Identifying the components of the solid–electrolyte interphase in Li-ion Batteries

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Abstract

The importance of the solid–electrolyte interphase (SEI) for reversible operation of Li-ion batteries (LIBs) has been well-established, but understanding of its chemistry remains incomplete. The current consensus on the identity of the major organic SEI component is that it consists of lithium ethylene di-carbonate (LEDC), which is thought to have a high Li-ion conductivity but a low electronic conductivity to protect the Li/C electrode. We report here on the synthesis, structural and spectroscopic characterizations of authentic LEDC and lithium ethylene mono-carbonate (LEMC). Direct comparisons of SEI grown on graphite anodes suggest that LEMC, instead of LEDC, is likely the major SEI component. Single crystalline X-ray diffraction (XRD) studies on LEMC and lithium methyl carbonate (LMC) reveal unusual layered structures and Li^+ coordination environments. LEMC has Li^+ conductivities of above 10^{-6} S/cm, while LEDC is almost an ionic insulator. The complex interconversions and equilibria of LMC, LEMC and LEDC in dimethyl sulfoxide (DMSO) solutions are also investigated.

Introduction

Li-ion batteries (LIBs) are ubiquitous in 21st century life and have an estimated 2018 global market of US$ 25 billion. Despite their technological importance and mass production, a molecular level understanding of ion transport mechanisms and the interfacial chemistry in these devices remain elusive. As evidenced by the history of LIBs,[1] misconceptions in fundamental chemistries often delay breakthroughs in new materials, for which interphases on graphite anodes are a conspicuous example. Graphitic materials serve as the standard anodes in the current LIBs. In the charge and discharge processes of a LIB, Li^+ intercalates into and de-intercalates from the graphene layers.[2-7] Due to the extremely low potentials where such intercalation/de-intercalation processes occur (~ 0.2 V vs. Li^+/Li),[4,8,9] commonly used carbonate-based electrolytes (*e.g.* 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC)) are electrochemically reduced at the anode surface in the first few charge/discharge cycles.[9-11] This electrochemical reduction generates an insoluble passivating film on the anode surface known as the solid–electrolyte interphase (SEI),[12-16] which constitutes a critical component of LIBs in that it prevents further parasitic electrolyte decomposition and stabilizes battery operation and capacity.[7,12,13] The SEI is still regarded as one of the most important but the least understood component in rechargeable LIBs although extensive efforts have been devoted to elucidating its composition and function.[17] While it is well accepted that the SEI is approximately 10 - 50 nm thick,[7,14,18-23] contains inorganic salts (*e.g.* Li_2CO_3 and LiF),[14,18,20,24,25] degraded carbonate molecules (semi-carbonates and polymers),[10,15,24,26-32] and prevents further solvent degradation as an electronic insulator while facilitating Li^+ transport as an electrolyte,[7,12,13] the precise structure, composition and the functional mechanism(s) of the SEI remain under debate.

It is well accepted that the organic SEI component primarily comes from electrochemical reduction of EC, as is often evidenced by a narrow shoulder in the discharge curve at *ca*. 0.8 V during the first discharge cycle (Fig. 1).[13,33,34] The importance of EC-originated products in the SEI is evidenced by the necessity of employing EC in essentially all commercial electrolytes, where preferential solvation of Li^+ by EC dictates SEI formation.[35,36] EC reduction is commonly believed to react via a "single-electron pathway" that generates lithium ethylene di-carbonate (LEDC) according to equation (1).[10,15,26,28,37] Identification of LEDC in authentic nanoscopic SEI films has been accomplished through multiple spectroscopic techniques including X-ray photoelectron spectroscopy (XPS),[10,14,33] Fourier-transform infrared spectroscopy (FTIR),[10,15,26,28,31,33,38] solid-state and solution phase nuclear magnetic resonance (NMR) spectroscopy,[14,32,39,40] to name a few. The SEI spectroscopic signatures were compared to those of synthetic LEDC standards, which have been independently reported by four separate laboratories, including one of us.[37,39,41,42] Unfortunately, these synthetic procedures for LEDC synthesis suffer from insolubility problems that lead to kinetic limitations in the carbonate formation process. Herein we report that these reported synthetic standards are not LEDC but are actually lithium ethylene mono-carbonate (LEMC) and, to our knowledge, LEDC has not been prepared prior to our work.

