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# Preparation and characterization of trifluoroethyl aliphatic carboxylates as co-solvents for the carbonate-based electrolyte of lithium-ion batteries

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## ABSTRACT

In this work, a series of trifluoroethyl aliphatic carboxylates with different carbon-chain lengths in acyl group are prepared and investigated as the co-solvents for the carbonate-based electrolyte of lithiumion batteries. The trifluoroethyl aliphatic carbonates are synthesized by a modified one-step approach, using aliphatic carboxylic acid and trifluoroethanol as the raw materials (molar ratio, 1.2:1), hydrogen ion exchange resin as the catalyst and silica gel drier as the de-hydration. The structure and electrochemical properties of the final products have been characterized by FTIR, <sup>1</sup>H NMR, GC-MS, viscosity, conductivity meter and electrochemical measurements. The structure characterizations show that the final products have high purity. Electrochemical tests present that the co-solvents are able to improve the electrochemical performances of graphite electrode at low temperature. In particular, we find that an addition of trifluoroethyl *n*-hexanoate (TFENH) into 1 M LiPF<sub>6</sub>/EC + EMC electrolyte can significantly decrease the Li de-intercalation potential of graphite by 540 mV and achieve a high capacity retention of 92% at 218 K. The electrochemical impedance spectroscopy (EIS) measurements indicate that the observed performance improvement at low temperature is associated with the decreased surface film resistance ( $R_{SEI}$ ) by the addition of co-solvents.

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## 1. Introduction

At present, the electrolytes composed of lithium hexafluorophosphate (LiPF<sub>6</sub>) salts and carbonate-based solvents are commonly used in commercialized lithium-ion batteries. However, the performances of graphite electrode in these electrolytes at low temperature are extremely poor, which can be ascribed to the following two reasons: (1) the decreasing ionic conductivity of the electrolytes caused by the increased viscosity at low temperature [1]; (2) the largely decreased lithium-ion diffusion rate across the solid electrolyte interface (SEI) film on graphite electrode at low temperature [2–3].

In order to improve the low temperature performance of current electrolyte, all-carbonate electrolytes with lower concentrations of EC have been developed by many groups [1,4–7]. Carbonate-based electrolyte consisting of 1.0 M LiPF<sub>6</sub> in EC + DEC + DMC (1:1:1) has been shown to have excellent performance at 253 K [4]. Under sponsorship by the Mars Exploration Program, Jet Propulsion

Laboratory (JPL) has developed three generations of successful electrolytes over the last two decades [1,4,5,7,8]. The two previous generations of low temperature electrolytes are based on all-carbonate mixed solvents, included EC:DEC:DMC:EMC(1:1:1:3) and EC:EMC (1:4) – Gen 1 and 2. Adding co-solvents with low freezing point, low viscosity and good electrochemical stability is another effective method to

enhance the low temperature performance of the electrolyte. The third generation of JPL electrolyte for low temperature is based on 1.0 M LiPF<sub>6</sub> in EC + EMC (1:4) mixtures with ester co-solvents (such as methyl propionate and ethyl butyrate). JPL have reported several type cells which show outstanding low temperature performances by using their electrolyte [6-8]. They have done more research on the polarize voltage and the residences at low temperature, but not explained the SEI formation mechanism when the ester co-solvents added. During the 1990s, several researchers have clearly discussed the surface chemistry on graphite anodes in several carbonate-based electrolyte systems which could form SEI film [9–11]. But why aliphatic carboxylates could enhance the low temperature performance of the carbonatebased electrolyte? And what role in forming SEI film does the aliphatic carboxylate co-solvent play? These problems have not reached agreement.



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A variety of compounds are investigated as the co-solvents for the carbonate electrolytes. Among them, fluorinated aliphatic carboxvlate is one of the most promising candidates. It has been proved that partially fluorinated esters can effectively decrease the viscosity of the electrolyte, and are favorable for the formation of stable SEI film on graphite electrode at low temperature [6,12,13]. Smith et al. described favorable results with trifluoroethyl butvrate. ethyl trifluoroacetate, and trifluoroethyl acetate and methyl pentafluoropropionate. The results showed that the electrolyte consisting of 1.0 M LiPF<sub>6</sub>/EC + EMC + trifluoroethyl butyrate (20:60:20 vol%) had a better performance in nearly all tests than the other fluorinated ester containing mixtures [6]. Nakajima et al. investigated methyl difluoroacetate, methyl hexafluoroisobutyrate and the other three fluorinated esters. They found a low molecular weight fluoroester CHF<sub>2</sub>COOCH<sub>3</sub>-mixed 1 M LiClO<sub>4</sub>/EC + DEC demonstrated the much larger charge capacities than the base-line electrolyte [12].

Moreover, most fluorinated esters have much higher flash points than that of hydrocarbon-based carbonates, which benefit the safety of lithium-ion battery [14-18]. Sato et al. did some research on the thermal stabilities of electrolytes containing a series of fluorinated carboxylic acid esters using differential scanning calorimeter. Among these fluorinated carboxylic esters, methyl difluoroacetate exhibited the highest onset temperature and the smallest amount of exothermic heat at the coexistence of lithium. In 2011, they investigated that the exothermically decomposed temperature of the methyl difluoroacetate - based LiPF<sub>6</sub> solution – was higher than 723 K. So, this electrolyte was considered to be a good candidate for safer Li-ion batteries [16,17]. Yamaki et al. studied the thermal stability of fluorinated ester electrolytes with and without lithium metal and the positive electrode material at the charged state. According to DSC measurement, LiPF<sub>6</sub>/methyl difluoroacetate also showed the best stabilization with both lithium metal and Li<sub>0.5</sub>CoO<sub>2</sub> [18].

