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Identification of Diethyl 2,5-Dioxahehexane Dicarboxylate (DEDOHC) and Poly-Ethylene Carbonate (Poly-EC) as Decomposition Products of Ethylene Carbonate (EC)-based Electrolytes by Fourier Transform Infrared (FTIR) Spectroscopy

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Abstract

The formation of passive films on electrode by electrolyte decomposition plays a crucial role in maintaining the reversibility of Li ion batteries (LIBs); however the understanding of the electrolyte decomposition process is still lacking. In this study, we investigated the decomposition of an electrolyte based on ethylene carbonate (EC) solvent, and identified the decomposition products on Sn and Ni surface by matching the IR spectra to that of synthesized reference compounds. The reference compounds diethyl 2,5-dioxahehexane dicarboxylate (DEDOHC) and polyethylene carbonate (poly-EC) were synthesized and the chemical structures were characterized by nuclear magnetic resonance (NMR) and Fourier transform infrared (FTIR) spectroscopy. Peak assignments were made based on quantum chemical (Hartree-Fock) calculations. By introducing the synthesized product compounds into the electrolyte, we studied the effect of Li-ion solvation on the IR spectra and were able to match the spectra of the decomposition products on Sn and Ni electrode surfaces to those of DEDOHC and poly-EC for the first time. This study clearly demonstrated the importance to include solvation effects in the IR spectra of reference compounds in identification of electrolyte decomposition products in LIBs.

Keywords: electrolyte decomposition, solvation effect, EC, DEDOHC, poly-EC, FTIR, Li ion battery

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Introduction

Li ion batteries (LIBs) have been widely applied in long-term energy storage, portable electronics and transportation; however the electrolytes are chemically unstable during operation, thus negatively affect the reliability and durability of battery. Ethylene carbonate (EC)-based electrolytes are the most commonly used electrolytes in LIBs, as a result of their superior bulk ion conductivity and interfacial properties¹. Also, due to a higher dielectric constant than that of linear carbonate co-solvents, EC has been identified as the primary molecule in the inner solvation shell of the lithium ion in EC-based electrolyte^{2,3}. Therefore, as an indispensable component of the electrolytes of state-of-art LIBs, EC decomposition primarily controls the electrolyte decomposition process⁴. The products are widely known to contain both organic and inorganic components such as lithium alkyl carbonates (e.g. $(\text{CH}_2\text{OCO}_2\text{Li})_2$, ROCO_2Li), oxalate, alkoxides (e.g. ROLi , HCOLi) and other lithium salts (e.g. LiF , Li_2CO_3 , Li_2O)¹. In this study, however, we focus on two lesser known compounds that are more difficult to identify, because of the close chemical structure to the solvent molecules presenting an analytical challenge. Diethyl 2,5-dioxahexane dicarboxylate (DEDOHC) and a polymerized form of ethylene carbonate (which we will refer to as poly-EC) have been suggested as products of electrochemical reduction of EC-based electrolytes in LIBs. Yoshida et al.⁵ first reported the formation of DEDOHC (referred to as a transesterification byproduct) in LIBs with 1 M $\text{LiPF}_6/\text{EC}+\text{DEC}$ (1:1 v/v) electrolyte. Other groups have detected DEDOHC formation by gas chromatography-mass spectroscopy (GC-MS),⁶⁻⁸ and storage tests

imply that this product is catalyzed by lithium alkoxide.^{8, 9} Poly-EC has also been identified to be a product of EC electrolyte degradation, initiated by a Lewis acid such as PF₅⁹⁻¹¹. The proposed reduction pathways of DEDOHC and poly-EC are shown in equations (1) and (2). However, neither DEDOHC nor poly-EC has been detected either *in-situ* or *ex-situ* by FTIR. This may be due to the lack reference spectra for these compounds and their close chemical structure to the solvent molecules that would require reference spectra to make chemical identification by FTIR.

