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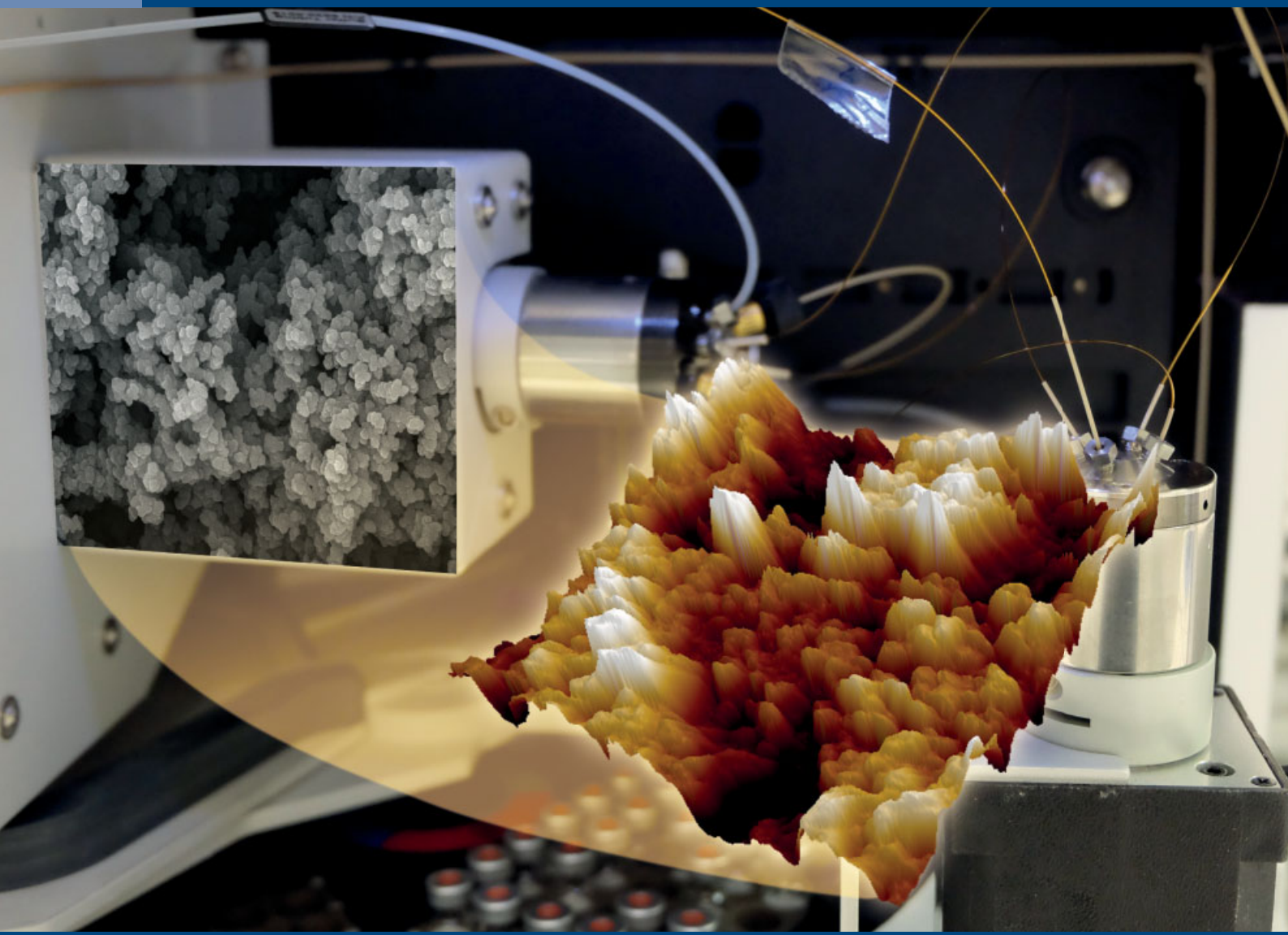

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Research Article

Method development for separating organic carbonates by ion-moderated high-performance liquid chromatography

An ion-moderated partition high-performance liquid chromatography method was developed for the separation and identification of common organic carbonates. The separation of organic carbonates was achieved on an ion exclusion column with an exchangeable hydrogen ion. An isocratic, aqueous mobile phase was used for elution and detection was performed with a refractive index detector. The developed method was validated for specificity, linearity, limits of detection and quantification, precision and accuracy. All calibration curves showed excellent linear regression ($R^2 > 0.9990$) within the testing range. The limits of detection were 3.8–30.8 ppm for the analyzed carbonates. Improvements in the peak resolution of the chromatograms were achieved by decreasing the column temperature. Addition of the organic modifier, acetonitrile, to the eluent was found to have insignificant effects on the peak resolution. The developed method was demonstrated for analyzing organic carbonate components in the electrolyte system of a commercial lithium ion battery.