Trifluoroethyl aliphatic carboxylates, a member of the fluorinated aliphatic carboxylates family, are usually synthesized by liquid phase esterification. Conventional esterification always involves strong acid catalysts such as H<sub>2</sub>SO<sub>4</sub>, HCl, HF, H<sub>3</sub>PO<sub>4</sub> and ptoluene sulfonic acid, etc. These acids are corrosive, and the neutralization of the excess acid after the reaction may pollute the environment. Furthermore, the side reaction caused by strong acid catalysts may generate acidic impurities which are harmful for lithium-ion batteries. In contrast, using solid-state catalysts in liquid phase esterification is one way of avoiding the problems above, and the catalysts could be easily separated from products by simple filtration. Hence, considerable attention has been paid to the heteropolyacid catalysts for the esterification reactions, such as  $H_4SiW_{12}O_{40}$ · $nH_2O$ , etc. [19,20] However, high cost prohibits their practical use. As alternative catalyst, hydrogen ion exchange resin has low cost and high efficiency for esterification reactions.

In this paper, a series of trifluoroethyl aliphatic carboxylates with different carbon-chain lengths in acvl group were prepared by modified one-step synthesis, using aliphatic carboxylic acid and trifluoroethanol as the raw materials (molar ratio, 1.2:1). In order to enhance the yield of ester, hydrogen ion exchange resin was used as the catalyst, and silica gel was selected as the dehydrating agent to remove water during esterification process. Both hydrogen ion exchange resin and silica gel, in this reaction, could be dried for reuse, showing that the method presented in this paper could be economic and green. The structure characterizations including FTIR, <sup>1</sup>H NMR and GC–MS, revealed that the final products had high purity. By adding the trifluoroethyl aliphatic carboxylates into 1 M LiPF<sub>6</sub>/ EC + EMC (1:4) electrolyte as co-solvents, the electrochemical performances of graphite electrode at low temperature were greatly improved. Further EIS measurements indicated that the improvement was related to the decreased surface film resistance ( $R_{SEI}$ ) with the addition of co-solvents.

## 2. Results and discussion

Trifluoroethyl aliphatic carboxylates were synthesized by a modified one-step approach using aliphatic carboxylic acid and trifluoroethanol as the raw materials (molar ratio, 1.2:1). After drying over anhydrous MgSO<sub>4</sub> and 4 Å molecular sieves, the moisture contents of products were controlled at a level of less than 20 ppm, which could meet the requirements of electrolyte for lithium-ion batteries. The final yield could reach about 85%. The four products, trifluoroethyl acetate (CH<sub>3</sub>COOCH<sub>2</sub>CF<sub>3</sub>), trifluoroethyl *n*-butyrate (CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>2</sub>CF<sub>3</sub>), trifluoroethyl *n*-hexanoate (CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>COOCH<sub>2</sub>CF<sub>3</sub>) and trifluoroethyl normal-octanoate acid (CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>COOCH<sub>2</sub>CF<sub>3</sub>) were denoted as TFEA, TFENB, TFENH and TFENO, respectively.

### 2.1. Chemical structure characterization

The FTIR spectra of TFEA, TFENB, TFENH and TFENO samples are shown in Fig. 1; at the same time the attribution of the main absorption peaks are listed in Table 1.

- (1) In the wave number region of 3000–2815 cm<sup>-1</sup>, all the peaks are attributed to the C–H bond stretching. In TFEA molecule, due to the strong electron-withdrawing effect of the C=O group, there is no marked peak in this region attributed to stretching vibration of –CH<sub>3</sub> at  $\alpha$ -site of C=O group. With the increase of the carbon-chain length in acyl group, the electronwithdrawing effect of the C=O group is gradually weakened. For this reason, in TFENH and TFENO, peaks attributed to C–H stretching vibration of long acyl group gradually become significant, and at the same time move to lower wave number.
- (2) The strong and sharp absorption peak at  $1790-1740 \text{ cm}^{-1}$  could be assigned to the C=O group stretching. This peak is shifted to a lower wave number as the alkyl group in the structure increases, which can be explained by the stronger electron repulsive effect in longer alkyl group.
- (3) There are two sharp strong absorption peaks at 1200–1050 cm<sup>-1</sup>, which can be indexed to the stretching vibration of C–O–C in ester group. Peaks at 1200–1130 cm<sup>-1</sup> with higher intensity and strong sensitivity on the length of the carbon-chain in acyl group are attributed to the anti-symmetric stretching vibration. The wave number of these peaks gradually decreased



Fig. 1. FTIR spectra of the products.

Table 1					
Attribution of absorption	peaks	in	FTIR	spectra.	

Attribution	TFEA	TFENB	TFENH	TFENO	More information
Stretching vibration of C–H in acyl group	_	2976	2962	2960	Symmetrical stretching vibration of C–H in $\beta$ -site
		2882	2937	2932	Symmetrical stretching vibration of C–H in –CH <sub>2</sub> –
			2876	2860	Symmetrical stretching vibration of C–H in terminal –CH <sub>3</sub>
Stretching vibration of C=O	1782	1767	1760	1760	
Stretching vibration of C-O-C	1185	1175	1169	1169	Anti-symmetrical stretching vibration of C-O-C
	1090	1104	1110	1110	Symmetrical stretching vibration of C-O-C
Deformation vibration of C–H	1411	1411	1411	1411	Deformation vibrations in O-CH <sub>2</sub> -CF <sub>3</sub>
	976	976	976	976	External deformation vibrations of C-H
C-F stretching vibration	1290 1225	1290	1290	1290	

with the increasing carbon-chain length. The peaks at 1130– 1050 cm<sup>-1</sup> with lower intensity belong to the C–O–C symmetric stretching vibration. With the extension of the carbon-chain, the peaks move to higher wave number gradually and ultimately overlap with the peak at 1200–1130 cm<sup>-1</sup>.

