

A Carboxylic Ester-Based Electrolyte with Additive to Improve Performance of Lithium Batteries at Ultra-Low Temperature

To cite this article: Pengbin Lai et al 2022 J. Electrochem. Soc. 169 100539

View the article online for updates and enhancements.



This content was downloaded from IP address 112.48.20.139 on 27/10/2022 at 08:03





A Carboxylic Ester-Based Electrolyte with Additive to Improve Performance of Lithium Batteries at Ultra-Low Temperature

Pengbin Lai,¹ Haiming Hua,¹ Boyang Huang,¹ Peng Zhang,^{2,z} and Jinbao Zhao^{1,2,z}

¹State-Province Joint Engineering Laboratory of Power Source Technology for New Energy Vehicle, Engineering Research Center of Electrochemical Technology, Ministry of Education, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, People's Republic of China ²College of Energy, Xiamen University, Xiamen 361102, People's Republic of China

Lithium metal batteries (LMBs) are the promising battery system to push energy density to high level at low temperatures. In this work, the linear carboxylic esters methyl propionate (MP)-based electrolyte with 4 wt% fluorinated ethylene carbonate (FEC) is reported. The low melting point and viscosity of MP makes it the candidate solvent for the low temperature field. Assisted with FEC, the optimized electrolyte shows quite high ionic conductivity and better compatibility with separator and lithium metal anode, resulting in stable cycling performance at room temperature. Besides, it keeps liquid state at -70 °C and exhibits lower binding energy with lithium ion, enabling the Li/LiCO₂ batteries to cycle at -40 °C for 60 cycles. Apart from that, this battery can retain 88.6% discharge capacity at -70 °C of that at room temperature, reaching the highest discharge capacity retention at this ultra-low temperature to the best of our knowledge. This work demonstrates a simple but effective way to design the electrolytes with excellent low temperature performance.

© 2022 The Electrochemical Society ("ECS"). Published on behalf of ECS by IOP Publishing Limited. [DOI: 10.1149/1945-7111/ac9a84]

Manuscript submitted July 4, 2022; revised manuscript received September 16, 2022. Published October 26, 2022.

Supplementary material for this article is available online

Due to their high energy density (\sim 300 Wh kg⁻¹), high power density and longer cycling life, lithium-ion batteries (LIBs) have been widely applied as the main power supply from large scale energy storage system to portable digital devices.¹⁻⁴ At the same time, LIBs have been accepted as the stream power source for the electric vehicles, military and aerospace whose working conditions are in wide temperature range.⁵ Although nowadays traditional LIBs can be adapted to the above -20 °C environment, their application in the ultra-low temperature (below -40 °C) is still limited.^{6,7}

Previous literatures have systematically studied the charging and discharging behavior of battery at sub-zero environment, and ascribed the poor performance to the following reasons: $^{8-13}$ (1) The traditional electrolyte inevitably freezed when temperature decreased to -30 °C, which could increase the viscosity and decrease the conductivity of electrolyte, inhibiting lithium ion transport between cathode and anode. (2) The desolvation process would be more sluggish at graphite anode surface when temperature decreased, slowing intercalating process of lithium ion into the graphite interlayer. (3) Much slower diffusion of lithium ion in the cathode. These factors were all proved to have impacts on low temperature performance and the lithium ion desolvation process at graphite/electrolyte interface is regarded to be the main reason in some recent works.^{10,11} Therefore, designing an electrolyte possessing wide liquid range and selecting suitable anode is of great importance to enhance battery's performance at low temperature.^{14,15}

First of all, electrolyte, which serves as the bridge connecting cathode and anode through the ionic conduction, is an essential part to determine whether the battery can work at low temperature.^{16,17} Once the ionic conduction shutdown between the electrodes, the electrochemical reaction in the cell could not take place anymore. However, traditional carbonate solvents, ethylene carbonate (EC) and dimethyl carbonate (DMC) are the indispensable component of commercial electrolyte. But the higher melting point of these carbonate solvents causes their conductivity easily decreased when temperature reduced to sub-zero, limiting their ability to facilitate lithium ion transport. What's worse, when the temperature of environment was further reduced to lower than -30 °C, the battery with such electrolyte doesn't work at all.⁷ To overcome this problem, recent studies demonstrate varied design principles of

electrolyte for low temperature application, in which optimizing the organic solvent system is the major strategy for improving low temperature performance.^{18,19} To obtain the excellent performance at cryogenic environment, organic solvent with lower melting point and higher permittivity is very critical. Table SI lists some representative organic solvents for the low temperature application. Among them, carboxylate ester solvents possess not only low enough freeze point and high permittivity, but also decent oxidative potential. Therefore, this kind of solvents has been widely-used as co-solvent to reduce the melting point of electrolyte.²⁰⁻²⁴ Holoubek et al.²⁵ reported the MP-based electrolyte (2 M LiPF6 MP +10% FEC) which enabled the dual ion battery (graphite/graphite battery) to discharge at -60 °C at 10 C high rate. Also, Cho et al. reported²⁶ high-content MP electrolyte (1 M LiPF₆ in MP:FEC 9:1 v/v) which delivers successful cycling of NCM811/graphite pouch cells at 0.5 C rate at -20 °C. Xia et al.²⁷ developed an ethyl acetate (EA)-based electrolyte (2 M in EA), with which the all-organic battery can work well at -70 °C and retain 70% of capacity at room temperature.

