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Analysis on Extraction Behaviour of Lithium-ion Battery Electrolyte Solvents in Supercritical CO_2 by Gas Chromatography

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The extraction behavior of Lithium-ion battery electrolyte components has been investigated in diverse parameters for supercritical CO_2. The components, containing ethylene carbonate, dimethyl carbonate and ethylmethyl carbonate that are commonly used in lithium ion battery electrolyte, have been quantitated by gas chromatography with flame ionization detector based on internal standard calibration. The extraction behavior, yield and order of extract components have shown the difference caused by the varied physical properties under selected extraction parameters--extraction pressure (15 to 35 MPa), temperature (30 to 50 °C) and time (25 to 65 min). In addition, the polarity and the melting point of carbonate has a strong influence on composition during the trapping process.

Keywords: Carbonate-based electrolyte, Extraction behavior, Supercritical CO_2.

1. INTRODUCTION

Lithium-ion batteries (LIBs) have been used widely in electric vehicles (EVs) due to their high energy density, low self-discharging and low memory effects [1-3]. Two chief issues--the gradual depletion of petroleum resources and the impact of greenhouse gas emissions on climate change, have generated considerable interest in the recent years on the research and development of EVs. A number of nations are introducing related policies to promote the development of EVs, at the same time, many automobile manufacturers have launched their own EVs, such as Nissan Leaf, Chevrolet Volt and Tesla Model S [4, 5]. Although, so far, EVs are not widely used yet, it is predicted that, the consumption of LIBs will explode with the popularity of EVs in future years [6]. The rapid growth of LIBs demand generates tremendous spent LIBs in both production process and end-of-life.

The spent LIBs contain lots of valuable components, such as cathode active material, aluminium (cathode current collector and LIBs casing), copper (anode current collector) and organic electrolyte [7-9]. More importantly, some of the battery components are considered toxic [10], including HF [11,12], organophosphates [13,14] and alkyl fluorophosphates [15-17]. Discarding spent LIBs into municipal solid waste will definitely pollute the soil and underground water. Therefore, the spent LIBs have to be recycled regarding for economic sustainability and environmental protection. Currently, various methods have been developed to recycle the valuable metals of spent LIBs, only a few studies have focused on the recovery of electrolyte [18-23]. One of the first reports in this field was made by Schmidt et al. in 2003. They dissolved out the organic carbonate and conducting salt with organic solvent. The organic solvent can be recovered through reduced pressure distillation, and the leaving solution containing organic carbonate and conducting salt can be stored for reuse [24]. It is generally believed that the conventional solvent extraction and distillation processes have several disadvantages, such as leaving solvent residue and giving low yields. Extraction by supercritical CO_2 can be considered as an alternative process because of no solvent residue in the product and considerable extraction yields. Several researchers have examined the suitability of supercritical CO_2 for the extraction of organic carbonate based electrolytes from spent LIBs. The patent of sloop was the first to introduce supercritical fluids (including supercritical CO_2) extraction for removing the electrolyte from energy storage devices [25]. Furthermore, we have performed an optimization of extraction condition and analyses of extract composition in our previous work [26]. Recently, extraction of LIB electrolytes with supercritical helium head pressure CO_2 was reported by Grützke and his colleagues [27]. In their latest work, the extraction behaviour of supercritical and liquid carbon dioxide was investigated, and the influences of several co-solvents on liquid CO_2 extraction procedure were demonstrated [28]. Time-dependence of extraction progress was illustrated in this report, but extraction behaviour changing over pressure and temperature, which are two most important factors for supercritical extraction, was not mentioned. To make clearer explication of the extraction of electrolyte as a whole, it is necessary to understand the extraction behaviour of particular components in this electrolyte. A typical experiment should use electrolyte as the study object. But due to hydrophobic and thermophobic nature of hexafluorophosphat, the decomposition of $LiPF_6$ may bring bias and imprecision in quantitative analysis [29]. Therefore, it is reasonable to use the same mixed carbonate compositions in our investigation. Furthermore, no data have been reported in the literature about the influence of physical properties of carbonate on supercritical extraction behaviour of mixed carbonate solvents.