(4) The peaks at 1411, 1290 and 976 cm<sup>-1</sup> are attributed to the deformation vibrations of  $-CH_2-$ , the stretching vibrations of C-F in  $-CF_3$ , and the external deformation vibrations of C-H in trifluoro-alcohol group, respectively. Stretching vibrations of C-F in  $-CF_3$ , often form multi-bands and peak group with high intensity from 1350 to 1120 cm<sup>-1</sup> [21]. These peaks in the FTIR spectra of TFEA, TFENB, TFENH and TFENO all hold at the identical wave number, for the same alcohol group  $-O-CH_2-CF_3$  and similar chemical environment in molecules of the four esters.

<sup>1</sup>H NMR spectra of the four products are shown in Fig. 2. There are quartets with the chemical shift between 4.50 and 4.43 ppm in

the <sup>1</sup>H NMR spectra of the four fluoro-esters respectively, which can be ascribed to the protons in  $-O-CH_2-$  group. As TFEA, TFENB, TFENH and TFENO have the same trifluoro-alcohol group  $-O-CH_2-$ CF<sub>3</sub> which stays in similar chemical environment, the corresponding chemical shift of the protons in  $O-CH_2-$  structure is identical. Due to the strong electronegativity of the oxygen atoms and electron withdrawing effect of the  $-CF_3$  group, the shielding effects of protons can be reduced, and then higher chemical shift ( $\delta$  values: 4–5 ppm) will be gained in  $-O-CH_2-$  group. Further, this peak split into a quartet, which is affected by the three <sup>19</sup>F atoms in consecutive  $-CF_3$  group.

According to Fig. 2, peaks at 2.50–2.00 ppm can be ascribed to the protons in  $\alpha$ -site C–H of the C=O group. As shown in Fig. 2a, a sharp single peak emerged at 2.15 ppm in <sup>1</sup>H NMR spectrum of TFEA, because there is only one methyl at the  $\alpha$ -site of the C=O group. By peak integration lines, atomic ratio of protons in trifluoro-alcohol group and  $\alpha$ -CH<sub>3</sub> could be determined; therefore, we could conclude that the molecule structure formula of TFEA



Fig. 2. <sup>1</sup>H NMR spectra.

sample is CH<sub>3</sub>COOCH<sub>2</sub>CF<sub>3</sub>. But in TFENB, TFENH, TFENO molecule structures, there is a methylene (-CH<sub>2</sub>-) at the  $\alpha$ -site of the C=O group. As another -CH<sub>2</sub>- stay at the  $\beta$ -site of C=O group, so the peak related to protons in  $\alpha$ -CH<sub>2</sub> will split into a triplet. As a result, sharp triplets at 2.39–2.42 ppm in <sup>1</sup>H NMR spectra of TFENB, TFENH and TFENO can be seen in Fig. 2b,c and d.

As shown in Fig. 2b,c and d, sharp multiplets at 1.75–1.60 ppm can be attributed to protons in  $-CH_2-$  at the  $\beta$ -site of the C=O group. In TFENB molecule structure, as there are one and one terminal-CH<sub>3</sub> ( $\gamma$ -site of the C=O group) close together, the peak related to protons in  $\beta$ -CH<sub>2</sub>– will split into a sextet; in TFENH and TFENO structure, the  $\beta$ -CH<sub>2</sub>– is next to the  $\alpha$ -CH<sub>2</sub>– and  $\gamma$ -CH<sub>2</sub>–, respectively. For this reason, the peak related to protons in  $\beta$ -CH<sub>2</sub>– will split into a quintet. With the carbon-chain extension in acyl groups, electron repulsive effect of  $\gamma$ -CH<sub>2</sub>– is increasing, which leads to the enhancement of the shielding effect in  $\beta$ -CH<sub>2</sub>– group. So the multiplets related to  $\beta$ -CH<sub>2</sub>– values could move to lower chemical shifts.

As shown in Fig. 2b, c and d, sharp split triplets below 1.00 ppm are ascribed to protons in terminal methyl ( $-CH_3$ ) of *n*-butyryl, *n*-caproyl and *n*-capryl group for the consecutive methylene. AS the weak shielding effect, the chemical shift value is close to the internal standard (TMS). With carbon-chain extension in the acyl group, terminal  $-CH_3$  could get less electron withdrawing effects from C=O group. Thus, shielding effects of terminal  $-CH_3$  become stronger, and the triplets move to lower chemical shift.

As shown in Fig. 2c and d, a series of broad peaks at 1.40–1.20 attributed to the protons in several –CH<sub>2</sub>– groups between  $\beta$ -CH<sub>2</sub>– and terminal –CH<sub>3</sub>. For the similar chemical environments, these multiplets couldn't be separated easily from broad peaks. But we are able to get atomic ratio of protons in different structure by the integration line. It can be concluded that the molecule structure formulas of major component of TFENB, TFENH, TFENO samples are CH<sub>3</sub>(CH<sub>2</sub>)<sub>2</sub>COOCH<sub>2</sub>CF<sub>3</sub>, CH<sub>3</sub>(CH<sub>2</sub>)<sub>4</sub>COOCH<sub>2</sub>CF<sub>3</sub> and CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>COOCH<sub>2</sub>CF<sub>3</sub>, respectively.