Keywords: High-performance liquid chromatography / Lithium ion batteries / Method development / Organic carbonates
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1 Introduction

The organic carbonate family of compounds has drawn intense research and commercial interest due to their stability, effectiveness as solvents, low volatility, and increasingly green methods of synthesis [1,2]. The organic carbonate family (also referred to as carbonate esters) takes the general formula of $R_1O(CO)OR_2$, and is generally subdivided into linear carbonates if R_1 and R_2 are two separate functional groups, or cyclic carbonates if R_1 and R_2 both link to the same cyclic functional group. As a family, the organic carbonates have a demand of around one megaton as of 2007 [1], primarily for use in the polycarbonate [3] and lithium ion battery industries [4, 5]. In addition, the organic carbonates have been proposed as volatile organic compound exempt solvents [1] and oxygenating fuel additives [6]. However, commodity applications for these compounds have largely been limited by their higher cost of production compared to volatile organic solvents [1].

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Abbreviations: DEC, Diethyl carbonate; **DMC**, Dimethyl carbonate; **EC**, Ethylene carbonate; **EMC**, Ethyl methyl carbonate; **GC**, Glycerol carbonate; **ICH**, International Conference on Harmonization; **PC**, Propylene carbonate

Currently, there are three primary methods of manufacturing organic carbonates: (i) the oxidative carbonylation of methanol to dimethyl carbonate (DMC) [1, 7] followed by transesterification to the desired carbonate in a two-step process, (ii) the phosgenation of alcohols to the corresponding carbonates, and (iii) the direct reaction of carbon dioxide with alcohols or diols [1, 2, 8]. The oxidative carbonylation of methanol is primarily limited to the production of DMC and requires a subsequent transesterification step to transform DMC to another organic carbonate by a two-step method [3,8]. Consequently, despite the high toxicity and expensive costs of handling phosgene gas ($COCl_2$), the phosgenation route is primarily used for the synthesis of organic carbonates [1] as it allows for a more direct conversion of an alcohol or diol to a linear organic carbonate or cyclic carbonate [9]. A third route to the production of organic carbonates that has been gaining increasing interest is the direct reaction of carbon dioxide with alcohols or diols to form the corresponding linear or cyclic carbonate. However, this pathway is characterized by slow rates and low percent conversions limited by the thermodynamic stability of CO_2, which has been an active focus of research in improved catalyst design [10–12]. Additionally, as glycerol is an abundant waste product of the refinement of biodiesel, the reaction of glycerol and CO_2 to form glycerol carbonate has attracted particular attention due to the opportunity to valorize these two "waste" molecules [13].

*Both authors contributed equally to this article.

For any synthesis, it is necessary to separate and quantify the product yield from the reaction mixture. In the case of organic carbonates, this generally requires the organic carbonate to be separated from a mixture containing corresponding alcohols (i.e. unused reactants in a phosgenation or direct CO_2 reaction process) and other carbonates (i.e. unused reactants in a transesterification process). This means that a useful analytic separation method should be able to separate not just the carbonates from the reagent alcohols, but also separate and quantify similar organic carbonates. Additionally, the lithium ion battery industry makes use almost exclusively of organic carbonate mixtures as the electrolyte solvent. Consequently, a method that can distinguish between similar organic carbonates and similar alcohols is expected to benefit the lithium ion battery as well as the synthetic and catalytic research communities.

In general, GC is utilized for separation and quantification of organic carbonates, either with the use of a flame ionization detector [14] or mass spectrometer [15]. Typical methods use an injection port temperature at 230°C and an oven ramp up to 230°C [14–16]. This has the unfortunate downside of being destructive to cyclic carbonates such as ethylene carbonate and glycerol carbonate [14,17] with decomposition of ethylene carbonate beginning as low as 120°C [14]. Alternately, HPLC has been used for analysis of organic carbonates. Typical HPLC methods make use of a C_{18} reversed-phase silica column, which separates analytes based on their hydrophobicity. Such HPLC methods have been shown to separate the electrolyte family of carbonates under optimized conditions [18,19]. Nonetheless, these methods require gradient pumps and mixers while offering poor resolution due to the similar hydrophobicity of electrolyte carbonates, with published methods showing both ethylene carbonate and propylene carbonate eluting within the first minute [18]. One alternative is an LC method making use of an ion-exchange resin column. Such a method has been demonstrated by Pelet et al. to be effective for separating ethylene carbonate and glycerol carbonate [14]. Unfortunately, the CarH column by Touzard and Matignon utilized in this study no longer appears to be commercially available and no follow-up research literature for the separation of other cyclic carbonates or any linear carbonates with an ion-exchange column is available.

Herein, we report the use of a simple, isocratic, aqueous ion-moderated partition HPLC method for separating and identifying six organic carbonates. Of the six carbonates selected, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, ethylene carbonate, and propylene carbonate (DMC, DEC, EMC, EC, and PC respectively) are common battery electrolyte carbonates [4,20] and plastic precursors [3], while glycerol carbonate (GC) was selected due to it being a promising green reagent and solvent [13]. Considering the similar chemical structures and properties of these carbonates, we applied a polymer-based ion-exclusion HPLC column that relies on multiple modes of interactions for separating and quantifying structurally similar (and frequently isomeric) molecules [21]. Although both the developed method and the cited work employed a refractive index detector for the detection of carbonates, the current work uses a simple, isocratic mobile phase as opposed to the previous work reported that used binary mobile phase for separations [14, 19]. We validated this developed method as per the widely acknowledged International Conference on Harmonization (ICH) guidelines [22]. Effects of column temperature and an organic modifier were studied for improving the peak resolution of the chromatograms. This method could also be applied to separate organic carbonates from their corresponding alcohols. Additionally, an application of the developed method was demonstrated in the identification of the carbonate components of a battery electrolyte from a functioning commercial lithium ion battery.