To further investigate the extraction of LIBs electrolyte in supercritical CO_2, we design a series of experiments to quantitatively analysis the composition of the particular electrolyte components in the pressure, temperature and time dependency of the extraction procedure. The compositions of extracts were quantitated by internal standard calibration based on gas chromatography with a flame ionization detector. The goal of this contribution is to provide a technical guidance for lithium ion battery electrolyte recovery through summarizing the inherent correlation between physical properties of carbonate and extraction regulation of mixed carbonate solvents under selected supercritical conditions.

2. EXPERIMENTAL

2.1. Materials

Dimethyl carbonate (DMC, 99.9%), ethylmethyl carbonate (EMC, 99.9%), ethylene carbonate (EC, 99.9%) and Diethyl carbonate (DEC, 99.9%) were used as received from Tinci Materials Technology Co., Ltd. (Guangzhou, China). For the convenience of our study, carbonate mixture was prepared based on TC-E201# electrolyte. The TC-E201# is a representative of commercial lithium-ion battery electrolytes, which consists of 1 M $LiPF_6$ and ethylene carbonate/dimethyl carbonate/ethyl methyl carbonate (EC/DMC/EMC with a volume ratio of 1:1:1) and most widely deployed in LIBs based on lithium cobalt oxide and its composites by excellent performance properties. Acetonitrile (99.9%, HPLC grade) was obtained from Dikma Technologies Inc. (California, USA). Commercial grade CO_2, supplied by Liming Gas Co., Ltd. (Harbin, China), was used with the purity of more than 99.95%. The JH ordinary type polypropylene separator was purchased from Jinhui Hitech Optoelectronic Material Co., Ltd. (Foshan, China), which was used as adsorbent of electrolytes.

2.2. Supercritical CO_2 extraction procedure

The Spe-ed SCF Prime supercritical CO_2 extraction system used in these studies was purchased from the Applied Separations, Inc.. Three reference compounds were mixed in dry environment, and stored under the ordinary temperature and away from light. 2g mixed solution was adsorbed in the lithium-ion battery separator, and enclosed into the extraction vessel in a dry room with a humidity of less than 20 ppm. The extraction vessel was installed in the constant temperature heater and connected to the extraction system. To study the influence of physical properties of mixed carbonate solvents on the particular component extraction behaviour, a series of experiments was designed to conduct under the pressure from 15 to 35 MPa, the temperature from 30 to 50 °C and the dynamical extraction time from 25 to 65 min. The extracts were then collected into a sample vial at a constant flow rate of 4.0 L/min. The collected sample was tightly sealed and stored in a refrigerator at 4 °C.

2.3. Preparation of standard and sample solutions

As an accurate and precision method, the internal standard calibration was employed for quantitating concentration of each carbonate in mixed solution. A schematic diagram of the method is shown in Fig. 1. Standard stock solutions DMC, EMC and EC were prepared separately by dissolving 1 g of each compound in 100 mL acetoni4trile. A stock solution of DEC (10 mg/mL) internal standard was prepared in acetonitrile. Various aliquots of the standard solutions were taken, the internal standard solution added, and further diluted to 10 mL with acetonitrile to reach the concentration range of 0.2~0.7 mg/mL for DMC, EMC and EC respectively. Triplicate 0.1 μL injections were made for each concentration and chromatographed under the specified chromatographic conditions described in detail later. The peak area ratios of analyte versus internal standard were plotted presenting the corresponding concentrations. Linear relationships were obtained. Table 1 lists the concentration range for calibration curves, regression parameters and limits of detection (LOD) of each analyte.