Another fact limiting battery's performance is the anode. Traditional anode material (i.e. graphite) with insertion/extraction process had sluggish desolvation process and suffered severe SEI film damage during cycling at low temperature, therefore researchers developed other types of anode material such as lithium metal,²⁸ silicon,²⁹ lithium titanate³⁰ (LTO) and titanium dioxide.³¹ Among these materials, lithium metal anode was the promising battery anode material for its high energy density (3860 mAh g^{-1}) and low reductive potential (-3.04 V vs SHE).³² Besides, lithium metal batteries' (LMBs) plating and stripping mechanism has shown better kinetic than graphite anodes' intercalation chemistry at low temperature.³³ Therefore, although LMBs' kinetic is slowed down as LIBs do at low temperature to some extent, LMBs are the promising battery system to push battery's energy to high level at low temperature. However, just as with room temperature cycling, LMBs suffer from lithium dendrite growth and continuous growth of solid electrolyte interphase (SEI) from reactions between anode and electrolyte when cycling at low temperature.33-35 Recently, extensive works had been exerted to enhance the LMBs' low temperature performance like using fluorinate solvent,^{36,37} local high concentration electrolyte,^{38,39} weak solvation electrolyte^{28,40} and so on.

In this work, we demonstrated an electrolyte containing single carboxyl ester solvent and additive to enhance battery's performance at low temperature. The single solvent with low melting point enabled electrolyte to keep liquid state even at -70 °C, exhibiting

appreciable high conductivity and low viscosity at that low temperature. Apart from the solvent, additive is also an important part for the cells' low temperature performance.^{41,42} To inhibit the side reaction between electrolyte and lithium metal anode, appropriate amount of additive, which can firstly react with lithium metal to form stable SEI, was added to the single solvent electrolyte. The Li/LCO cells (cathode mass loading = 5 mg cm^{-2}), with the optimized electrolyte provided excellent performance at ultra-low temperature, which could deliver 88.6% capacity retention at -70° C at 0.1 C after charged at room temperature. And also, they can be cycled at -40 °C for 60 cycles at 0.1 C. To explore how the improved performance is achieved, we verify that fluorinated ethylene carbonate (FEC) additive contributes to the improved cycling and low temperature performance by forming the LiF-rich SEI which not only protected electrode but also facilitated the Li⁺ transportation by reducing the charge transfer resistance (R_{ct}) . The design of adding little amounts of additive into single carboxyl ester solvent enabled LMBs to cycle stably at room temperature and to work at low temperature with superior performance. This work provides a strategy for the rational design electrolyte applicable at low temperature.

Experimental

Preparation of materials.—Lithium cobalt oxide (LCO) active material was provided by Beijing Easpring Material Technology Co. Ltd (China). LCO, acetylene black conductive agent and polyviny-lidene fluoride (PVDF) binder were mixed and grinded in the mass ratio of 8:1:1. N-methyl-2-pyrrolidone (NMP) was added to disperse the mixed powder, and then the formed slurry was magnetically stirred for 8 h to make sure its consistency. And the high loading cathode was prepared in the mass ratio of 94.5%:2.5%:3.0%. The stirred-slurry was coated on Al foil and dried in a vacuum oven at 80 °C for 12 h. The normal loading mass of active material in cathode was around 5 mg cm⁻² and the high-loading cathode was around 12 mg cm⁻². The diameter of lithium metal foil was 12 mm and the thickness of it was 1 mm. The separator was purchased from Asahi Kasei Company and punched into pieces.

The lithium Bistrifluoromethanesulfonimide (LiTFSI) salt, FEC solvent and commercial electrolyte containing 1 M Lithium hexafluorophosphate (LiPF₆) in EC and DMC mixture (1:1 by volume) were provided by Guotaihuarong Company. The methyl propionate (MP) solvent (>99%) was purchased from Sigma-Aldrich. The pure MP electrolyte was prepared by adding LiTFSI into single organic solvent MP. The addition of FEC with different weight ranged from 1% wt to 5% wt was marked MF1, MF2, MF3, MF4 and MF5, respectively. The molar concentration of our electrolytes was 1 mol 1⁻¹. The amount of electrolyte for every battery was controlled around 80 μ l in total. The batteries used for electrochemical test and characterization were assembled in 2016 type coin cell. The Li/LCO cells were assembled by putting a separator between LCO cathode and lithium metal anode and adding electrolyte in the glove box (M. Braun GmbH) filled with argon gas.

Computational detail.—All the DFT calculation was conducted on the Gaussian09 package.⁴³ The geometry structure of all molecules were optimized by B3LYP-D3⁴⁴ method at 6-311+G(d, p) basis set.^{45,46} Frequency analysis was performed to guarantee that all the structures were the minimum points on potential energy surface. The binding energy was calculated by the following equation:

$$E_b = E_{total} - E_{sol} - E_{Li^+}$$
^[1]

 E_{total} , E_{sol} and E_{Li}^+ represented the single point energy of lithium complex, solvent and lithium ion respectively.

In the first principle calculation, the geometry structure of FEC molecule was optimized in DMol3 module⁴⁷ in Materials Studio 2019 with B3LYP functional.⁴⁸ The double numerical plus

polarization (DNP) basis set was used during calculation with basis file of 4.4. The convergence tolerance was set 1.0×10^{-5} Ha, 0.002 Ha Å⁻¹, and 0.005 Å for energy, maximum force, and maximum displacement, respectively. The ab initio molecular dynamics (AIMD) was performed in CASTEP module⁴⁹ with general gradient approximation⁵⁰ (GGA) and Perdew–Burke–Ernzerhof⁵¹ (PBE) exchange-correlation functional. The lithium metal model was built as following method: a five-layer 2×2 supercell of lithium (110) surface with a vacuum layer of 15 Å. The optimized FEC molecule was put in 15 Å vacuum space to simulate its reaction with lithium metal. A minimization calculation was conducted first in Forcite module packed in Material Studio and then 2.0 ps AIMD was exerted in CASTEP with NVT ensemble. The time step was set to 1.0 fs and temperature was set to 300 K to simulate the room temperature environment. What's more, the temperature was controlled by Nose thermostat with a Nosé⁵² Q ratio of 0.5.