2 Materials and methods

2.1 Materials

Diethyl carbonate (DEC) (anhydrous, ≥ 99%), ethylene carbonate (EC) (98%), ethyl methyl carbonate (EMC) (98%), glycerol carbonate (GC) (4-hydroxymethyl-1,3-dioxolan-2-one, ≥90%), propylene carbonate (PC) (anhydrous, 99.7%) and sulfuric acid (99.999%, HPLC grade) were purchased from Sigma–Aldrich (St. Louis, MO). Dimethyl carbonate (DMC) (99+%) was acquired from Acros Organics (Bridgewater, NJ). DriSolv Methanol (anhydrous, 99.8%) was obtained from EMD Millipore (Billerica, MA). 18650 type lithium ion battery was obtained from McMaster-Carr (Elmhurst, IL). All purchased chemicals were used as received and were selected due to them being the highest purity commercially available. 18.2 MΩ· cm deionized water was generated using a Millipore Synergy filtration system (VWR, Radnor, PA). 0.2 μm polytetrafluoroethylene (PTFE) syringe filters were purchased from VWR (Radnor, PA).

2.2 Instrumentation

The HPLC analysis was conducted on a Waters instrument comprised a Waters 717 plus auto sampler (Waters, Milford, MA), a Waters 515 pump (Waters, Milford, MA), a PerkinElmer series 200 vacuum degasser (PerkinElmer, Waltham, MA) and a Waters 410 Differential refractometer (Waters, Milford, MA). The chromatographic separations were performed using a 300 mm x 7.8 mm Aminex HPX-87H column with 9 μm particle size in conjunction with a 30 mm x 4.6 mm micro-guard Cation-H guard column cartridge (Bio-Rad Laboratories, Hercules, CA). Data acquisition was performed with Chrom Perfect Spirit Version 5.5.6 chromatography software (Justice Laboratory Software, Denville, NJ).

2.3 Chromatographic conditions

The organic carbonate samples were analyzed using a modified HPLC method previously developed by the National Renewable Energy Laboratory for analyzing carbohydrates

[21]. The mobile phase consisted of 5 mM sulfuric acid which had been sonicated under vacuum for 1 h before passing it through the in-line degasser. An injection volume of 10 μL was maintained for all experiments. In a typical experiment, the column and the detector were kept at 55 and 35°C, respectively, with a mobile phase flow rate of 0.6 mL/min. The effect of the addition of an organic modifier on the carbonate separation was similarly studied by using 5% acetonitrile in 5 mM sulfuric acid as the mobile phase. Peak resolution studies were conducted by varying the column temperature (25, 35, 45, and 55°C) and the mobile phase flow rate (0.2, 0.3, 0.4, and 0.6 mL/min) while keeping the remaining parameters constant.

2.4 Preparation of standard solutions

The calibration curves for all selected organic carbonates (DEC, DMC, EC, EMC, GC, and PC) were obtained from their respective standard solutions. A stock solution of 15,000 ppm was prepared for each of the carbonates. The calibration standards were then prepared by serial dilutions of the stock solution of the respective carbonate. The concentrations of the standard solutions for the six carbonates ranged from 50 to 15,000 ppm. While the water-soluble cyclic carbonate samples (EC, GC, PC) were diluted in deionized water, the linear carbonates (DEC, DMC, EMC), on account of their low water solubility, were diluted in methanol. Peak areas were plotted against the corresponding concentration to construct the calibration graphs. Linear regression equations were obtained from these calibration graphs. The linearity, LOD and LOQ were estimated from these linear regressions for the analyzed carbonates. Serial dilutions of separately prepared stock solutions at three different concentration levels were prepared and triplicate determinations for each concentration were performed on the same day to estimate the accuracy and precision of the developed method. Solutions containing linear carbonates and their corresponding alcohols were prepared in deionized water in a 1:2.5, v/v ratio. Cyclic carbonates and their corresponding alcohols were prepared similarly using 2:1, v/v ratio. The ratios were such selected so as to provide optimum peak intensity for the analyzed carbonates and alcohols. To evaluate the HPLC system conditions for best separations of the carbonates, a 100 mM solution containing all six selected organic carbonates was prepared in deionized water. Note that to avoid introducing additional matrix peaks, the 100 mM solution was prepared in deionized water.

2.5 Evaluation of carbonate components of a lithium ion battery

A commercial 18650 type lithium ion battery cell was disassembled so as to obtain rinses of the anode and cathode with deionized water for evaluating the carbonate components in the battery electrolyte. The cell was first fully discharged, followed by removing the battery case and unrolling a 1 inch length segment of the cathode and anode. The segment of cathode and anode were put in separate beakers containing 25 mL of deionized water immediately after unrolling to prevent solvent evaporation. Samples were centrifuged and filtered with 0.2 μm PTFE syringe filters before HPLC analysis.