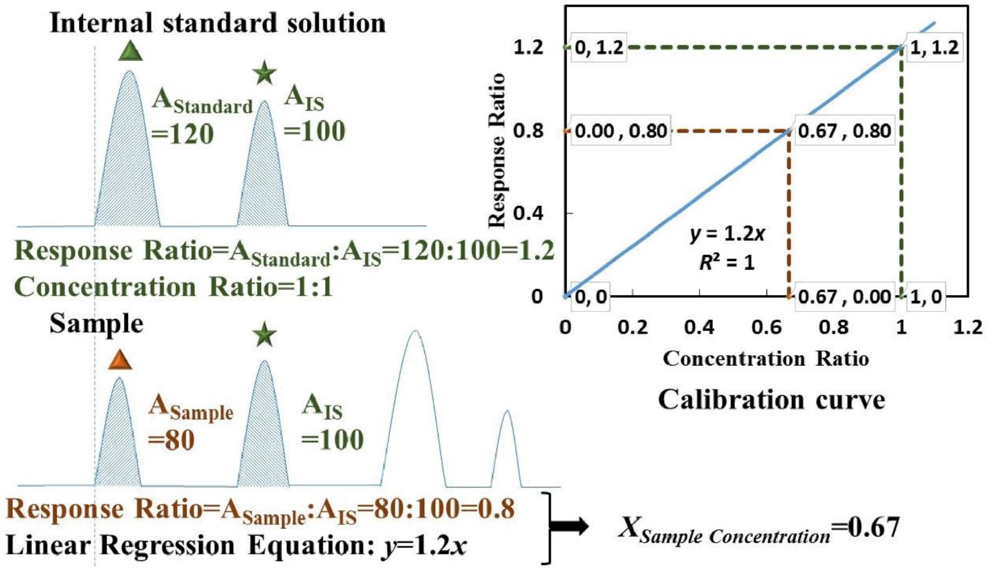

Figure 1. Schematic diagram of quantitate by internal standard calibration. The internal standard solution to be tested was first profiled by GC-FID. The peak area of the standard and internal standard was recorded as $A_{Standard}$ and A_{IS}, respectively. Internal standard solutions were subsequently spiked into the extract. Their peak areas were recorded again as A_{Sample} and A_{IS}.

Table 1. Typical linear regression data for the analysis of DMC, EMC and EC in a spiked mixture.

Analyte	Concentration range (mg/ml)	R^2 (n=6)	Slope	Intercept	LOD (s/n>3) (μg/ml)
DMC	0.2~0.7	0.99317	0.00124	0.11307	56
EMC	0.2~0.7	0.99503	0.00175	0.1585	41
EC	0.2~0.7	0.99885	0.000260	0.09776	217

The collected samples were weighed to calculate the yield of extraction. A collected sample (500 μL) was added into 300 μL internal standard stock solution and diluted to 250 mL with acetonitrile before being injected into the GC-FID system. The peak area ratios of each analyte were used to determine the amount of each analyte in the collected sample using the slope and intercept data generated from the linear regression analysis of calibration data.

2.4. GC-FID analysis

In this work, chromatographic analysis was performed on an Agilent 7890A (Agilent Technologies, China) GC system equipped with a G4513A autosampler system, a flame ionization detector and a 5975C mass spectrometry detector. The instruments were controlled by the MSD ChemStation G1701EA E.02.02.1431GC/MS software.

Chromatographic separation was achieved using a HP-5MS 5% phenyl methyl silox capillary column (30 m × 250 μm × 0.25 μm), purchased from Agilent Technologies (Beijing, China). Helium (purity 99%) was the GC carrier gas and maintained at a constant flow rate of 1.0 mL/min. Injection of 0.1 μL extract was accomplished in splitless injection mode operated at 250 °C. The oven temperature profile was ramped from 35 to 250 °C as follows: after holding the initial temperature (35 °C) for 5 min the temperature was increased with a rate of 30 °C /min up to 85 °C and hold for 5 min; subsequently the temperature was increased up to 250 °C with a rate of 30 °C/min and then held for 1 min. The resulting total run time was 19.4 min.

3. RESULTS AND DISCUSSION

Each component in the mixed solvents has great different extraction behaviour, which can be understood intuitively through the measurement of the content variation. As with extraction yield, content variation also depends on rate-limiting factors, which include temperature, pressure and other factors. A systematic study on the composition variation of the components in the mixed carbonate solvents was conducted to demonstrate the influence of physical properties of carbonate on supercritical extraction behaviour of mixed carbonate solvents under extraction parameters in term of pressure, temperature and time. In the experiment process, a single factor was evaluated while all others were kept constant.