Classical Molecular dynamic (MD) simulation was conducted to investigate the solvation structure of electrolyte. An amorphous cell was conducted with LiTFSI, MP and FEC with certain ratio. The cell was first geometry-optimized with the COMPASS⁵³ (Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies) force field and the associated charges are listed in Fig. S18. The long-range electrostatic interaction was calculated by Ewald summation⁵⁴ and the van der Waal interaction was truncated at 18.5 Å. The electrolyte density was calculated based on MD stimulation with NPT ensemble at 298 K using Nosé algorithm to control the temperature and the Berendsen⁵⁵ algorithm to control the pressure. The NPT simulation time was set to 200 ps and the converge density of electrolyte was calculated as the average density of the last 100 ps. The similar density between theoretical calculation and experiment data confirmed the validation of the calculation method. The structure of lithium ion was determined by analyzing the radial distribution function (RDF) and coordination number (CN) in the MD trajectory of last 100 ps.

Material characterization.—The conductivity of electrolyte was tested by alternating current (AC) impedance module assembled in CHI660D electrochemical workstation. The conductivity of electrolyte at different temperatures was obtained by the following equation:

$$\sigma = \frac{l}{Ra}$$
[2]

In which σ represented the conductivity of electrolyte, l represents the length of two platinum plane, a means the area of platinum plane, R is determined by the section point value of AC impedance. To guarantee the thermal equilibrium, the conductivity measurement was carried out after staying at setting temperature for 30 min.

The viscosity value of electrolyte was measured by the viscometer (VM-10A-L). Contact angle test was conducted by contact angle tester (JC-2000C1) at 25 °C. Scanning electron microscope (SEM) images was obtained from Gemini SEM 500 field emission scanning electron microscope manufactured from Zeiss company. Xray photoelectron spectroscopy (XPS) spectral data was taken from Escalab Xi+ equipment. The batteries were cycled for 20 cycles and then dissembled in glove box to take out the cycled lithium metal anode for further characterization. The lithium metal sample of SEM and XPS was obtained from dissembled cells and rinsed with Dimethyl Carbonate (DMC) solvent for 3 times in Ar-filled glovebox. During the transferring process, the prepared sample was protected in the well-sealed container filled with Ar gas to avoid the contact with oxygen in the air. Nuclear Magnetic Resonance (NMR) of⁷Li was tested by Ascend 500 MHz spectrometer. During NMR test, the NMR tube with a capillary tube containing 0.1 M LiClO₄ salt dissolved in D₂O solution for locking field in the⁷Li-NMR tests, as introduced in our previous work.³⁹ The Raman test was conducted by HORIBA FRANCE and the wavelength of the laser was 532 nm.

Electrochemical characterization.-Electrochemical impedance spectroscopy (EIS) was taken from Solartron Metrology at a frequency range from 10^{-1} Hz to 10^5 Hz under amplitude of 10 mV. The Li/LCO cells in the EIS test was in discharge state. The batteries were cycled for 5 cycles at room and -40 °C respectively before testing. The high loading cathode was used in the low temperature discharge test and the low loading cathode was used in other tests. LSV (linear sweep voltammetry) data was tested with a three-electrode system containing a working electrode of stainless steel, reference electrode and counter electrode of Li sheet at a sweeping speed of 1 mV s⁻¹ on electrochemical station (CHI 660E). The average coulombic efficiency of different electrolytes was calculated using a modified Aurbach method 3⁵⁶ with Li-Cu cells, which were cycled at a current density of 0.5 mA cm^{-2} . The cell was firstly deposited and stripped at amount of 5 mAh cm⁻² on the Cu for precycling, and then 5 mAh cm⁻² amount of 5 mAh cm⁻² about of lithium was deposited on Cu as a Li reservoir. (Q_r) After that, 1 mAh cm⁻² amount of lithium (Q_c) was stripped and deposited for ten cycles. Finally, the cells were charged to 1 V to strip all the lithium. The average coulombic efficiency (CE) was calculated as the following equation:

$$CE = \left(\frac{n \times Q_c + Q_s}{n \times Q_c + Q_r}\right)$$
[3]

Where n is the cycle number (here n = 10) and Q_s is the final charge capacity.

All of the batteries were assembled in Braun glove box full of Ar gas with water and oxygen content less than 0.5 ppm. The galvanostatic test data was obtained on the Neware test system. The potential of Li/LCO battery was ranged from 3.0 V-4.2 V at various current densities and at different temperature. For the room temperature cycling test, the cells were firstly cycled at 0.1 C for one cycle and then followed by the cycling at 1 C rate. For the low temperature testing, the low temperature environment was provided by DC-8006 incubator for discharge test and Meiling Biology&Medical DW-HW50 ultra-low freezer for cycling test. The temperature of the chamber was ranged from -39 °C to 41 °C. In order to form the SEI film, all of tests of the batteries in low temperature environment was conducted after two activation cycles at 0.1 C rate at room temperature. To guarantee the thermal equilibrium, the low temperature performance test of cells was carried out after staying at setting temperature for 2 h.

Results and Disccusion

FEC is beneficial for the cycling performance of LMBs, but the ultra-low temperature performance is limited due to its high melting point and high viscosity. Therefore, FEC is used as additive instead of co-solvent in our work. The amount of FEC additive in most literatures are around 5%.^{57,58} By comprehensively comparing the property of different amount of FEC additive, 4% wt was selected for the following tests and was marked as MF4. (Figs. S1, S2, Table SII).