2.6 Method validation

The developed method was validated for specificity, linearity, precision, accuracy, LOD and LOQ as per the International Conference on Harmonization (ICH) guidelines [22]. The peak resolution (R_s) for DMC-EC was calculated by measuring the retention times and peak widths at half-max height of the analytes using the equation:

$$R_s = \frac{1.18(t_{EC} - t_{DMC})}{w_{1/2,DMC} + w_{1/2,EC}} \quad (1)$$

where R_s is the resolution for DMC-EC, t_{DMC} is the retention time of DMC, t_{EC} is the retention time of EC, $w_{1/2,\,DMC}$ is the peak width at half-height of DMC and $w_{1/2,\,EC}$ is the peak width at half-height of EC.

3. Results and discussion

3.1 HPLC analysis of organic carbonates standard solution

The HPLC column employed for the separation and identification of organic carbonates is a strong acid cation-exchange column with a polystyrene-divinylbenzene resin backbone and exchangeable hydrogen ion (H^+) as the counter ion [23]. This single column employs multiple modes of interactions such as reverse phase, normal phase, ion exclusion, ion exchange, ligand exchange and size exclusion between the analyte and the mobile and stationary phase [24] for separating the analytes. This mechanism is termed as ion-moderated partition [25]. As a result, this column is commonly used for a variety of applications including biomass hydroxylate [26] and biological fluid analysis, fermentation monitoring as well as acetylated amino sugar separations [27]. However, to our best knowledge, the application of this column for the separation of organic carbonates has never been reported.

The separation and identification of organic carbonates was initially conducted by using a simple, aqueous isocratic method originally developed for biomass analysis [28]. A 10 μL injection of the 100 mM solution containing a mixture of pure organic carbonates was performed on the HPLC with the column temperature maintained at 55°C. The detector temperature was kept at 35°C and the mobile phase flow rate was held at 0.6 mL/min. Under these conditions, in *ca.* 42 min, this method separated four (GC, PC, EMC, and DEC) out of six carbonates as indicated in the chromatogram in Fig. 1A. However, DMC and EC co-eluted as a single peak. Glycerol, a common impurity, along with some other

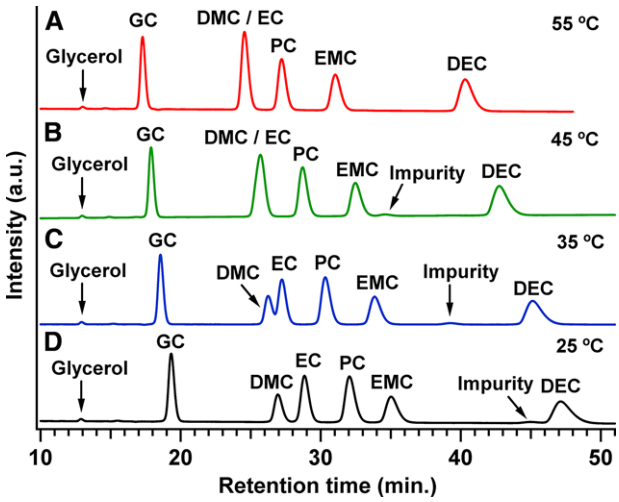


Figure 1. HPLC chromatograms of a 100 mM solution mixture of six organic carbonates (GC: glycerol carbonate; DMC: dimethyl carbonate; EC: ethylene carbonate; PC: propylene carbonate; EMC: ethyl methyl carbonate; DEC: diethyl carbonate) at four different column temperatures: (A) 55°C, (B) 45°C, (C) 35°C, and (D) 25°C. HPLC conditions– detector temperature: 35°C, mobile phase: 5 mM H_2SO_4, mobile phase flow rate: 0.6 mL/min and injection volume: 10 μL.

minor unidentified impurities found in GC samples, was also detected along with the carbonates.

3.2 Effect of the column temperature on the elution of dimethyl carbonate and ethylene carbonate

Chromatographic variables such as column temperature are known to affect the separation of co-eluting peaks in organic acid metabolites [29] and biomass hydrolysate samples [30]. To improve the separation between DMC and EC, the effect of the change in column temperature on the resolution of these carbonates was studied at four temperatures (55, 45, 35 and 25°C) while keeping the remaining parameters the same (Fig. 1). The peak resolution (R_s) was used to evaluate the effect of column temperature on the separation of these two analytes. Although a decrease in the column temperature from 55 to 45°C did not improve the peak resolution of DMC and EC, lowering of the column temperature to 35°C led to the separation of these two carbonates. The R_s for DMC and EC at this temperature was 0.93. For two analytes to be baseline resolved, their R_s value should be greater than 1.5 [31]. Further decreasing the column temperature to 25°C not only resulted in the baseline separation of DMC and EC but also drastically improved the R_s to 1.75 (Fig. 1D).