The electrochemical reduction of the electrolyte (either solvent or salt) is believed to play a central role in the electrolyte decomposition at the anode of LIBs,^{12, 13} and individual ion solvation and ion pairing are important parts of the reduction chemistry. Several theoretical and experimental studies have been performed to determine the effect of Li^+ solvation on IR vibration spectra of electrolytes solvent and electrolyte decomposition.^{4, 14-17} . Even though neither DEDOHC nor poly-EC is lithium compounds, lithium salt can be dissolved in these compounds and therefore it is essential that FTIR reference spectra include the solvation contribution. In the present study, we synthesized two important electrolyte decomposition products (i.e. DEDOHC and poly-EC) and characterized them by FTIR and NMR. Vibration frequencies of these compounds were assigned based on theoretical calculations and experimental findings. The reference spectra were acquired by introducing the synthesized pure compounds into battery electrolyte environments, such as LiPF_6 , EC/LiPF_6 and DEC/EC/LiPF_6 . By matching the IR spectra of Sn and Ni surfaces after electrolysis to that of reference compounds, with the

solvation effect included, we were able to identify DEDOHC and poly-EC as electrolyte decomposition products.

Experimental section

Equation (3) shows the synthetic scheme of diethyl-2,5-dioxahehexane carboxylate (DEDOHC), which are based on a literature procedure^{18, 19}.

Anionic polymerization of EC (Eq. 4) follows a literature procedure using phosphazene base *t*-BuP₄²⁰. The product is precipitated in diethyl ether to remove the unreacted monomer. The polymer obtained was then dissolved in dichloromethane and precipitated in diethyl ether, this dissolution-precipitation was repeated for 3 times to get a pure product.

All reagents were purchased from Sigma-Aldrich and used without further purification. Battery grade ethylene carbonate (EC) is purchased from BASF and used without further purification. Bruker Biospin Advance II 500 MHz NMR spectrometer is used to collect the proton and carbon NMR spectra of the synthesized products.

Infrared (IR) spectra were acquired in attenuated total reflection mode with a spectrometer (Nicolet Nexus 670 Fourier) equipped with a broad band mercury-cadmium-telluride detector. Spectra

were collected with a 4 cm^{-1} resolution and added 512 scans; details of ATR mode for FTIR analysis has been reported in earlier works^{21,22}. The electrolytes used in this study were 1 M $\text{LiPF}_6/\text{EC}/\text{DEC}$ (diethyl carbonate) (Novolyte Technologies, BASF) with EC: DEC = 1:2 v/v, in which DEDOHC and poly-EC were dissolved (1:5 v/v), referred as DEDOHC/EC/DEC/ LiPF_6 and poly-EC/EC/DEC/ LiPF_6 in the text. These electrolyte samples were then dried in a glove box to remove DEC from the mixtures. Hereafter, these samples are referred as DEDOHC/EC/ LiPF_6 and poly-EC/EC/ LiPF_6 . LiPF_6 salt was added into the synthesized compound ($\sim 1\text{M}$), referred as DEDOHC/ LiPF_6 and poly-EC/ LiPF_6 . Electrolyte decomposition product-to-electrolyte ratios were chosen to be sufficiently high ($\sim 20\%$ v/v) in order to facilitate the identification of new features in the electrolyte background spectrum. Pure DMC ($>99\%$ anhydrous, Sigma-Aldrich) and EC solvents were used as control samples. Sample handling was performed under an inert atmosphere without any exposure to the ambient air.

A single compartment Teflon cell with two electrodes was used for the Sn foil electrochemical experiments. Lithium metal serves as both counter and reference electrodes; Sn foil (99.99% Sigma Aldrich) as working electrode. All the potentials reported in this work are refer to the Li/Li^+ redox couple. All the electrochemical cells were assembled in an Ar-filled glove box (water and oxygen contents <10 ppm). For the *ex-situ* FTIR experiments, the Sn electrode was cycled between 0 to 2 V for two cycles at 1mV/s . The spectra were obtained in ATR mode directly on the electrode surfaces after DMC rinsing to remove bulk electrolyte. After allowing the volatile electrolyte component DEC to evaporate in the glove box and rinsed with DMC to remove residual electrolyte, the anodes were transferred directly to the N_2 -purged spectrometer sample cavity before FTIR analysis. Details of *ex-situ* FTIR-ATR analysis have been reported in earlier publications.^{21, 23, 24} The Ni foil IR experiments and spectra are from a previous paper⁴.