Figure 1a demonstrated the conductivity of the three electrolytes at different temperature. At room temperature, the ionic conductivity of commercial electrolyte was slightly higher than that of pure MP and MF4. However, when the temperature decreased to sub-zero, the commercial electrolyte was beginning to freeze and its conductivity dramatically reduced to 0.20 mS cm⁻¹ at -30 °C. While the pure MP and MF4 electrolyte still maintain liquid state even at -70 °C (Fig. S3) and demonstrate decent conductivity. The conductivity of MF4 was slightly lower than pure MP for the little addition of FEC (1.33 mS cm⁻¹ at 1.24 mS cm⁻¹ at -70 °C) at low temperature. As shown in Fig. 1b, the viscosity of these electrolytes was increased as temperature decrease. However, in the temperature-viscosity plot

of commercial electrolyte, there was an obvious turning point around -40 °C where the viscosity increased remarkably from 4.75 mPa·s at room temperature to 308 mPa.s at -40 °C, which can be attributed to the freezing of the electrolyte. The viscosity of pure MP and MF4 was significantly lower than commercial electrolyte under sub-zero temperature while MF4 (5.82 mPa·s at -50 °C) is slightly higher than pure MP (5.50 mPa·s at -50 °C) due to the addition of FEC. (Fig. 1c).

The compatibility of the electrolytes with the lithium metal was established by a storage test where the lithium metal anode was immersed in the electrolyte for a few days. The result was shown in Figs. 1c, 1d and 1e. The commercial electrolyte was clear even after 20 days, while the MP electrolyte became yellow and slimy after just 2 days in contact with the lithium metal (Fig. S4), indicating side reaction between lithium metal and electrolyte. This may be ascribed to the high reactivity of carboxylate solvents with lithium metal [44]. However, with the addition of FEC, the electrolyte (MF4) did not change the color even after 20 days, suggesting the initially formed stable interphase with FEC can prevent the side reaction of the electrolyte. This phenomenon was probably because that FEC can inhibit this side reaction. The wettability between electrolyte and separator is also an important part to guarantee the battery's charge and discharge performance. The contact angle test was used to measure electrolytes' wettability, as Figs. 1g, 1h and 1i shown. Compared to the commercial electrolyte which has a contact angle of 46.9°, the pure MP electrolyte has a much lower angle (31.7°) , which leads to better wettability with separator. The introduction of FEC doesn't significantly influence the contact angle, which is slightly increased (32.9°) and still lower than that of commercial electrolyte. Based on the results above, the addition of FEC could assist to improve the compatibility between anode and electrolyte and doesn't have significant negative impact on the electrolyte in conductivity, viscosity or wettability.

The function of FEC is investigated by theoretical calculation and experiments. Firstly, the oxidizing and reducing properties of electrolyte component can be described by the value of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), respectively. Fig. S5a shows the HOMO and LUMO values of different solvents obtained by density function theory (DFT) calculation. It suggests that fluorinated ethylene carbonate (FEC) possesses much lower LUMO value (-0.39 eV) than EC (-0.28 eV), DMC (0.069 eV) and MP (-0.022 eV), which means that FEC would be reduced prior to these solvents and participate in the formation of SEI film at the surface of lithium metal anode. To explore mechanism of film-forming property of FEC, ab initial molecular dynamics (AIMD) is taken to stimulate the reaction mechanism between FEC and lithium metal. As shown in Fig. S5b, the bond of C-F was about to break at 120 fs and Li-F bond was formed at around 2000 fs, indicating the formation of LiF, which is thought to aid in charge transfer reactions between the lithium metal and the electrolyte (faster ionic conduction thought the SEI) and to have better mechanical properties.⁵⁹ According to the calculation results discussed above, we propose a FEC reduction mechanism as shown in Fig. S5c, in which F atom was detached from FEC molecule after gaining an electron and combine with lithium ion to form the LiF.

The result of theoretical calculation is proved by X-ray photoelectron spectroscopy (XPS) spectra. The chemical components of the surface on lithium metal anode are shown in Fig. 2a. In the F1s spectra, there are two distinct peaks: one belongs to LiF at 684.9 eV and the other is C–F bond at 688.6 eV, which is probably derived from the lithium salt and additives.⁵⁷ It is very clear that the F content of LiF in MF4 electrolyte is higher than that in the pure MP electrolyte, indicating more LiF-formed F element in the FECintroduced electrolyte than that in the FEC-free electrolyte.

This result is also proved by Li 1s spectra in Fig. 2b. According to pervious literature,⁵⁷ the peak of Li 1s can be divided into three peaks: LiF at 56.4 eV, ROCO₂Li at 54.9 eV and Li₂CO₃ at 55.5 eV, respectively. Among these peaks, ROCO₂Li and Li₂CO₃ could come



Figure 1. The property of different electrolytes. (a) Conductivity of different electrolytes at different temperature. (b) Viscosity of different electrolytes at different temperature (c) Enlarge image of (b). (d)–(f) Reactivity of lithium metal foil in different electrolytes at 20th day. (g)–(i) Contact angle test result tested at the room temperature.



Figure 2. XPS characterization of SEI film of lithium metal anode in Li/LCO cells after 20 cycles at room temperature. (a) F 1s spectra. (b) Li 1s spectra. The SEM images of lithium anode surface form the Li/LCO cells at 1 C rate after cycling for 50 cycles at room temperature. (c) pure MP. (d) MF4. The SEM images of lithium anode surface form the Li/LCO cells at 0.1 C rate after cycling for 50 cycles at low temperature (-40 °C). (e) pure MP. (f) MF4.

from the decomposition of MP molecule and LiF is from the lithium salt and additive. It is obvious that the peaks at 54.9 eV and 55.5 eV of pure MP electrolyte is higher than that of MF4 electrolyte, indicating more MP solvent is consumed during cycling. On the other hand, the higher LiF peak at 56.4 eV of MF4 suggests that more F from LiF formed on the surface on lithium metal, which is correspond to the result of F 1s. Therefore, these observations indicate that the addition of FEC prevents the consumption of MP solvent and promotes the formation of LiF-rich SEI film.