The elution order of the evaluated cyclic and linear organic carbonates in our HPLC analysis was postulated to follow a reverse phase separation mechanism. Among the three cyclic carbonates evaluated (EC, PC, and GC), GC eluted first, followed by EC and then PC. Since GC is the most polar molecule and PC being the least polar one among these three

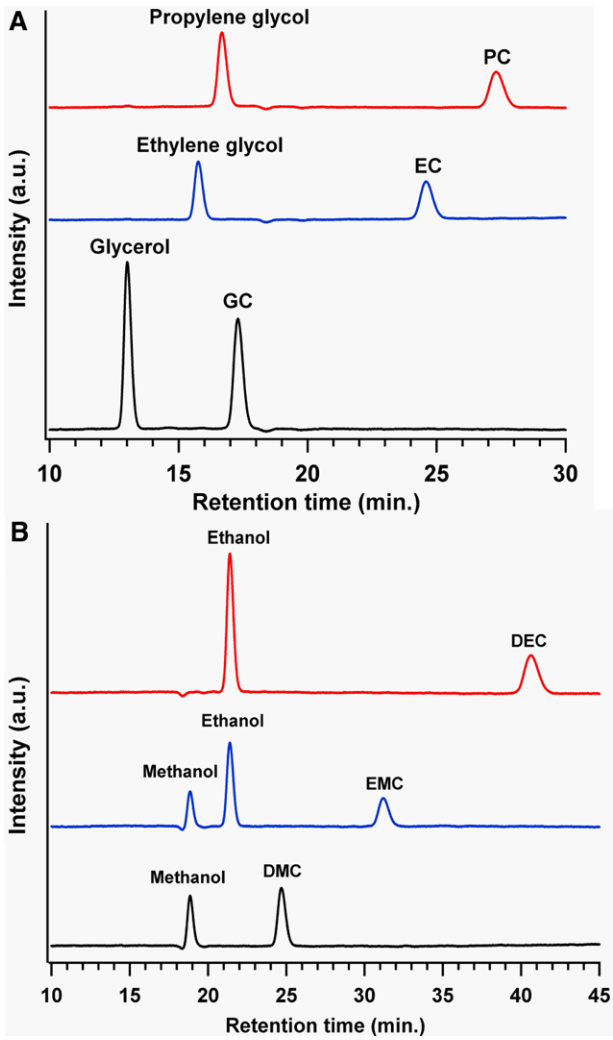


Figure 2. HPLC chromatograms of (A) cyclic carbonates and their respective alcohols (B) linear carbonates and their respective alcohols. Note that the corresponding alcohols for EMC are methanol and ethanol. HPLC conditions– column temperature: 55°C, detector temperature: 35°C, mobile phase: 5 mM H_2SO_4, mobile phase flow rate: 0.6 mL/min and injection volume: 10 μL.

carbonates [32], this order of elution implied that the polarity of these three carbonates governed their order of elution. Accordingly, the elution of these cyclic carbonates likely followed a reverse phase mechanism similar to the one reported in phenols separation [33]. Similarly, for the three evaluated linear carbonates, the elution of DMC was followed by EMC and then DEC. This result suggested that the elution order followed the increasing chain length of the alkyl groups in these carbonates which is similar to the increase in lipophilicity, suggesting possible reverse phase separation mechanism as well. Lowering the column temperature was also found to increase band spreading [27]. This was confirmed by the alteration in the shape of the DEC peak shape as the temperature decreased from 55 to 25°C. Nevertheless, such change in column temperature only marginally affected the total analysis time which remained under 50 min at the four evaluated

Table 1. Calibration curves, limits of detection (LOD) and limits of quantification (LOQ) for six organic carbonates: DMC, EMC, DEC, EC, PC, and GC

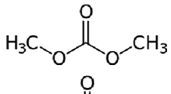
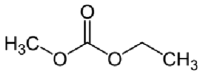
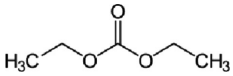
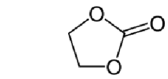
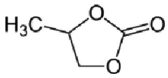
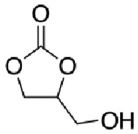
Carbonate	Abbreviation	Linear regression	R^2	LOD (ppm)	LOQ (ppm)
	DMC	y = 510,152 x	0.99995	7.3	24.3
	EMC	y = 621,458 x	0.99990	14.6	48.5
	DEC	y = 684,302 x	0.99901	30.8	102.7
	EC	y = 699,826 x	0.99998	7.5	25
	PC	y = 910,020 x	0.99991	8.2	27.2
	GC	y = 1,112,670 x	0.99997	3.8	12.7

Table 2. Accuracy and precision for six organic carbonates

Carbonate	Nominal value (v/v)	Found ± SD (v/v)	RSD (%)	Er (%)
	1.5	1.501 ± 0.003	0.22	0.06
DMC	0.15	0.142 ± 0.002	1.94	4.93
	0.015	0.0153 ± 0.0001	1.1	2.57
	1.5	1.501 ± 0.005	0.36	0.09
EMC	0.15	0.142 ± 0.0004	0.26	5.26
	0.015	0.0149 ± 0.0004	2.66	0.61
	1.5	1.501 ± 0.002	0.1	0.09
DEC	0.15	0.144 ± 0.003	1.75	3.8
	0.015	0.0145 ± 0.0002	1.35	3.42
	1.5	1.500 ± 0.007	0.45	0.01
EC*	0.15	0.147 ± 0.0005	0.35	1.41
	0.015	0.0149 ± 0.0001	0.27	0.55
	1.5	1.500 ± 0.001	0.06	0.02
PC	0.15	0.147 ± 0.0005	0.37	1.93
	0.015	0.0151 ± 0.0001	0.75	0.94
	1.5	1.501 ± 0.018	1.17	0.1
GC	0.15	0.152 ± 0.002	1.37	1
	0.015	0.0149 ± 0.0003	1.82	0.56