Computation

Ab initio quantum chemical calculations were performed with Gaussian 09 at the Hartree-Fock (HF) theory level with a 6-31+G(d,p) basis set. Before the frequency calculations, the molecular structure was optimized at the same theory level and with the basis set. The systematic error in the calculated vibrational frequencies at the HF level was corrected by using an empirical scaling factor of 0.8929.²⁵

Results and discussions

Structural Identification of Synthetic DEDOHC and poly-EC

Figures 1a and 1b show the synthesized DEDOHC ^1H and ^{13}C NMR spectra, respectively, collected from a suspension in CDCl_3-d . The high molecular symmetry of DEDOHC produces fairly simple ^1H and ^{13}C spectra. The triplet at 1.31 ppm for $-\text{CH}_3$ indicates a $-\text{CH}_2-\text{CH}_3$ substructure, while the quartet at 4.19 ppm represents a characteristic split pattern and proton position of the $-\text{O}-\text{CH}_2-\text{CH}_3$ substructure. The triplet at 4.38 ppm indicates a $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ substructure. Peak area integration further confirmed the former substructures with a proton ratio of 3:2:2. ^{13}C NMR detected four nonisotropic ^{13}C nuclei located at 14.22 ppm ($-\text{CH}_3$), 64.81 ppm ($-\text{O}-\text{CH}_2-\text{CH}_3$), 65.13 ppm ($-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$) and 155.03 ppm ($-\text{C}(\text{O})-$). The $-\text{C}(\text{O})-$ carbon at 155.03 ppm shows a relatively lower abundance compared to other carbons because it is an sp^2 -hybridized carbon peak.

Figures 1c and 1d show the synthesized poly-EC ^1H and ^{13}C NMR spectra, respectively, collected from a suspension in CDCl_3-d . As the molecular structure shows, the polymerized form of EC is actually a copolymer of alkylcarbonate and ethylene oxide functional groups. The triplet at 3.63 ppm represents a $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$ substructure, while the triplets at 3.72 and 4.31 ppm indicate $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$ and $-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ substructures, respectively. Peak area integration further confirmed the former substructures with a proton ratio of 1:1:1. Although poly-EC was extensively washed to remove the residual monomers and initiator, a small amount of monomer was left on the product, as indicated by the signals at 4.57 ppm, assigned to the $-\text{CH}_2-\text{CH}_2-\text{O}-$ substructure of the EC monomer. ^{13}C NMR detected four nonisotropic ^{13}C nuclei located at 66.22 ppm ($-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$), 66.81 ppm ($-\text{C}(\text{O})-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$), 69.13 ppm ($-\text{C}(\text{O})-\text{O}-\text{CH}_2-$) and 152.23 ppm ($-\text{C}(\text{O})-$). The $-\text{C}(\text{O})-$ carbon at 152.23 ppm shows a relatively lower abundance compared to the other carbons because it is an sp^2 -hybridized carbon peak. All chemical shifts of ^1H and ^{13}C nuclei are given in Table S1 (Supporting Information).

Figure 2 shows the FTIR spectrum of synthesized DEDOHC and poly-EC. To aid the interpretation of the FTIR spectrum, vibrational frequencies of the compounds were obtained from *ab*

initio quantum chemical calculations. Comparisons between calculated and experimental frequencies of pure DEDOHC and poly-EC can be found in Tables S2 and S3 (Supporting Information), respectively. Table 1 gives characteristic vibrational frequencies with their group frequency assignments. The vibrational mode at $\sim 1744\text{ cm}^{-1}$ is characteristic of the delocalized carbonyl group C=O stretching mode, while the strongest vibrational mode at $\sim 1234\text{ cm}^{-1}$ is attributed to the O–C–O asymmetric stretching mode. The weak vibrational mode at $\sim 857\text{ cm}^{-1}$ originates from the carbonate group O–C–O–O out-of-plane bending mode. All of these peak features are common to DEDOHC and poly-EC; what distinguishes the spectra of these two compounds is the ether structure C–O–C vibration stretch at 1103 cm^{-1} , which is only present in the spectrum of poly-EC.