The standard deviation (*SD*) of extract quantity was calculated by following expression:

$$SD = \sqrt{\frac{1}{n-1}\sum_{i=1}^{n}(x_i - \bar{x})^2} \quad (1)$$

where in, x_i is the experimental value of extract quantity, $\bar{x}$ is the average value of extract quantity and *n* is the number of experimental data.

3.1. Effect of extraction pressure

Pressure is one of the most critical physical parameters with both theoretical and practical implications in supercritical CO_2 extraction [30]. The effect of pressure on the components acquired from mixed carbonate solvents in the supercritical CO_2 extraction was examined at five levels in the range of 15~35 MPa. The chromatogram (GC-FID) of pressure influence experiments reveal that the carbonate mixture extraction is a pressure dependency procedure compared with the effect of temperature and time. From the aspect of pressure-resolved, the large amount of the extract is obtained in the initial stage with low experiment pressure, but overall extraction yield is gradually enhanced with the increase of extraction pressure (Fig. 2). Composition analysis of the extracts indicate that the extraction yields of DMC and EMC are of the same order of magnitude and maintain relatively constant amount (about 79.78±1.35% and 76.33±1.29% respectively). The increase in the overall extraction yield (from 81.09±1.48% to 85.78±1.34%) are mainly contributed by EC extraction yield enhancement (from 89.62±1.46% to 98.19±1.26%, Fig. 3). This can be explained by regulating effect of pressure on polarity of supercritical CO_2. Supercritical CO_2 is a relatively non polar solvent, while increasing the pressure could enhance the polarity of supercritical CO_2 within a certain scope [31]. Since EC is a cyclic carbonate and thus more polar than linear carbonate like DMC and EMC, the enhancement of supercritical CO_2 polarity can help to improve solubility of EC in it. DMC and EMC are nonpolar carbonate and therefore are easily soluble in supercritical CO_2 at low pressure.

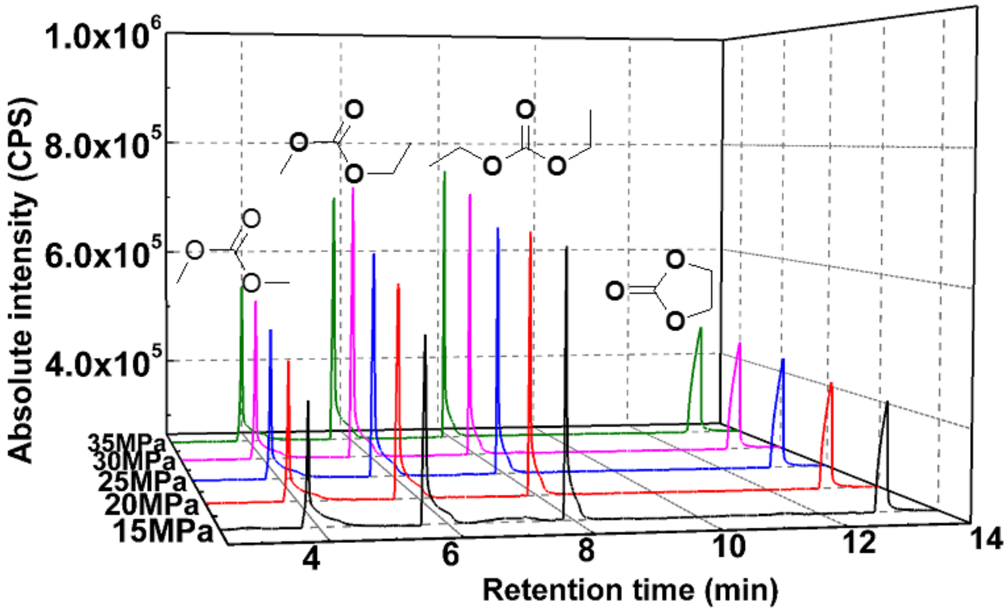

Figure 2. Chromatograms (GC-FID) of extracts with the course of pressure from carbonate mixture by supercritical CO_2.