Note that Found ± SD stands for Mean ± Standard deviation for three concentrations.
*Nominal values and Found ± SD values are reported as v/v, except for EC which was reported as w/v.

column temperatures. Apart from the column temperature, mobile phase flow rate is known to affect the separation of closely eluting biomass hydroxylate compounds on the Aminex column [30]. Alteration in the mobile phase flow rate did not have a significant influence on the separation of DMC and EC in this study. The addition of 5% acetonitrile to the mobile phase (5 mM aqueous sulfuric acid) was also found to have no significant effect on the separation of DMC and EC (Supporting Information Fig. S1). While the overall analysis time was reduced by *ca*. 10 min, a wavy baseline was observed in the chromatograms similar to ones reported in biomass hydrolysis byproducts analysis [34]. An unidentified negative peak at *ca*. 18 min was also observed in the chromatogram as reported by Cheng et al. [35].

3.3 Method validation results

The proposed HPLC method was validated for organic carbonates separation according to the ICH guidelines on validation of analytical procedures [22].

3.3.1 Specificity

The specificity of the method for the determination of alcohols, diols and the corresponding organic carbonates obtained from them was established from the retention times of these compounds. The retention times of the alcohols, diols and their corresponding organic carbonates were acquired by injecting their mixtures (Fig. 2). All of the six carbonates are readily separated from their precursor alcohols with 4+ min of separation between each. This means that the developed method has excellent specificity for separating reaction mixtures containing alcohols and their corresponding carbonates at the standard 55°C column temperature. However, solution mixtures containing unknown carbonates should be run with a column temperature of 25°C due to low specificity for DMC and EC.

3.3.2 Linearity, limits of detection, and quantification

The LOD was determined as the concentrations corresponding to S/N = 3 and LOQ was determined as the concentrations corresponding to S/N = 10 [36]. The noise was determined as the root mean square (RMS) noise of the baseline and the signal was obtained as the peak height using Chrom Perfect Spirit Version 5.5.6 data acquisition software.

External standard calibration curves were employed for the quantification of six organic carbonates (DEC, DMC, EC, EMC, GC, and PC). Five standard solutions covering a broad range of concentrations (50–15,000 ppm) were used to obtain the calibration curves. The linear regression of each calibration curve was analyzed using Microsoft Excel 2010 software. Linear relationships were found between the peak areas and the concentration of all carbonates evaluated with $R^2 >$ 0.9990. (Table 1) The sensitivity of this analytical method for carbonate mixtures analysis was determined by calculating the LOD and LOQ of each of the carbonates. (Table 1)

3.3.3 Precision and accuracy

The precision and accuracy for the developed method was studied as reported by Baker et al. [37]. The studies were conducted at three concentration levels (150, 1500, and 15,000 ppm) for each carbonate using three replicate determinations for each concentration through the same day. High precision (<3% RSD) and accuracy (<6% error) of the developed method was found for the investigated organic carbonates (Table 2).

3.4 Application of the developed method for the identification of organic carbonates in the electrolytes of a lithium ion rechargeable battery

A major focus in lithium ion batteries (LIBs) research is the development of novel materials for electrolytes and electrodes to increase the lifetime of these batteries. We applied the developed HPLC method to identify the organic carbonate components in the electrolytes present in the anode and cathode of a commercial LIB. Since the battery contained an unknown carbonate mixture, the column was held at 35°C for identifying all the carbonate components. In the analyzed battery electrolytes, DMC, EC and PC were revealed as major carbonate components in the anode electrolyte wash, whereas EC and PC constituted the major carbonate components in the cathode electrolyte wash. (Fig. 3) A shoulder at the beginning of the EC peak hinted the possible presence of DMC in the cathode extract. The difference in the peak areas of DMC in the cathode and anode electrolyte extract suggests poor electrolyte diffusion across the separator, a feature previously observed by GC studies of LIBs [15]. Along with these carbonates, some unidentified impurities and possible additives were observed. Some unidentified peaks, likely due to the differences between the compositions of the sample solvent and the mobile phase [38], were also detected in the chromatograms. By analyzing the peak areas in chromatogram, the ratio of DMC/EC/PC in the anode electrolyte extract was found to be 1:5:1, v/v, while that of EC/PC in the cathode electrolyte extract was determined to be 4:1, v/v. The amount of