The morphology of lithium metal anode can be confirmed by Scanning Electronic Microscopy (SEM). The Li/LCO cell was cycled for 50 cycles at 1 C rate at room temperature before SEM was taken. As Fig. 2c shown, the surface of lithium metal in pure MP electrolyte is loose and porous, exhibiting the existence of dead lithium and broken of SEI film during cycling. While with the MF4 electrolyte in Fig. 2d, the morphology of lithium anode is dense and uniform. Even though at the low temperature, the lithium metal cycled in MF4 is still relatively dense. (Figs. 2e and 2f). It is worth noting that when the FEC amount was between 0% and 4% (2%), the surface still shows porous morphology as with pure MP with some dense and uniform localized areas. SEM images and XPS spectra of the surface layer formed on lithium with the MF2 electrolyte is given in Fig. S6. These results indicate that sufficient amount of FEC is necessary to improve the morphology of lithium metal anode upon cycling.

The kinetics of lithium ion diffusion can be described by the impedance value, therefore the electrochemical impedance spectroscopy (EIS) was applied to investigate the impedance of every part of cell. As previous literatures shown,¹¹ the EIS of traditional LIB is composed of four parts. Such an EIS curve can be fitted by equivalent circuit, as Fig. S7a shown. The left side of the curve at high frequency (higher than 10^5 Hz) means the bulk resistance of cell (R_b), which corresponds to the conductivity of electrolyte. The frequency ranged from 10^5 to 10^3 Hz represents the resistance of solid-state interface (Rsei) layer formed at the surface of electrode. The medium frequency region (from 10^3 to 10^0 Hz) is the charge transfer resistance (R_{ct}), including the desolvation and diffusion process of lithium ions. And the straight line at low frequency (lower than10⁰ Hz) indicates the Warburg diffusion (W) resistance of lithium ion in electrode. It was generally believed that the charge transfer resistance would increase remarkably when temperature was decreased. 10,11,60

Figures 3a and 3b demonstrate the Nyquist plots of cell in pure MP and MF4 electrolyte after 5 cycles at various temperature. With the decrease of temperature, the whole resistance of cells increases, which can be attributed to the slower kinetic of the cells. By comparing the increasement of different part of the cell, it was found that the temperature had a significant impact on charge transfer resistance (R_{cl}) but little influence on R_{sei} . Generally speaking, MF4 demonstrates lower resistance than pure MP, especially in charge transfer resistance, indicating faster kinetics at low temperature. The calculated activation energy of R_{ct} and resistance of SEI (R_{sei}) of the two electrolytes is shown in Figs. 3c and 3d, respectively. As the result shown, the activation energy of pure MP is higher than MF4

whatever in R_{ct} or R_{sei} , suggesting that addition of the FEC could promote the lithium ion transport at the electrode/electrolyte interphase by forming the LiF-rich SEI at low temperature. In addition, by comparing activation energy of 5 cycles with the pristine (without any cycling), it can be found that several cycles at lower rate (0.1 C) at room temperature is of great importance before low-temperature testing. (Fig. S8) Therefore, in the following electrochemical test, two activation cycles at room temperature were all conducted before low temperature test.

The cycling stability at room temperature was firstly tested before the low temperature performance test. In order to reveal the electrochemical performance of these electrolyte, lithium cobalt oxide (LCO) is selected as the battery cathode for its high capacity and structure-steady property at room and low temperature. The electrochemical performance of Li/LCO batteries at 25 °C were shown in Fig. 4. Due to an absence of a SEI forming additive, the MP electrolyte was continuously consumed during the cycling until it is dried out, so there is a sharp capacity decay appeared at 90th cycle for the pure MP electrolyte, as shown in Fig. 4a. With less amount of pure MP electrolyte, the occurrence of capacity decay is becoming earlier. (Fig. S9). Also, the result above is in agreements with Li-Li symmetric cell test result. (Fig. S10) As for the MF4 electrolyte (Fig. 4b), there was no sharp capacity decay appeared. maintaining 93.6% capacity retention after 200 cycles at 1 C rate, showing similar cycling performance with commercial electrolyte. (Figs. 4c and S11) This result is because that the introduction of FEC can contribute to the formation of the LiF-rich film and assist to the uniform Li deposition (Fig. 4d).

The low temperature performance is shown in Fig. 5. Previous literature⁶¹ had demonstrated that the voltage drops of discharge curve at low temperature is predominantly caused by charge transfer process of lithium ion at the electrode-electrolyte interface. The comparison of discharge performance of the three electrolytes at room temperature, -40 °C and -70 °C is shown in Fig. 5a. It can be seen that there is a huge discharge curve drop in the commercial electrolyte, showing the large polarization at low temperature, which



Figure 3. EIS of Li/LCO cell in pure MP and MF4 electrolyte at various temperature. Nyquist plot of (a) MP 5cycles. (b) MF4 5 cycles. Calculate activation energy of (c) R_{ct} and (d) R_{sei} of pure MP and MF4 electrolyte.