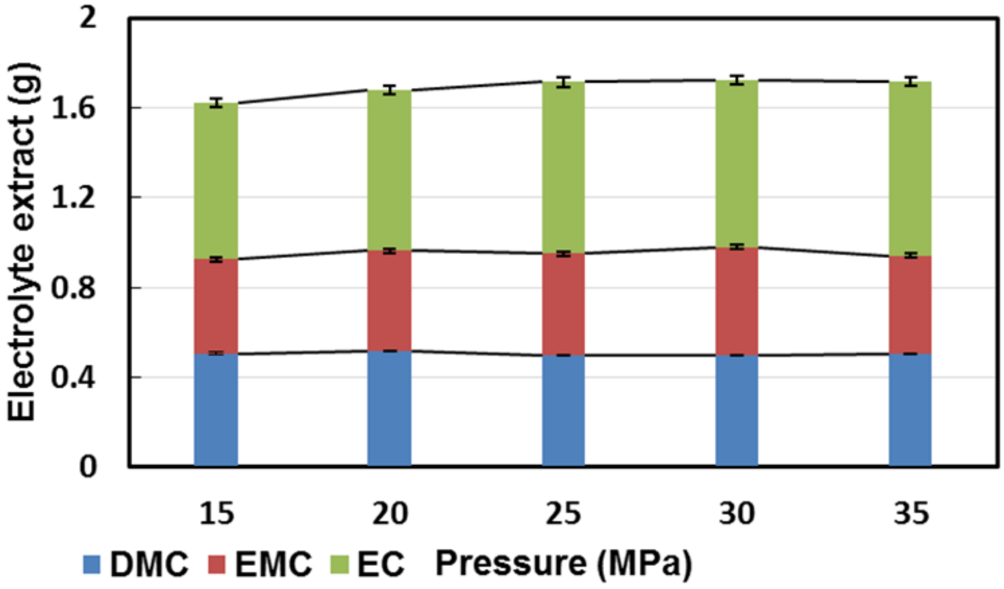

Figure 3. Compositions of the extracts corresponding to Fig. 2. green, top: EC; crimson, middle: EMC; blue, bottom: DMC

3.2. Effect of extraction temperature

Temperature is also an important variable for the supercritical CO_2 extraction process. The extraction behaviour of the particular electrolyte component was further investigated in the course of temperature from 30 to 50 °C.. Although chromatogram (GC-FID) of the temperature-resolved experiments is much less intuitive than pressure-resolved, trend of overall extraction yield is identical to that of the pressure-resolved experiments from signal intensity ratio of particular carbonate to internal standard (Fig. 4).