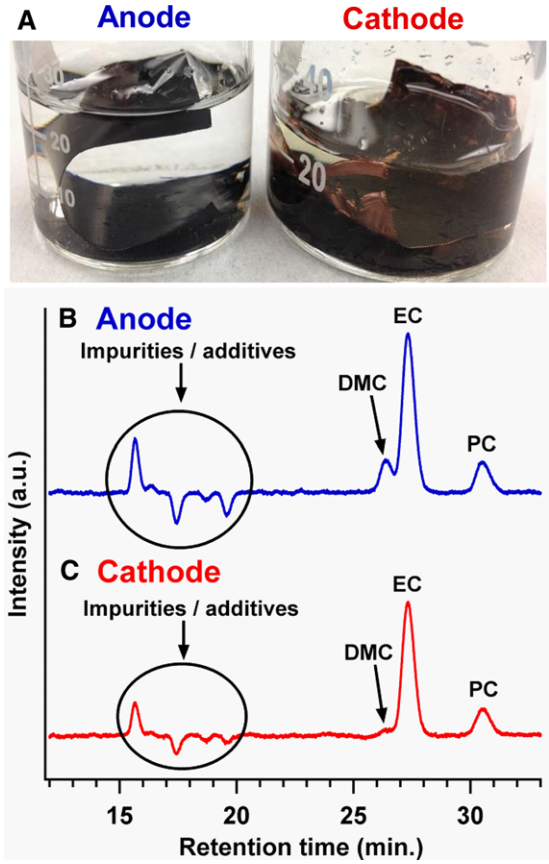


Figure 3. (A) Photos of (left) a piece of anode and (right) a piece of cathode of a disassembled commercial lithium ion battery immersed in water. (B) and (C) HPLC chromatograms of electrolytes extracted from anode and cathode, respectively. HPLC conditions: column and detector temperature: 35°C, mobile phase: 5 mM H_2SO_4, mobile phase flow rate: 0.6 mL/min, and injection volume: 10 μL.

DMC in the cathode washing solution was below the LOD and could not be calculated. Since commercial LIBs are generally composed of binary or ternary mixtures of various organic carbonates, this HPLC method can be tuned to identify the individual carbonate contents of these batteries.

4 Concluding remarks

An ion-moderated partition HPLC method was developed for analyzing six common organic carbonates including glycerol carbonate, dimethyl carbonate, ethylene carbonate, propylene carbonate, ethyl methyl carbonate, and diethyl carbonate. This method applies a single ion-exclusion HPLC column originally designed for biomass hydroxylate analysis using an isocratic, aqueous mobile phase. It needs no additional sample preparation in the form of derivatization. Further, this method provides excellent qualitative and quantitative separation of organic carbonates from their precursor alcohols as well as individual organic carbonates present in a carbonate mixture. The method was illustrated to be applicable in the characterization of organic carbonates of a functional commercial lithium ion battery.

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The authors have declared no conflict of interest.

5 References

[1] Schäffner, B., Schäffner, F., Verevkin, S. P., Börner, A., Organic carbonates as solvents in synthesis and catalysis. *Chem. Rev.* 2010, *110*, 4554–4581.

[2] Sakakura, T., Choi, J.-C., Yasuda, H., Transformation of carbon dioxide. *Chem. Rev.* 2007, *107*, 2365–2387.

[3] Brunelle, D. J., in: Kroschwitz, J. I. (Ed.), *Kirk-Othmer Encyclopedia of Chemical Technology*, 5th Edition, Wiley, New York 2004, *19*, pp. 797–827.

[4] Xu, K., Electrolytes and interphases in Li-ion batteries and beyond. *Chem. Rev.* 2014, *114*, 11503–11618.

[5] Zhang, S. S., A review on electrolyte additives for lithium-ion batteries. *J. Power Sources* 2006, *162*, 1379–1394.

[6] Arteconi, A., Mazzarini, A., Di Nicola, G., Emissions from ethers and organic carbonate fuel additives: a review. *Water Air Soil Pollut.* 2011, *221*, 405–423.

[7] Buysch, H.-J., Krefeld, B. A., in: Gerhartz, W. (Ed.), *Ullmann's Encyclopedia of Industrial Chemistry*, 5th Edition, VCH, New York 1985, *A5*, pp. 197–202.

[8] Shukla, K., Srivastava, V. C., Diethyl carbonate: Critical review of synthesis routes, catalysts used and engineering aspects. *RSC Adv.* 2016, *6*, 32624–32645.

[9] Van, V. C. H., Ten, K. A. J. B., De, G. M. T., Process for the preparation of cyclic organic carbonates, WIPO Patent WO 2013189861 A1 PCT/EP2013/062456, publ. date December 27, 2013.

[10] Santos, B. A. V., Pereira, C. S. M., Silva, V. M. T. M., Loureiro, J. M., Rodrigues, A. E., Kinetic study for the direct synthesis of dimethyl carbonate from methanol and CO_2 over CeO_2 at high pressure conditions. *Appl. Catal., A* 2013, *455*, 219–226.

[11] Aresta, M., Dibenedetto, A., Pastore, C., Angelini, A., Aresta, B., Papai, I., Influence of Al_2O_3 on the performance of CeO_2 used as catalyst in the direct carboxylation of methanol to dimethylcarbonate and the elucidation of the reaction mechanism. *J. Catal.* 2010, *269*, 44–52.

[12] Aouissi, A., Al-Othman, Z. A., Al-Amro, A., Gas-phase synthesis of dimethyl carbonate from methanol and carbon dioxide over $Co_{1.5}PW_{12}O_{40}$ Keggin-type heteropolyanion. *Int. J. Mol. Sci.* 2010, *11*, 1343–1351.

[13] Sonnati, M. O., Amigoni, S., Taffin de Givenchy, E. P., Darmanin, T., Choulet, O., Guittard, F., Glycerol carbonate as a versatile building block for tomorrow: synthesis, reactivity, properties and applications. *Green Chem.* 2013, *15*, 283–306.

[14] Pelet, S., Yoo, J. W., Mouloungui, Z., Analysis of cyclic organic carbonates with chromatographic techniques. *J. High Resol. Chromatogr.* 1999, *22*, 276–278.