Figure 4. The room temperature performance of Li/LCO cells in the three electrolytes. The cells were firstly cycled at 0.1 C for two cycles and then followed by the cycling at 1 C rate. The charge and discharge profile of (a) MP, (b) MF4 and (c) Commercial electrolyte at room temperature. (c) Cycling stability and coulombic efficiency of pure MP and MF4 at room temperature.

is probably due to the restricted desolvation process resulted from the large binding energy with lithium ion in carbonate solvents.⁶¹ (Table SIII) Therefore, at -40 °C, the commercial electrolyte delivers discharge capacity of 26.0 mAh g⁻¹, only 17.7% of its room temperature capacity (146.9 mAh g⁻¹), while the MP and MF4 electrolyte could deliver over 90% of capacity retention. It is worthnoting that the traditional commercial electrolyte in this work is expected to have poor low temperature performance compared with other carbonate-based electrolytes. When the linear carbonate solvent changed from DMC to other solvents with low melting point, the discharge performance at low temperature is improved, which is compared and discussed in Fig. S12.^{19,62}

When the temperature further decreases to -70 °C, pure MP shows a huge voltage drop, merely delivering 45.7 mAh g⁻¹ (31.1%) capacity, which is probably related to the huge charge transfer resistance at lower temperature. Discharge capacity of different amount of FEC at -70 °C is displayed in Fig. S13. The discharge capacity of addition of FEC ranged from 0% to 5% is 45.7 mAh g⁻¹, 50.0 mAh g⁻¹, 81.3 mAh g⁻¹, 104.0 mAh g⁻¹, 130.5 mAh g⁻¹ and 122.0 mAh g⁻¹, respectively. It is obvious that 4% of FEC into pure MP electrolyte could significantly improve Li/LCO battery's discharge performance at -70 °C, with the capacity retention of 88.6%, indicating the addition of FEC improves the discharge performance of Li/LCO battery at ultra-low temperature. These electrolytes' discharge capacity value was listed in Fig. S14, in which lower amount of additive couldn't fully form stable LiF-riched SEI to cover the surface of lithium metal and higher amount of FEC may slightly increase the melting point and viscosity of electrolyte.

With the well-formed SEI, the cell with MF4 electrolyte demonstrates better high-rate discharge performance than MP electrolyte as shown in Fig. 5b. What's more, the high loading Li/LCO cell with MF4 electrolyte can also work at the extreme temperature, delivering 121.5 mAh g⁻¹ and 104.2 mAh g⁻¹ capacity at -40 °C and -70 °C respectively. To our surprise, with this electrolyte, the battery could even power LED light at -70 °C. (Supporting video) And after discharging at ultra-low temperature,

the battery with the optimized MF4 electrolyte could still cycle at room temperature at 1 C (1 C = 150 mAh g⁻¹) rate as Fig. 5d shown. (Fig. S15) Apart from discharging at low temperature, the battery with our electrolyte can be cycled at 0.1 C rate at -40 °C, as Fig. 5e shown. MF4 electrolyte could deliver capacity of 111.6 mAh g⁻¹ at 60th cycle while pure MP delivered only 32.3 mAh g⁻¹. (Fig. S16) This result can ascribe to the uniform SEI film formed by addition of FEC, which can prevent fresh lithium metal from the direct contact of electrolyte and can facilitate the diffusion of lithium ion as previous results shown.⁶³

It is worth-noting that when the addition amount of FEC is higher than 5% (e.g. 10%, MF10), although the batteries in MF10 electrolyte show similar room temperature cycling performance with those in MF4 electrolyte, they deliver only 82.8 mAh g⁻¹, which are lower than those in MF4 electrolyte. (Fig. S17) This result can be ascribed to the high melting point and viscosity of FEC. Therefore, higher amount of FEC in previous literature is not suitable for this ultra-low condition.⁶⁴

Some previous literatures had been reported that additive could have impact on the solvation structure of lithium ion.^{65,66}To verify whether FEC has an effect on the solvation structure of lithium ion, nuclear magnetic resonance (NMR) and Raman spectra were conducted to explore its solvation structure, as Figs. 6a and 6b shown. In the⁷Li NMR spectra, the chemical shift of lithium species in pure MP and MF4 electrolytes are both near 0.66 ppm, indicating the similar solvation structure of lithium ions. Also, the raman spectra demonstrates addition of FEC doesn't obviously affect the vibration of C=O bond in MP molecule (1745 cm^{-1}) and the vibration of S=O bond in LiTFSI⁶⁷(745 cm⁻¹), (Fig. S18) which corresponds to the result of molecular dynamic (MD) calculation as Figs. 6c and 6d shown.(Figs. S19, S20) The calculated coordinate number (CN) of Li-O in solvents and salt were listed in Table SIV. These results suggested that the function of FEC was not the affection of the solvation structure of the lithium ion. To further confirm the film-forming function of FEC, the Li/LCO battery with MF4 electrolyte was cycled at room temperature at 0.1 C rate for two



Figure 5. The low temperature performance of Li/LCO cells in MP and MF4 electrolytes. Before the low temperature testing, the cells were kept at the setting temperature for 2 h. (a) Li/LCO (cathode mass loading = 5 mg cm⁻²) cells' discharge profile of the three electrolytes at various temperature at 0.1 C after charged at room temperature. (b) Li/LCO discharge profile of MP and MF4 at -40 °C at different rate. (c) High loading (12 mg cm⁻²) Li/LCO discharge profile of MF4 electrolyte at low temperature. (d) Li/LCO charge/discharge profile at room temperature after discharged at -70 °C. (e) Cycling stability and coulombic efficiency of pure MP and MF4 at -40 °C at 0.1 C rate.

cycles and dissembled in glove box, and then transformed into the pure MP electrolyte system. As the Figs. 6e and 6f shown, the filmforming battery demonstrated nearly the same performance as the MF4 electrolyte in the low temperature. (Fig. S21) This result may be ascribed to the reduction of FEC and is proved in XPS spectra. (Fig. S22) These observations suggested that pre-filming of lithium metal was significant to enhance the low temperature performance of battery.