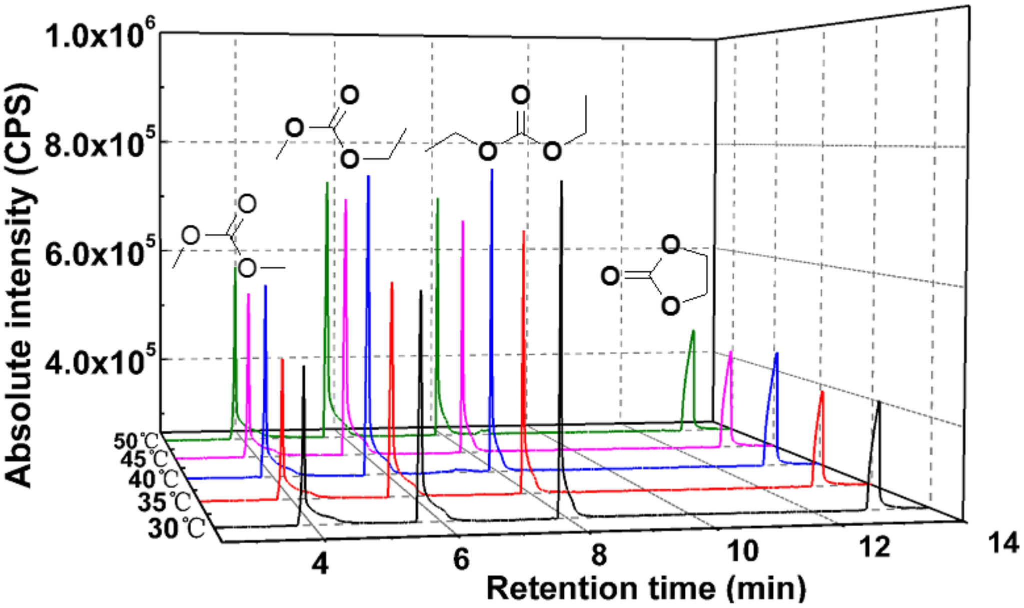

Figure 4. Chromatograms (GC-FID) of extracts with the course of temperature from carbonate mixture by supercritical CO_2.

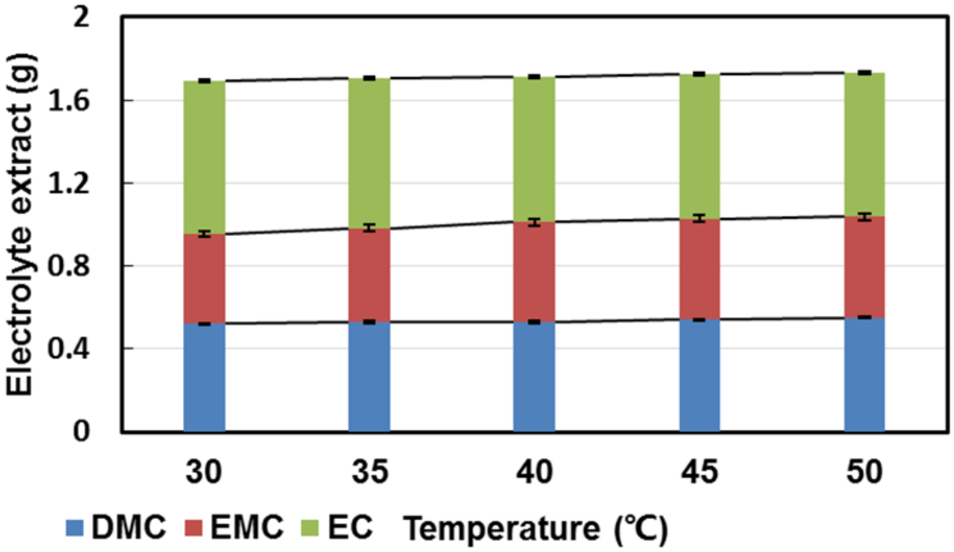

Figure 5. Compositions of the extracts corresponding to Fig. 4. green, top: EC; crimson, middle: EMC; blue, bottom: DMC.

This result was confirmed by composition analysis of the extracts (Fig. 5). Nevertheless, the extraction yield of EC is slip with increasing temperature (from 95.11±1.48% to 89.44±1.26%) and the trend is contrary to the pressure-resolved experiments. Extraction yields of DMC and EMC remain ~~a~~ slow growth rates (from 82.67±1.39% to 87.44±1.21% and from 72.39±1.25% to 80.81±1.33% respectively). This extraction behaviour can be ascribed to the decreasing of supercritical CO_2 polarity by raising the temperature from 30 to 50 °C at 25 MPa [31]. Furthermore, the contrary trends reveal that polarity plays a more important role than the supercritical fluid density and solute compounds diffusivity in pressure- and temperature-resolved extraction experiments [32]. A rule of thumb that chemists first learn regarding solvation is that “like dissolves like”. In general, while polar solvents dissolve polar solutes, nonpolar solvents dissolve nonpolar solutes [33,34]. Thus, polar carbonate are able to obtain higher extraction yield with more polar supercritical carbon dioxide. Investigations by Grützke and co-workers show that only the linear carbonates, DMC and EMC, can achieved higher extraction yield with liquid carbon dioxide [27]. Compared to liquid carbon dioxide, extraction with supercritical carbon dioxide is better suited for EC. Their research also suggested that the polarity play a significant role in the solvation of such carbonate solvents.