Analysis of Li ion solvation effect on DEDOHC and poly-EC IR spectrum

The FTIR spectra of the synthesized standard compounds are of great importance to the identification of the electrolyte decomposition product in both *in-situ* and *ex-situ* experiments.^{26,21,27} The spectra of organic compound would be especially affected by the presence of solvents and ions of the battery's electrolyte, collectively referred to as solvation effects. Thus, DEDOHC and poly-EC were introduced into the electrolyte, and FTIR spectra were acquired under the same condition as in *in-situ* and *ex-situ* experiments. Figure 3 (a, b) shows FTIR spectra of pure DEDOHC, DEDOHC/LiPF₆, DEDOHC/EC/LiPF₆, and DEDOHC/EC/DEC/LiPF₆ in the ranges 800–2000 and 2700–3100 cm^{-1} . A salient peak at $\sim 841\text{ cm}^{-1}$ can be observed for the electrolytes containing the LiPF₆ salt, while the spectrum of pure DEDOHC does not contain this characteristic vibrational mode. Quantum mechanical calculations²⁸ show that free perfluorate anion (PF₆[−]) with O_h symmetry gives rise to two IR active modes at 860 and 540 cm^{-1} . Additional changes in spectral features due to the presence of LiPF₆ are the carbonyl group (C=O) stretching mode at 1718 cm^{-1} and the shift of the 1316 and 1238 cm^{-1} peaks (O–C–O stretch). Compared to the FTIR spectrum of Li⁺-free DEDOHC, Li solvation weakens the C=O bond and strengthens the C–O bond, resulting in red and blue shifting of the C=O and O–C–O vibrational stretches, respectively. Collectively, these spectral features induced by the salt addition to DEDOHC reflect interactions between solvent molecules and ions, which are consistent with the findings of previous

electrolyte solvent studies.^{2, 17, 27, 29} We also noticed that with addition of both EC and LiPF₆ to DEDOHC, the vibration of O-C-O stretch is shift to even higher wave number, from 1238 to 1253 cm⁻¹, which may come from the co-solvation of EC and DEDOHC with Li ion. And once DEDOHC is introduced to EC/DEC/LiPF₆ electrolyte, due to the similarity with DEC, DEDOHC peaks were hard to recognize in the spectrum.

The effect of Li⁺ solvation on the FTIR vibration spectrum of poly-EC was investigated by adding poly-EC into DEC/EC/LiPF₆, EC/LiPF₆ and LiPF₆. Figure 3(c, d) shows FTIR spectra of pure poly-EC, poly-EC/LiPF₆, poly-EC/EC/LiPF₆, and poly-EC/EC/DEC/LiPF₆. Similar changes and vibrational frequency shifts due to ion solvation can also be seen in the poly-EC spectra, namely a new band on the low-frequency side of the carbonyl group (C=O) vibration at 1720 cm⁻¹ and a new band on the high-frequency side of the carbonate group O-C-O asymmetric stretching at 1303 cm⁻¹. Additional changes in the FTIR spectrum of poly-EC containing the LiPF₆ salt include shifting of the alkyl group on the high-frequency side of the C-H stretch at 2887 cm⁻¹. Poly-EC/EC/LiPF₆ has the same shifts as poly-EC/LiPF₆, only the relative intensity changed, but poly-EC/EC/DEC/LiPF₆ shows a combination of Li ion solvation and co-solvent effects.

Analysis of Surface species formed on Sn and Ni

The Sn electrode was swept from 2V to 0 V at a scan rate of 1mV/s for two cycles in 1M LiPF₆, EC: DEC (1:2 v/v) electrolyte. The cyclic voltammetry curve is shown in Figure S1 (Supporting Information). Fig. 4 shows the analysis of electrolyte decomposition species formed on Sn foil by FTIR. Details about the absorption bands of the residual electrolyte have been shown in previous publication, including complete assignments²¹. FTIR spectra show that the Sn foil surface species is mainly DEDOHC with Li ion solvated (1744, 1316 cm⁻¹), though residual electrolyte EC/LiPF₆ is detected as well. The DEDOHC O-C-O vibration peak shifts from 1278 to 1316 cm⁻¹ with Li solvation effect, which matches exactly the new surface species feature on the Sn electrode. This observation confirms that the unstable product detected in previous studies was indeed DEDOHC^{30, 31}. Without considering the Li ion solvation effect, it would be hard to identify DEDOHC as the electrolyte decomposition product in IR.