According to Table 2, with the acyl carbon-chain extension from TFEA to TFENO, the melting points, boiling points, and the refractive indexes are increased gradually. TFEA, TFENB and TFENH all have very low freezing point (<197 K). Meanwhile, at both room temperature and low temperatures, they have good mutual solubility in ethyl methyl carbonate (EMC), which is one of the main solvent components in lithium-ion battery electrolyte. But TFENO only shows partial solubility in EMC at room temperature. When temperature was below 263 K, phase separation would be occurred between TFENO and EMC. For this reason, only TFEA, TFENB and TFENH may be suitable as low temperature co-solvents of lithium-ion battery electrolyte.

From the physical properties of aliphatic carboxylic acid (reactants) and aliphatic carboxylate (products) listed in Table 2, we can see that  $\text{RCOOCH}_2\text{CF}_3$  could be easily separated from RCOOH by distillation as they have quite different boiling points.



Fig. 3. GC-MS spectra of TFEA samples.

GC-MS spectra have been used to further analyze the purities of products and the types of impurities, as shown in Figs. 3-5. It can be seen from Fig. 3, TFEA sample contains two components. By contrast to standard mass spectra, the tiny peak whose retention time arrives at 1.5 min is attributed to the CF<sub>3</sub>CH<sub>2</sub>OH impurity. But there is no standard mass spectrum that could match the prominent peak related to the major constituent whose retention time arrives at 1.7 min. Analysis of mass spectrometry is shown in Table 3. The molecular weight of the main component is about 142. Connecting with <sup>1</sup>H NMR and MS spectrum analysis it can be speculated that the peak at 1.7 min is attributed to CH<sub>3</sub>COOCH<sub>2</sub>CF<sub>3</sub>. By peak area ratio, it can be determined that the purity of TFEA sample is about 98%. However, due to the close boiling point, it is difficult to separate CF<sub>3</sub>CH<sub>2</sub>OH from TFEA completely by rectification. There are reactive hydrogen atoms in the  $\alpha$ -CH<sub>3</sub> (pK<sub>a</sub> = 12.5) [22], which could react with Li<sub>x</sub>C on graphite negative electrode and affect the cycle performance of lithium-ion battery. Therefore, it is essential for TFEA sample to remove the CF<sub>3</sub>CH<sub>2</sub>OH impurity before adding it to the lithium-ion battery electrolyte as a cosolvent. We have selected CaH<sub>2</sub> to remove impurities with hydroxyl group. After rectification, CF<sub>3</sub>CH<sub>2</sub>OH impurity could be removed from TFEA sample and meet the requirements of cosolvent, which can be confirmed by gas chromatogram.

From the gas chromatogram in Fig. 4, the purity TFENB sample is 99.1%, but also contains trace impurities. Compared the standard mass spectrum, main peak at 4.0 min is attributed to the TFENB,

Table 2	1								
Some p	hysical	properties	of the	reactants	and	RCOOCH <sub>2</sub> CF	31	orodu	cts

Reactant		B.p./K		M.p./K	n <sub>D</sub> (293 K)
CF <sub>3</sub> CH <sub>2</sub> OH		346.6		228.0	1.2907
CH <sub>3</sub> COOH		390.9		289.6	1.3716
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>2</sub> COOH 436.5			265.1	1.3991	
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOH 478.0			1.4170		
CH <sub>3</sub> (CH <sub>2</sub> ) <sub>6</sub> COOH 512.3		512.3		1.4268	
RCOOCH <sub>2</sub> CF <sub>3</sub>	MWt B.p./K		M.p./K	n <sub>D</sub> (293 K)	Solubility in (EMC)
TFEA	TEA 142.08 350.0		<193.0	1.3038	Mutual solubility
TFENB	FENB 170.13 385.0		<193.0	<193.0 1.3436	
TFENH	198.18	423.0	196.8	1.3798	Mutual solubility
TFENO	226.24	463.5	232.5	1.3808	Partial solubility



Fig. 5. GC-MS spectra of TFENH samples.

Table 3Mass spectrum analysis of TFEA sample (t = 1.7 min).

M/Z	Species
142 122 83 69 63	CH <sub>3</sub> COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup> CH <sub>3</sub> COOCH-CF <sub>2</sub> <sup>+</sup> $^{\bullet}$ CH <sub>2</sub> CF <sub>3</sub> <sup>+</sup> $^{\bullet}$ CF <sub>3</sub> <sup>+</sup> CH <sub>3</sub> COO $^{\bullet+}$
00	engeoo

but the negligible peak at 5.7 min may be ascribed to the 4-heptanone impurity, which exists in starting material *n*-butyric acid. Unlike TFEA samples,  $CF_3CH_2OH$  can be completely separated from TFENB by distillation and not be found in the gas chromatogram for the larger boiling points difference (about 38 K). The  $pK_a$  value of  $\alpha$ -H in the aliphatic ketone carbonyl (in DMSO) is about 27.1–28.3 [23], which are far less than that of



Scheme 1. Possible reaction between aliphatic ketone and lithium or Li<sub>x</sub>C<sub>6</sub>

alcohols, at room temperature. However, there is equilibrium between ketoform and enolic form in aliphatic ketone [22], and the hydroxyl group from enolic form may react with  $\text{Li}_xC_6$ , as shown in Scheme 1. Therefore, the synthetic product was contacted with lithium metal at reflux temperature for 5 h to eliminate the 4-heptanone impurity. After redistillating, middle distillate was selected as a co-solvent of lithium-ion battery electrolyte.