3.3. Effect of dynamic extraction time

Extraction time can also influence the extract quantity of organic carbonate solvents. In order to attain the impact of extraction time on the content, the organic carbonate solvents were initially exposed to the dynamic supercritical CO_2 for 25 min and gradually increase to 65 min (Fig. 6.) It can be seen that overall extraction yield can be effectively improved by prolonging the exposed time (from 82.53±1.21% to 86.94±0.95%). Fig. 7 demonstrates the GC-FID measurements corresponding to the compositions of the volatile components in Fig. 6. Nonetheless, an increase in the extraction time produced a reduction in the extraction yields of DMC and EMC longer than 45 min in this experiment (from 88.71±0.87% to 84.89±0.98% and from 82.49±1.17% to 76.93±1.13% respectively). During the reduced pressure trapping of supercritical fluids, since CO_2 is relatively non polar, the EC was first separated due to their strong polarity, and EC was crystallized in the trap due to its high melting point. Then, DMC and EMC was collected into the trap after EC. Although extending the extraction time may be able to increase extraction yield, longer extraction time may also cause unwanted loss of extracts from the trap. Therefore, the extracts were being blown off from the trap, as well as the volatilization of extracts being accelerated, which is not beneficial to the collection enhancement.

An overall view of the influence of extraction parameters on compositions of the extract components, which is intimately related to physical property. The physical properties of organic carbonate solvents mentioned in this paper are listed in Table 2. The polarity of organic solvents is given as the dielectric constant. Carbonate with high dielectric constants tend to be more polar. First of all, the extraction behaviour of DMC and EMC have shown the same trend with the course of pressure and temperature for their similar structure and polarity.

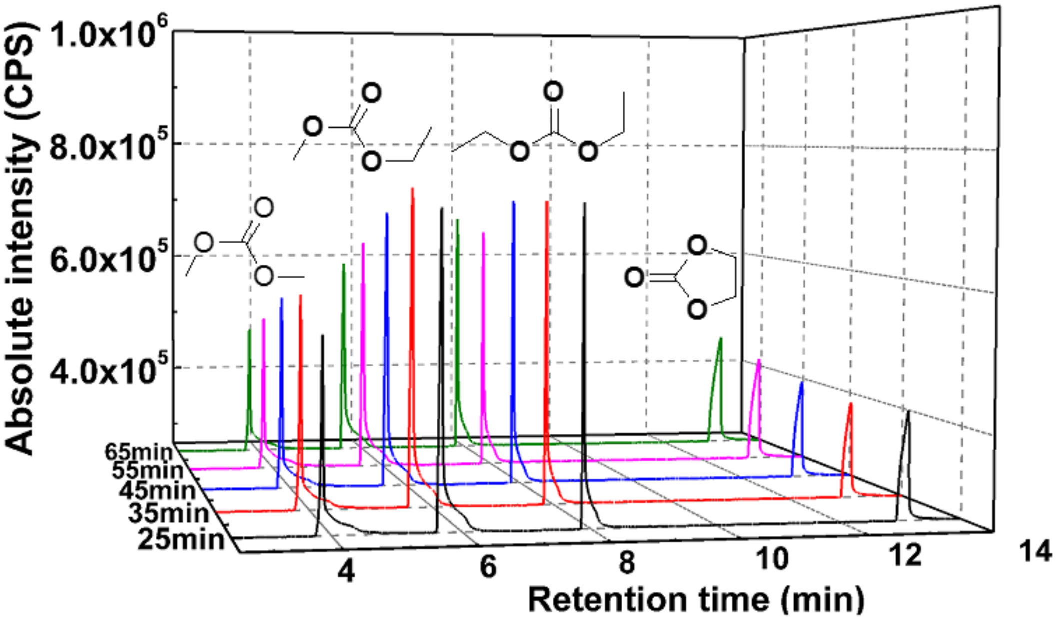

Figure 6. Chromatograms (GC-FID) of extracts with the course of time from carbonate mixture by supercritical CO_2.