Conclusions

To summarize, we developed an electrolyte of carboxylate ester methyl propionate as the main solvent with low melting point and high permittivity, which could keep the electrolyte in liquid state at ultra-low temperature. The carboxylate ester-based electrolytes demonstrate high conductivity and low viscosity at low temperature, enabling Li/LCO cells to work at -70 °C. And the addition of small amount of FEC can inhibit side reaction between MP solvent and lithium metal anode by forming LiF-rich SEI, showing better compatibility with lithium metal anode and separator. The cell with the optimized electrolyte can achieve a very high capacity retention of 88.6% at -70 °C and can be even cycled at -40 °C. Compared with traditional strategy to improve LiB's performance at low temperature by utilizing solvent with low melting point into the traditional electrolyte system as co-solvent or additives, our work presents a method to use the only-one solvent dissolving lithium salts, companied with a little amount of functional additive. This kind of electrolyte not only possesses higher conductivity, but also improves the battery's performance at ultra-low temperature, which provides a reference for the design of low temperature electrolyte in the future.

Acknowledgments

We gratefully acknowledge the financial support of National Key Research and Development Program of China (2021YFB2400300), National Natural Science Foundation of China (21875198,21875195), the Fundamental Research Funds for the Central Universities (20720190040) and the key Project of Science and Technology of Xiamen (3502Z20201013). And we are grateful to Tan Kah Kee Innovation Laboratory (IKKEM) for help with XPS, SEM, NMR and Raman measurements.



Figure 6. Further confirmation of function of FEC. (a) ⁷Li NMR and (b) Raman spectra of pure MP and MF4 electrolyte. RDF and coordinated number of (c) Pure MP and (d) MF4. (e) Discharging capacity file of film-forming anode cell at -70 °C at 0.1 C rate after charged at room temperature. (f) Charge/discharge profile of film-forming anode cell at -40 °C at 0.1 C rate.

ORCID

Jinbao Zhao (1) https://orcid.org/0000-0002-2753-7508

References

- 1. J.-M. Tarascon and M. Armand, *Nature*, **414**, 359 (2001).
- 2. H. K. Bruce Dunn and J.-M. Tarascon, Science, 334, 928 (2011).
- 3. R. V. Noorden, *Nature*, 507, 26 (2014).
- 4. B. Scrosati, J. Hassoun, and Y.-K. Sun, Energy Environ. Sci., 43287 (2011).
- R. Schmuch, R. Wagner, G. Hörpel, T. Placke, and M. Winter, *Nat. Energy*, 3, 267 (2018).
- 6. X. Dong, Y. G. Wang, and Y. Xia, Acc. Chem. Res., 54, 3883 (2021).
- 7. J. Hou, M. Yang, D. Wang, and J. Zhang, *Adv. Energy Mater.*, **10**, 1904152 (2020).
- 8. M. Petzl, M. Kasper, and M. A. Danzer, J. Power Source, 275, 799 (2015).
- 9. Y. Q. Qiao, J. P. Tu, X. L. Wang, and C. D. Gu, J. Power Sources, 199, 287 (2012).
- Q. Li, D. Lu, J. Zheng, S. Jiao, L. Luo, C. M. Wang, K. Xu, J. G. Zhang, and W. Xu, ACS Appl. Mater. Interfaces, 9, 42761 (2017).
- 11. S. S. Zhang, K. Xu, and T. R. Jow, *Electrochim. Acta*, 49, 1057 (2004).
- G. Yue-ru, Z. Wei-min, S. Chang-Hu, L. Chuan-jun, Z. Zhong-ru, X. Xu-jin, and Y. Yong, J. Electroanal. Chem., 24, 488 (2018).
- G. Zhang, X. Wei, S. Chen, G. Han, J. Zhu, and H. Dai, ACS Appl. Energy Mater., 5, 6462 (2022).
- 14. R. Petibon, J. Harlow, D. B. Le, and J. R. Dahn, *Electrochim. Acta*, 154, 227 (2015).
- 15. A. Ohta, H. Koshina, H. Okuno, and H. Mural, J. Power Source, 6, 6 (1995).
- E. R. Logan, D. S. Hall, M. M. E. Cormier, T. Taskovic, M. Bauer, I. Hamam, H. Hebecker, L. Molino, and J. R. Dahn, *The Journal of Physical Chemistry C*, **124**, 12269 (2020).
- M. C. Smart, B. V. Ratnakumar, A. Behar, L. D. Whitcanack, J. S. Yu, and M. Alamgir, J. Power Sources, 165, 535 (2007).
- S. Herreyre, O. Huchet, S. Barusseau, F. Perton, J. M. Bodet, and P. Biensan, J. Power Source, 97-98, 576 (2001).