As shown in Fig. 5, the purity of TFENH sample is about 98.3%, containing one impurity. By the standard mass spectrum we could make a judgment that the impurity peak at 3.8 min may be attributed to TFENB. This impurity may stem from the small amount of *n*-butyric acid in the analytical reagent *n*-caproic acid. Main peak at 5.9 min could not be ascribed to any standard mass spectrum, whose analysis is shown in Table 4. The molecular weight of the corresponding component is about 198. Connecting MS and <sup>1</sup>H NMR analysis, it can be confirmed that the peak at 5.9 min is attributed to TFENH. Low content of impurities TFENB could not significantly affect the action of TFENH as a co-solvent of electrolyte.

## 2.2. Properties of the modified electrolyte with co-solvents

As a co-solvent, the purified product was added into original electrolyte 1 mol  $L^{-1}$  LiPF<sub>6</sub>/EC + EMC (1:4, vol). The obtained  $0.75 \text{ mol } L^{-1}$  $LiPF_{6}/EC + EMC + TFEA$ modified electrolytes  $(15:60:25, vol), 0.75 mol L^{-1} LiPF_6/EC + EMC + TFENB (15:60:25, vol))$ vol) and 0.75 mol  $L^{-1}$  LiPF<sub>6</sub>/EC + EMC + TFENH (15:60:25, vol) were presented in simplified form as electrolyte A, B and C. As a contrast, the base-line electrolyte 1 mol  $L^{-1}$  LiPF<sub>6</sub>/EC + EMC (1:4, vol) was named electrolyte D. In order to eliminate the influence of lower ECcontent and lower LiPF<sub>6</sub> concentration after adding co-solvent, two electrolytes composed by 1 mol  $L^{-1}$  LiPF<sub>6</sub>/EC + EMC (15:85, vol) and 0.75 mol  $L^{-1}$  LiPF<sub>6</sub>/EC + EMC (15:85, vol) was prepared and assigned as electrolyte E and F, which added the same volume of EMC instead of RCOOCH<sub>2</sub>CF<sub>3</sub> co-solvent. However, electrolyte E kept an equal salt concentration with base-line electrolyte. On the contrary, electrolyte F held a similar salt concentration in accord with three modified electrolytes (electrolyte A, B and C).

Table 4											
Mass	spectrum	analysis	of	TFENH	sample						
(t = 5.9)	min).										

M/Z	Species
198	CH <sub>3</sub> (CH <sub>2</sub> ) <sub>4</sub> COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup>
169	CH <sub>2</sub> (CH <sub>2</sub> ) <sub>2</sub> COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup>
155	CH <sub>2</sub> CH <sub>2</sub> COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup>
141	CH <sub>2</sub> COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup>
127	COOCH <sub>2</sub> CF <sub>3</sub> <sup>+</sup>
99	${}^{\bullet}\text{OCH}_2\text{CF}_3^+$
83	$^{\bullet}CH_2CF_3^+$
57	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> <sup>•+</sup>
43	$CH_3CH_2CH_2^{\bullet^+}$



Fig. 6. Temperature dependence of the viscosity.

Temperature dependence of the viscosity of base-line electrolyte and electrolyte with one co-solvent is shown in Fig. 6. It could be seen from the figure that the viscosity of the six electrolytes were all increased obviously below 278 K. However, electrolytes containing co-solvent (included RCOOCH<sub>2</sub>CF<sub>3</sub> or EMC) could clearly slow the increasing trend of viscosity at lowing-temperature. It might be ascribed to the lower content of EC which has a high viscosity. Viscosity of electrolyte E was a little higher than that of electrolyte F, it is concluded that higher concentration of LiPF<sub>6</sub> could slightly increase the viscosity. From electrolyte A, B, C and F, it could be found that trifluoroethyl aliphatic carboxylates are more suitable as the co-solvent to reduce the viscosity of electrolyte than aliphatic carbonate. Electrolyte A (with TFEA) exhibited the lowest viscosity increasing during the cooling process. From 298 K to 238 K, the viscosity of the electrolyte only increased four times. The viscosity is macro-reflection of internal migrating friction of solvent molecules in the electrolyte. Due to its smaller molecule-scale than that of TFENB or TFENH, and weaker solvent-solvent molecular interaction than that of linear carbonate, TFEA could reduce the viscosities of the electrolyte systems more obviously.



Fig. 7. Temperature dependence of the ionic conductivity.

Temperature dependence of the ionic conductivity of carbonate-based electrolytes and modified electrolytes with RCOOCH<sub>2</sub>CF<sub>3</sub> co-solvent is shown in Fig. 7, including the fitting curve by VTF equation [24-26]. Adapting to the lowering temperature, the conductivities of the six electrolytes were all decreased. The electrolyte D could perform a higher ionic conductivity above 223 K. Comparing electrolyte E with electrolyte F, a little higher salt concentration would be helpful to hold a larger ionic concentration at room temperature. But at low temperature. higher salt concentration means larger viscosity, which is not helpful to enhance the ionic conductivity. In contrast, the decreasing ionic conductivity of the electrolyte with RCOOCH<sub>2</sub>CF<sub>3</sub> co-solvent was slowed down significantly, comparing with that of the carbonate-based electrolyte (electrolyte A, B and C). In keeping with the temperature dependence of the viscosity, electrolyte A containing TFEA has a better performance, due to the lower viscosity at lower temperature. It could be conjectured that RCOOCH<sub>2</sub>CF<sub>3</sub> with shorter acyl group in molecules would participate in Li<sup>+</sup> solvation process and reduce the ionic radius of the solvated Li<sup>+</sup>, which could provide weaker internal friction in the fluid during the ionic migration.