In previous work⁴, the Ni electrode was swept from an open circuit voltage (OCV) of 2.9 to 0.5 V, followed by reverse scan from 0.5 to 2.5 V vs Li/Li, at a scan rate of 1 mV/s in 1.2 M LiPF₆/EC:EMC (3:7,w/w) electrolyte. By comparison of IR experimental spectrum (referred to as Ni(1) in Figure 5) with the synthesized compound lithium ethylene dicarbonate (LiEDC), LiEDC was determined to be the major surface species on Ni electrode. Since lithium metal is not deposited in this potential region, LiEDC is the product of electrochemical reduction of EC in the electrolyte and not the chemical reaction of EC with freshly deposited lithium. When the lower potential of cycling was shifted to – 0.5 V to include deposition of metallic lithium (referred to as Ni(2) in the figure), the same product was observed only with greater intensity. However, after a total nine cycles between -0.5 and 2.5V (referred as Ni (3)), the FTIR spectrum of Ni electrode shows a new feature at around 1103 cm⁻¹, a shoulder at 1302 cm⁻¹, and dramatic changes in the multiple C-H stretching bands in the 2800 – 3200 cm⁻¹ can be attributed to the formation of poly-EC after long-term cycling. The ratio of the carbonate and ethylene oxide segments will affect the relative intensities of the C=O and C-O bands, so the synthesized poly-EC may not have exactly the same ratio as electrolyte decomposition products; however the vibrational frequencies will be essentially the same. Intuitively the kinetics of polymerization of EC might be expected to be much slower than the kinetics of reduction to LiEDC, as indicated in these experimental results. It is also intuitive that the polymerization in-situ is anionically initiated, although it is not clear what the initiator is. In the previous study from which these spectra were taken, poly-EC could not be identified as a product because a reference spectrum was not available, although it was clear that after extended cycling another product besides LiEDC was present.

Conclusions

In this study, we investigated the decomposition of EC-based electrolyte using FTIR-ATR vibrational spectroscopy and identified the decomposition products by matching the IR spectra to that of synthesized reference compounds. Reference IR spectra of DEDOHC and poly-EC compounds were obtained and detailed peak assignments were made based on quantum chemical (Hartree-Fock) calculations. Solvation effect was studied by introducing the synthesized compounds into various

electrolyte environments (LiPF₆, EC/LiPF₆ and EC/DEC/LiPF₆). Significant peak shift and broadening of spectra were observed when solvation effect is included. By analyzing the surface species on Sn electrode, the unstable product was detected to be DEDOHC; and on Ni electrode, poly-EC generated after extended cycling, besides previously identified product LiEDC. These examples have revealed the importance to include solvation effect in the identification of electrolyte decomposition products, using ex-situ IR spectroscopy, which is also applicable to in-situ IR spectroscopy, as well as other vibrational spectroscopy analysis of decomposition process.

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Table 1. Characteristic Vibration Frequencies of DEDOHC and Poly-EC and Corresponding Group Frequency Assignments

Group frequency assignment	Wavenumber (cm ⁻¹)	
	DEDOHC	Poly-EC
Alkyl (asymmetric or symmetric stretch)	2986, 2944, 2913, 2878	2872, 2948
C=O stretch	1744	1743
O–C–O stretch	1278, 1234	1259
C–O–C stretch (ether structure)		1103 (wide)
O–C–O–O (out-of-plane bending)	857	859

Figure 1. (a) ^1H and (b) ^{13}C NMR spectra of DEDOHC, and (c) ^1H and (d) ^{13}C NMR spectra of poly-EC. The spectra were collected in CDCl_3-d . Solvent signals arising from proton residuals due to incomplete deuteration are denoted by an asterisk.

Figure 2. FTIR spectra of DEDOHC and poly-EC.

Figure 3. FTIR spectra of DEDOHC (a,b) and poly-EC (c,d) for various Li^+ solvation conditions.

Figure 4. FTIR spectra of Sn electrode cycled between 0 and 2V vs. Li/Li^+ and DEDOHC reference spectra (DEDOHC/EC/LiPF₆, DEDOHC/LiPF₆, DEDOHC).

Figure 5. FTIR spectra of Ni (1), Ni electrode cycled between 0.5 and 2.5V vs. Li/Li⁺; Ni (2), cycled between -0.5 and +2.5V vs. Li/Li⁺; Ni (3), after total nine cycles between -0.5 and +2.5V vs. Li/Li⁺; LiEDC and poly-EC reference spectra (poly-EC /LiPF₆)