- 19. E. J. Plichta and W. K. Behl, J. Power Source, 88, 192 (2000).
- N. Kim, Y. Myung, H. Kang, J. W. Lee, and M. Yang, *ACS Appl. Mater. Interfaces*, 11, 33844 (2019).
- M. C. Smart, B. V. Ratnakumar, and S. Surampudi, J. Electrochem. Soc., 149, A361 (2002).
- B. Liang, F. Cheng, X. Ge, X. Tan, C. Fang, and J. Han, ACS Appl. Energy Mater., 5, 5867 (2022).
- X. Ma, R. S. Arumugam, L. Ma, E. Logan, E. Tonita, J. Xia, R. Petibon, S. Kohn, and J. R. Dahn, J. Electrochem. Soc., 164, A3556 (2017).
- M. C. Smart, B. V. Ratnakumar, K. B. Chin, and L. D. Whitcanack, J. Electrochem. Soc., 157, A1361 (2010).
- J. Holoubek, Y. Yin, M. Li, M. Yu, Y. S. Meng, P. Liu, and Z. Chen, *Angew. Chem. Int. Ed. Engl.*, 58, 18892 (2019).
- 26. Y.-G. Cho, M. Li, J. Holoubek, W. Li, Y. Yin, Y. S. Meng, and Z. Chen, ACS Energy Lett., 6, 2016 (2021).
- 27. X. Dong, Z. Guo, Z. Guo, Y. Wang, and Y. Xia, Joule, 2, 902 (2018).
- 28. J. Holoubek et al., Nat. Energy, 2021, 303 (2021).
- 29. E. Markevich, G. Salitra, and D. Aurbach, J. Electrochem. Soc., 163, A2407 (2016).
- 30. T. Yuan, X. Yu, R. Cai, Y. Zhou, and Z. Shao, J. Power Source, 195, 4997 (2010).
- 31. J. Li, Y. Li, Q. Lan, Z. Yang, and X.-J. Lv, J. Power Source, 423, 166 (2019).
- 32. J. Liu et al., Nat. Energy, 4, 180 (2019).
- 33. A. C. Thenuwara, P. P. Shetty, and M. T. McDowell, Nano Lett., 19, 8664 (2019).
- 34. S. Li, M. Jiang, Y. Xie, H. Xu, J. Jia, and J. Li, Adv. Mater., 30, e1706375 (2018).
- 35. A. C. Thenuwara, P. P. Shetty, N. Kondekar, S. E. Sandoval, K. Cavallaro, R. May,
- C.-T. Yang, L. E. Marbella, Y. Qi, and M. T. McDowell, ACS Energy Lett., 5, 2411 (2020).
- 36. X. Fan et al., *Nat. Energy*, 4, 882 (2019).
- 37. J. Holoubek et al., ACS Energy Lett., 5, 1438 (2020).
- 38. J. Holoubek et al., Energy Environ. Sci., 15, 1647 (2022).
- 39. S. Lin, H. Hua, P. Lai, and J. Zhao, Adv. Energy Mater., 11, 2101775 (2021).
- T. Ma, Y. Ni, Q. Wang, W. Zhang, S. Jin, S. Zheng, X. Yang, Y. Hou, Z. Tao, and J. Chen, Angew. Chem. Int. Ed. Engl., 61, e2022079 (2022).

- 41. J.-P. Jones, M. C. Smart, F. C. Krause, and R. V. Bugga, J. Electrochem. Soc., 167, 020536 (2020).
- 42. M. C. Smart, B. L. Lucht, S. Dalavi, F. C. Krause, and B. V. Ratnakumar, M. C. Smart, B. E. Eddit, S. Dauri, T. C. Hause, and L. H. Hanne, J. *Electrochem. Soc.*, **159**, A739 (2012).
 M. J. Frisch, G. W. Trucks, and D. J. Fox, (2013), Gaussian 09, Revision E. 01,
- Gaussian, Inc., Wallingford CT.
- 44. P. J. Stephens*, F. J. Devlin, C. F. Chabalowsk, and M. J. Frisch, J. Phys. Chem., 98, 11623 (1994).
- 45. T. Clark, C. Jayaraman, G. W. Spitznagel, and P. V. R. Schleyer, J. Comput. Chem., 4, 294 (1982).
- 46. R. Krishnan, J. S. Binkley, R. Seeger, and J. A. Pople, J. Chem. Phys., 72, 650 (1980).
- 47. B. Delley, J. Chem. Phys., 113, 7756 (2000).
- 48. A. D. Becke, J. Chem. Phys., 98, 5648 (1993).
- 49. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, and Z. Kristallogr, Cryst. Mater, 220, 567 (2005).
- 50. J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, and C. Fiolhais, *Phys. Rev. B*, **46**, 4978 (1992).
- 51. J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett., 77, 3865 (1996).
- 52. S. NosÉ, Mol. Phys., 100, 191 (2002).
- 53. H. Sun, J. Phys. Chem. B, 102, 7338 (1998).
- 54. U. Essmann, L. Perera, and M. L. Berkowitz, J. Chem. Phys., 103, 8577 (1995).

- 55. H. J. C. Berendsen, J. P. M. Postma, W. F. van Gunsteren, A. DiNola, and J. R. Haak, J. Chem. Phys., 81, 3684 (1984).
- 56. B. D. Adams, J. Zheng, X. Ren, W. Xu, and J. G. Zhang, Adv. Energy Mater., 8, 1800802 (2017).
- 57. X.-Q. Zhang, X.-B. Cheng, X. Chen, C. Yan, and Q. Zhang, Adv. Funct. Mater., 27, 1605989 (2017).
- 58. L. Liao, X. Cheng, Y. Ma, P. Zuo, W. Fang, G. Yin, and Y. Gao, *Electrochim. Acta*, 87, 466 (2013).
- 59. G. Zheng et al., Energy Stor. Mater., 29, 377 (2020).
- 60. A. Nickol, C. Heubner, M. Schneider, and A. Michaelis, J. Electrochem. Soc., 169 (2022).
- 61. J. Xu, X. Wang, N. Yuan, J. Ding, S. Qin, J. M. Razal, X. Wang, S. Ge, and Y. Gogotsi, Energy Stor. Mater., 23, 383 (2019).
- 62. S. S. Zhang*, K. Xu, J. L. Allen, and T. R. Jow, J. Power Source, 216, 216 (2002). 63. D.-J. Yoo, Q. Liu, O. Cohen, M. Kim, K. A. Persson, and Z. Zhang, ACS Appl Mater Interfaces, 14, 11910 (2022).
- 64. G. Cai, J. Holoubek, D. Xia, M. Li, Y. Yin, X. Xing, P. Liu, and Z. Chen, Chem Commun (Camb), 56, 9114 (2020).
- 65. T. Li, X. Q. Zhang, N. Yao, Y. X. Yao, L. P. Hou, X. Chen, M. Y. Zhou, J. Q. Huang, and Q. Zhang, Angew. Chem. Int. Ed. Engl., 60, 22683 (2021).
- C. Jiang et al., Angew. Chem. Int. Ed. Engl., 60, 10871 (2021).
 D. M. Seo, P. D. Boyle, R. D. Sommer, J. S. Daubert, O. Borodin, and W. A. Henderson, J. Phys. Chem. B, 118, 13601 (2014).