According to the fitting results by VTF equation in Table 5,  $T_0$  of the three modified electrolytes were markedly lower than that of the carbonate-based electrolyte. Furthermore, the values of  $T_0$  went down with the decreasing of the number of carbon atoms in the co-solvents. At the same time, after trifluoroethyl aliphatic carboxylate co-solvents added, n values of modified electrolytes were close to zero, indicating that the mechanism of Li<sup>+</sup> migration in electrolyte A at low temperature was similar to that at room temperature. Ion-migration in modified electrolytes could be described by ionic atmosphere model in the test temperature range, which is related to the structure of Li<sup>+</sup> solvation.

Temperature dependence of ionic conductivity and viscosity of the modified electrolytes containing co-solvents suggests that trifluoroethyl aliphatic carboxylate with shorter carbon-chain in acyl group (such as TFEA) should be fit for the co-solvents to reduce the viscosity and enhance the ionic conductivity of the electrolyte at low temperature.

## 2.3. Electrochemical characterization

Fig. 8 shows the charge/discharge curves of graphite electrode in the carbonate-based electrolyte and three modified electrolytes at 0.2 C rate under different temperatures. As can be seen in Fig. 8a, the initial coulombic efficiency of the graphite in three carbonate-based electrolytes (electrolyte D, E and F) was slightly higher than that in the three modified electrolytes (electrolyte A, B and C) at 298 K, which suggested trifluoroethyl aliphatic carboxylate could cause a larger irreversible capacity loss than linear carbonate co-solvent. After five cycles, according to Fig. 8b, both of them had an identical coulomb efficiency above 99%, which indicated the electrolyte containing trifluoroethyl aliphatic carboxylate co-solvents could form effective passivation of graphite electrode but not affect the cycling performance of graphite at room temperature.

When tested at low temperature of 238 K, the charge capacity of graphite in base-line electrolyte (electrolyte D) dropped to about

Table 5Non-linear fitting result by VTF function.

Electrolyte	$T_0/K$	n	Α	$E_{\rm a}/{ m J}{ m mol}^{-1}$
Α	$122.8\pm5.5$	$-0.03\pm0.00$	$-0.86\pm0.09$	$3972\pm406$
В	$130.2\pm6.3$	$-0.02\pm0.00$	$-0.87\pm0.29$	$4207\pm616$
С	$132.2\pm9.2$	$-0.23\pm0.09$	$1.22\pm0.24$	$4473 \pm 534$
D	$156.9\pm13.0$	$-0.50\pm0.01$	$1.90\pm0.19$	$2970 \pm 153$
E	$152.5\pm13.8$	$-0.18\pm0.01$	$-1.53\pm0.06$	$2496 \pm 153$
F	$151.0\pm12.3$	$-0.12\pm0.01$	$-1.40\pm0.07$	$1739 \pm 115$



Fig. 8. Specific capacity - voltage curve at different temperature.

80% of that at 298 K. Electrolytes E and F with lower EC-content could provide higher Li<sup>+</sup> de-intercalation capacity at 238 K. By comparing electrolyte E with electrolyte F, it could be observed that higher salt concentration could present a little lower initiate polarizing voltage but a slightly smaller final capacity. In contrast, the capacity retention in electrolyte A, B and C could reach 85%, 92% and 95%, respectively. Furthermore, the typical charge potential was lowered from 0.95 V to 0.90 V, 0.80 V to 0.70 V by the addition of co-solvents. This contrast was magnified at 218 K, as we could see that the capacity retention of graphite in electrolyte F was only 50%, far lower than that in electrolyte B and C. Especially the capacity retention maintain at 92% in electrolyte C, which was the highest value reported so far as we know. At the same time, the charge potential was decreased from 1.30 V in electrolyte F to 0.89 V in electrolyte C. These data demonstrate that the addition of trifluoroethyl aliphatic carboxylate co-solvents in carbonate-based electrolyte can effectively improve the electrochemical performance of graphite at low temperature.

In order to gain further insight into the electrochemical mechanisms operating for the improvement, EIS measurements were conducted by discharging graphite to 0.1 V at five different temperatures (298, 278, 258, 238 and 218 K). As shown in Fig. 9, the Nyquist plots can be fitted by the equivalent circuit model comprising four parts: (i) lithium-ion transport in an electrolyte and electron transport in electrode ( $R_0$ ), (ii) lithium-ion transport in an SEI ( $R_{SEI}$ ), (iii) lithium-ion (charge) transfer at a graphite/ electrolyte interface ( $R_{ct}$ ), (iv) lithium-ion diffusion inside graphite

electrode. In this case, equivalent circuit which has been shown in Fig 9f as used for fitting the Nyquist plots [27–29].

At 298 K and 278 K, there were straight lines with an angle of about 60° from the  $Z_{\rm rm}$  axis at low frequency region, which refers to the Li<sup>+</sup> solid-phase diffusion. But at 258 K, 238 K and 218 K, Warburg impedance didn't appear notably in the Nyquist plots. The reason might be that the ability of lithium-ion diffusion inside graphite electrode was significantly decreased at low temperature. Lithium-ion diffusion inside graphite electrode should be presented below a much lower frequency. At every testing temperature, impedance in all-carbonate electrolytes (electrolyte E and F) was close to that in base-line binary electrolyte (electrolyte D). Electrolytes contained trifluoroethyl aliphatic carboxylates provided obviously lower impedance. The fitting results of the six ones have been listed in Table 6.