[15] Terborg, L., Weber, S., Passerini, S., Winter, M., Karst, U., Nowak, S., Development of gas chromatographic methods for the analyses of organic carbonate-based electrolytes. *J. Power Sources* 2014, *245*, 836–840.

[16] Grutzke, M., Monnighoff, X., Horsthemke, F., Kraft, V., Winter, M., Nowak, S., Extraction of lithium-ion battery electrolytes with liquid and supercritical carbon dioxide and additional solvents. *RSC Adv.* 2015, *5*, 43209–43217.

[17] D'Alelio, G. F., Organic cyclic carbonates, U.S. Patent 3225063, publ. date December 21, 1965.

[18] Shimadzu, Co., Analysis of Electrolytic solvents for lithium-ion rechargeable battery, *Application News*, L403, Shimadzu, Co., Tokyo.

[19] Cheng, H., Gadde, R. R., Determination of propylene carbonate in pharmaceutical formulations using liquid chromatography. *J. Pharm. Sci.* 1985, *74*, 695-696.

[20] Etacheri, V., Marom, R., Elazari, R., Salitra, G., Aurbach, D., Challenges in the development of advanced Li-ion batteries: a review. *Energy Environ. Sci.* 2011, *4*, 3243-3262.

[21] Sluiter, A., Hames, B., Ruiz, R., Scarlata, C., Sluiter, J., Templeton, D., Technical Report, 2008, NREL/TP-510-42623, National Renewable Energy Laboratory, Golden.

[22] Validation of analytical procedures: Text and methodology Q2(R1), ICH 2005, (www.ich.org).

[23] Blake, J. D., Clarke, M. L., Richards, G. N., Determination of organic acids in sugar cane process juice by high-performance liquid chromatography: improved resolution using dual Aminex HPX-87H cation-exchange columns equilibrated to different temperatures. *J. Chromatogr. A* 1987, *398*, 265–277.

[24] Jupille, T., Gray, M., Black, B., Gould, M., Ion moderated partition HPLC. *Am Lab.* 1981, *13*, 80–86.

[25] Albarrán, G., Collins, C. H., Separations using ion-moderated partition chromatography: Comparisons of

efficiency and resolution with several different columns. *J. High. Resolut. Chromatogr.* 1989, *12*, 486–488.

[26] Scarlata, C. J., Hyman, D. A., Development and validation of a fast high pressure liquid chromatography method for the analysis of lignocellulosic biomass hydrolysis and fermentation products. *J. Chromatogr. A* 2010, *1217*, 2082–2087.

[27] *Overview and strategies for bio-organic molecule purification, Rev B*, Bio-Rad Laboratories, Hercules 2012.

[28] Bhalkikar, A., Gernhart, Z. C., Cheung, C. L., Recyclable magnetite nanoparticle catalyst for one-pot conversion of cellobiose to 5-hydroxymethylfurfural in water. *J. Nanomater.* 2015, *2015*, 8.

[29] Bell, D. J., Blake, J. D., Prazak, M., Rowell, D., Wilson, P. N., Studies on yeast differentiation using organic acid metabolites part 1. Development of methodology using high performance liquid chromatography. *J. Inst. Brew.* 1991, *97*, 297–305.

[30] Pecina, R., Bonn, G., Burtscher, E., Bobleter, O., High-performance liquid chromatographic elution behaviour of alcohols, aldehydes, ketones, organic acids and carbohydrates on a strong cation-exchange stationary phase. *J. Chromatogr. A* 1984, *287*, 245–258.

[31] Xie, R., Tu, M., Wu, Y., Adhikari, S., Improvement in HPLC separation of acetic acid and levulinic acid in the profiling of biomass hydrolysate. *Bioresour. Technol.* 2011, *102*, 4938–4942.

[32] Chernyak, Y., Dielectric constant, dipole moment, and solubility parameters of some cyclic acid esters. *J. Chem. Eng. Data* 2006, *51*, 416–418.

[33] Wood, R., Cummings, L., Jupille, T., Recent developments in ion-exchange chromatography. *J. Chromatogr. Sci.* 1980, *18*, 551–558.

[34] Soleimani, M., Tabil, L., Simultaneous quantification of carbohydrates, alcohols, and toxic components in a bio-based medium using dual-detection HPLC analysis. *AJAC*. 2013, *4*, 265–272.

[35] Yuan J.P, Chen, F., Simultaneous separation and determination of sugars, ascorbic acid and furanic compounds by HPLC - dual detection. *Food Chem*. 1999, *64*, 423–427.

[36] Shrivastava, A., Gupta, V. B., Methods for the determination of limit of detection and limit of quantitation of the analytical methods. *Chron. Young Sci.* 2011, *2*, 21.

[37] Baker, M. M., Belal, T. S., Mahrous, M. S., Ahmed, H. M., Daabees, H. G., High-performance liquid chromatography with diode array detection method for the simultaneous determination of seven selected phosphodiesterase-5 inhibitors and serotonin reuptake inhibitors used as male sexual enhancers. *J. Sep. Sci.* 2016, *39*, 1656–1665.

[38] Snyder, L. R., Kirkland, J. J., Dolan, J. W., *Introduction to modern liquid chromatography*, Second Edition, John Wiley & Sons, New York 1979.