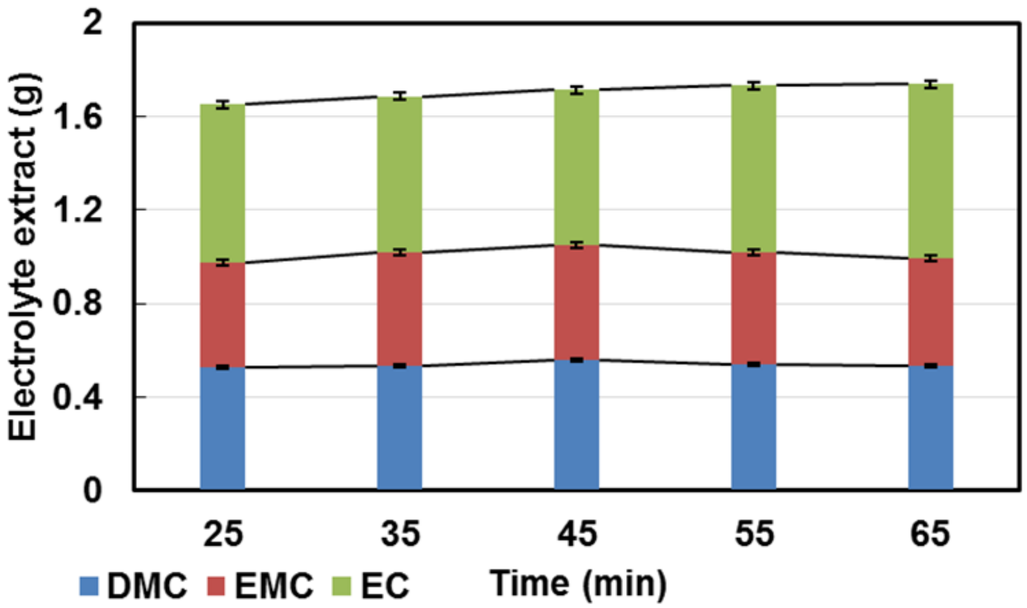

Figure 7. Compositions of the extracts corresponding to Fig. 6. green, top: EC; crimson, middle: EMC; blue, bottom: DMC.

The extraction behavior of EC is completely opposite to that of DMC and EMC in the same experiment. Furthermore, collection order and status of extract are associated respectively with the polarity and melting point of solute in the time-resolved extractions. To conclude, the components of TC-E201# electrolyte should be extracted in relatively low polarity supercritical CO_2, which maintain a high extraction yield of DMC and EMC. At the same time, medium polarity co-solvent should be added in the process to enhance the efficiency of EC.

Table 2. Melting point and dielectric constant of carbonate

Solvent	Molecular Formula	Melting Point (°C)	Dielectric Constant (F/m)
DMC	$C_3H_6O_3$	2-4	2.6
EMC	$C_4H_8O_3$	-14.5	2.9
EC	$C_3H_4O_3$	35-38	89.6

4. CONCLUSION

In the present paper, the influence of physical properties of carbonate on supercritical extraction behaviour of mixed organic carbonates or carbonate-based electrolytes was performed under selected extraction parameters using gas chromatography-flame ionization detector with internal standard calibration. The experiment results showed that the extraction of carbonate is a polarity predominant process. The nonpolar carbonate should be executed under relatively non or weak polar extraction medium which can both reduce energy consumption and obtain a considerable extraction yield. Polar carbonate should be extracted under polar solvents or add medium polarity co-solvents in nonpolar solvents. Meanwhile, the collection of carbonate is controlled by polarity and volatility of itself during the trapping process. The polar carbonates is fractionated before the nonpolar carbonate. It is worth mentioning that ingenious application of such physical properties such as polarity, melting point of carbonate could effectively separate and fractionate the carbonate-based electrolytes in recovery process by supercritical CO_2 extraction, which may enhance the recyclability of carbonate-based electrolytes.

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