According to Table 6, when the cells were evaluated at one temperature (both room temperature and low temperature), it was observed modified electrolytes with RCOOCH<sub>2</sub> CF<sub>3</sub>co-solvents performed a higher  $R_0$  compared with the all-carbonate solution. Adapting to the increasing number of carbon atoms in the co-solvent structure,  $R_0$  was continuously raised. These results could be confirmed by the temperature dependences of the ionic conductivities of electrolytes in Fig. 7. It could be concluded that the co-solvent with long carbon-chain in acyl group was harmful to increase the ionic conductivities.

But the values of  $R_{SEI}$  were provided another order: when the impedance spectra of the cells containing modified electrolytes



Fig. 9. Nyquist plots of graphite electrode in every electrolyte at different temperature.

were compared to the three carbonate-based electrolytes at room temperature, the electrodes in contact with electrolyte A, B and C generally displayed low film polarization characteristics as determined from the low  $R_{SEI}$  values observed. Especially, electrode in electrolyte C containing TFENH with longer carbon-

chain performed the lowest  $R_{SEI}$  values among those in electrolyte B and A. When impedance measurements were performed on the cells at low temperatures, more dramatically lower film resistances were observed for the modified electrolyte containing cells. TFENH with longer carbon-chain could also helped to form a SEI

## Table 6

Fitting result of AC impedance spectroscopy.

Temperature/K	$R_0/\Omega$					$R_{\rm SEI}/\Omega$				
	298	278	258	238	218	298	278	258	238	218
Electrolyte A	2.6	3.7	5.5	7.2	13.8	18.7	42.0	87.3	324.4	3114.0
Electrolyte B	3.1	4.0	5.7	8.0	18.8	13.2	31.7	67.8	206.3	1854.0
Electrolyte C	3.7	6.1	8.2	11.7	21.5	8.6	24.7	36.9	128.1	538.3
Electrolyte D	2.5	3.2	4.4	6.4	11.7	32.9	68.1	267.9	728.8	6690
Electrolyte E	2.6	3.3	4.4	6.3	11.5	30.4	70.2	304.6	699.4	6809.2
Electrolyte F	2.9	3.5	4.5	6.4	10.8	31.3	69.3	288.7	705.2	6470.1



**Fig. 10.** Temperature dependences of SEI film conductivities  $(1/R_{SEI})$  at 0.1 V.

film with low polarization on the graphite electrode, for the lowest  $R_{SEI}$  values were obtained during the tests at 258 K, 238 K and 218 K.

Fig. 10 shows the temperature dependences (Arrhenius plots) of the SEI film conductivities  $(1/R_{SEI})$  at 0.1 V in all-carbonate and three modified electrolytes. The activation energies were evaluated from the slopes of the Arrhenius plots with the Arrhenius equation [30],  $\ln (1/R_{SEI}) = A - E_a/RT$ . The symbols A,  $E_a$ , R, and T denote the frequency factor, activation energy, gas constant, and absolute temperature, respectively. In three carbonate electrolytes, the activation energy was close to 35 kJ mol<sup>-1</sup>. However, electrolyte A, B and C gave a smaller activation energy of 33, 32, 27 kJ mol<sup>-1</sup>. Smaller activation energy suggests that it is much easier for the diffusion of lithium-ions in the SEI film. It could be conjectured that RCOOCH<sub>2</sub>CF<sub>3</sub> might change the mechanism of forming SEI film in the carbonate-based electrolyte. Although TFENH with long carbon-chain in acyl group isn't fit for reducing the viscosity of the electrolyte, it is helpful to form a better SEI film with higher Li<sup>+</sup> conductive ability.



Fig. 11. Schematic diagram of esterification reactor.

From Table 6, it was generally observed that the  $R_0$  and  $R_{SEI}$  were continuously increased upon going to lower temperatures in each electrolyte. But adapting to the decreasing of temperature,  $R_{SEI}$  was growing exponentially, which increased much faster than  $R_0$ . Comparing with the low temperature performances of the graphite electrode, a conclusion could be observed that the nature of the SEI layer on the graphite electrode plays a more significant role in determining the low temperature performance than the bulk resistivity of the electrolyte.

The composition and microstructure of SEI film in the modified electrolytes containing trifluoroethyl aliphatic carboxylate cosolvents has not been studied clearly. Further research on the formation mechanism is needed in the future.

## 3. Conclusions

- (1) Hydrogen ion exchange resin as a catalyst and silica gel drier as a de-hydration, a series of trifluoroethyl aliphatic carboxylates were prepared by one-step approach with different carbonchain length in acyl group.
- (2) By FTIR, <sup>1</sup>H NMR and GC–MS analysis, the products have the expected chemical structures and high yields by the synthetic route. Species and structures of the impurities in the products were confirmed and then feasible approaches for purification were founded.
- (3) Temperature dependence of ionic conductivity and viscosity of the modified electrolytes containing co-solvents suggests that trifluoroethyl aliphatic carboxylate with shorter carbon-chain in acyl group (such as TFEA) should be fit for the co-solvents to reduce the viscosity and enhance the ionic conductivity of the electrolyte at low temperature.
- (4) According to the Li<sup>+</sup> de-intercalation curves of the graphite electrode and analysis of AC impedance spectroscopy, modified electrolyte containing TFENH could improve the low temperature performances of graphite electrode obviously. It could be confirmed that the nature of the SEI layer on the graphite electrode plays a more significant role in determining the low temperature performance than the bulk resistivity of the electrolyte.

## 4. Experiments

## 4.1. Reagents

Trifluoroethanol, acetic acid, *n*-butyric acid, *n*-hexanoic acid, *n*-octanoic acid, sodium ion exchange resin, NaHCO<sub>3</sub>, anhydrous MgSO<sub>4</sub>, 4 Å molecular sieves, CaH<sub>2</sub>, silica gel, hydrochloric acid, ethanol, all the reagents were of analytical grade, and directly used for the synthesis reaction without any treatment. Original electrolyte 1 mol  $L^{-1}$ LiPF<sub>6</sub>/EC + EMC (1:4) was provided by Novolyte Company.

## 4.2. Co-solvent synthesis

Preparation of hydrogen ion exchange resin catalyst: sodium ion exchange resin about 5 g was mixed with 50 mL 1 mol  $L^{-1}$  HCl. After stirring for 6 h, ion exchange resin was washed by deionized water till the pH value is about 7, and then dried at 350 K for 5 h.

The schematic diagram of esterification reaction device is shown in Fig. 11. 0.1 mol CF<sub>3</sub>CH<sub>2</sub>OH was added into the dropping funnel, and 50 g silica gel was added into the Soxhlet's extractor. Three-necked flask (100 mL volume) with 2 g hydrogen ion exchange resin and 0.12 mol fatty acid was heated to the reflux temperature with magnetic stirring. After adding CF<sub>3</sub>CH<sub>2</sub>OH drop by drop, the mixture was heated at reflux for about 6 h, and then Soxhlet's extractor was replaced by the distillation apparatus. The intermediate fraction was collected as the primary product, and added NaHCO<sub>3</sub> powder until no gas emission. Then collected filtrate was added an appropriate amount of anhydrous MgSO<sub>4</sub>, and dried for 24 h. Purified RCOOCH<sub>2</sub>CF<sub>3</sub> were obtained by collecting the intermediate fraction during distillation. Finally, activated 4 Å molecular sieves were added into the distilled RCOOCH<sub>2</sub>CF<sub>3</sub>.

The moisture content of the product was measured by the Karl-Fisher coulometric moisture analyzer (831 KF Coulometer, Metrohm). Boiling point was observed by distillation. Moiling point was tested in low temperature environment which was provided by cryostat circulation tank (YU HUA, DFY-80, minimum temperature 193 K). Refractive index was measured by using an Abbe refractometer (2 W Abbe refractometer) at 293 K.

### 4.3. Structure characterization

FTIR spectrum was obtained by Fourier Transform Infrared Spectrometer (Bruke V70, KBr tablet, wave number 4000– $600 \text{ cm}^{-1}$ , resolution 4 cm<sup>-1</sup>)

<sup>1</sup>H NMR characterization was dependent upon the Fourier transform NMR spectrometer (Bruker AVANCE 600), using CDCl<sub>3</sub> as a solvent and tetramethylsilane (TMS) as the internal standard.

MS–GC spectrum was characterized in gas chromatography– mass spectrometry (Agilent Technologies 7890A GC System and 5975C inert MSD), using He as eluant gas. The temperature in vaporizer was set 30 K higher than the boiling point of the sample.

## 4.4. Electrochemical characterization

As a co-solvent, the purified product was added into original electrolyte 1 mol L<sup>-1</sup> LiPF<sub>6</sub>/EC + EMC (volume ratio 1:4) in a volume ratio of 3:1, to obtain a new electrolyte whose composition could be approximately represented by 0.75 mol L<sup>-1</sup> LiPF<sub>6</sub>/EC + EMC + RCOOCH<sub>2</sub>CF<sub>3</sub> (volume ratio 15:60:25). The low-temperature ionic conductivity of the electrolyte was measured by conductivity meter (RIDAO, DDS-307), using conductivity electrode (conductivity cell constant was about 1, which was calibrated by 0.1 mol L<sup>-1</sup> KCl solution before the experiment). The viscosity of the electrolyte was tested by Ubbelohde viscometer in a constant temperature water bath (298 K) and cryostat circulation tank (<273 K).

The graphite electrode was prepared by combining 80 wt.% graphite negative electrode material (AGP-8, BTR New Energy materials INC.), 10 wt.% acetylene black, and 10 wt.% polyvinylidene fluoride (Kynar 741, Arkema Inc., USA) in N-methyl-2pyrrolidone. Then the slurry was uniformly coated on a copper foil (highly pure) and fully dried in vacuum oven. A separator (Celgard 2320) was placed between the cathode and the anode. Lithium foil (China Energy Lithium Co., Ltd., China) was used as counterelectrode. The CR2016 type (20 mm diameter, 1.6 mm thick) graphite/lithium cells were assembled in a high purified argonfilled dry box. Charge and discharge performances were tested by LAND testing system (CT2001-A). At 298 K, both charge and discharge performances of graphite electrodes were measured at 0.2 C rate. The Li<sup>+</sup> de-intercalation test at low temperature (238 or 218 K) was carried out in the following procedure: firstly, the graphite-Li cells were discharged to 0.02 V at 298 K; secondly, the batteries were held at low temperature for 2 h, and then charged to cut-off voltage 1.5 V at 0.2 C rate.

AC impedance spectroscopy was carried out by Versa STAT MC (Princeton) over a frequency range of 10<sup>6</sup>–0.1 Hz with an applied

ac voltage of 10 mV. Measurements were conducted for each cell after the formation process (after five cycles), the polarization potential of the graphite electrode was kept on 0.1 V. The analysis of resultant Nyquist plots was conducted by Zview software.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.02. 006http://dx.doi.org/10.1016/j.jfluchem.2014.02.006.

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