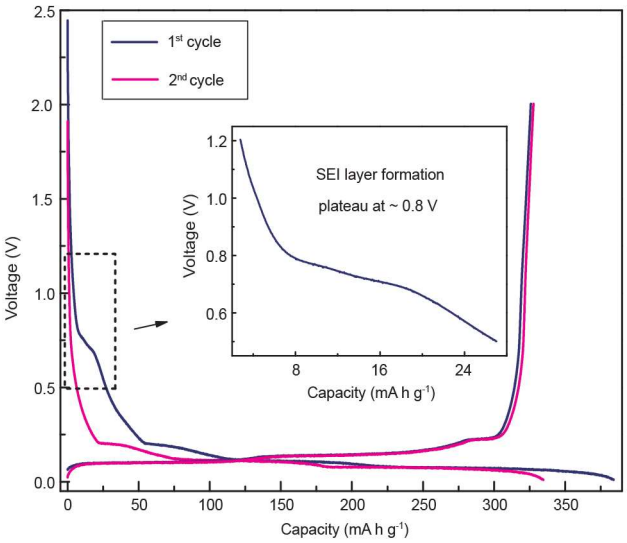
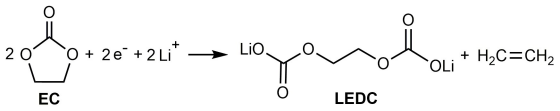


Figure 1. Electrochemical behavior of a graphite electrode. The dark blue and red curves show the 1st and 2nd battery cycles, respectively, with 1M $LiPF_6$ in EC/DMC (v: v = 1: 1) as electrolyte solution and Li foil as the counter electrode. The inset indicates formation of SEI layers at a plateau of ~ 0.8 V in the 1st lithiation process of the graphite electrode.

We describe here high-yield synthetic routes to LEDC•2DMSO, LEMC and lithium methyl carbonate (LMC). These compounds have been fully characterized using FTIR, 1D and 2D solution and solid-state NMR spectroscopy (^{1}H, ^{13}C and ^{7}Li), as well as powder X-ray diffraction (XRD) for all compounds and single crystal X-ray studies for LEMC and LMC. In addition, we also show that LEMC is a facile Li^+ ion conductor whereas LEDC and LMC are not. Spectroscopic comparisons between authentic EC/DMC derived SEI films and the synthetic model compounds suggest that the SEI likely contains an "LMC-capped LEMC organic layer" and it is *unlikely* that LEDC is present in the SEI at all.



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Results and discussion

Synthesis and characterization. LEMC was conveniently prepared in high yield as a white polycrystalline solid through the lithiation/deprotonation of ethylene glycol (EG) with n-BuLi according to Fig. 2a. Single crystals of LEMC were obtained from EG solutions layered with pyridine in *ca.* 10% yield. LMC was prepared in high yield in a similar manner, according to published procedures (Fig. 2b).[37,39,41] Single crystals of LMC were grown from a MeOH/Et_2O solution in *ca.* 30% yield. Synthetic details for both compounds are given in the supplementary information along with full spectroscopic, analytical and structural data (FTIR, solution and solid-state NMR, elemental analysis, powder and single crystal X-Ray diffraction, XPS, Supplementary Fig. 1 – 10 and Supplementary Table 1 - 5). These white crystalline solids are soluble in rigorously dried DMSO but insoluble in ethereal and hydrocarbon solvents. LEMC is also soluble in dry EG, moderately moisture sensitive and will slowly decompose in air. LMC is soluble in MeOH and dimethylformamide, is air/moisture sensitive and also undergoes hydrolysis in solution.

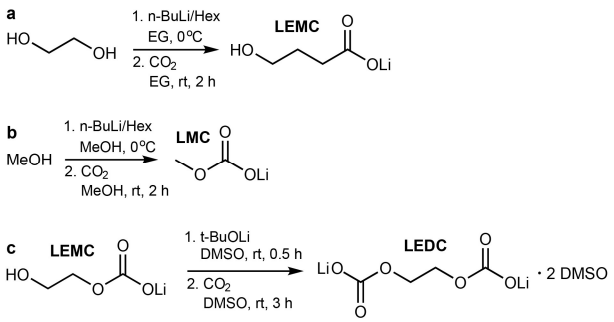


Figure 2. Chemical synthesis of (**a**) LEMC, (**b**) LMC and (**c**) LEDC·2DMSO.

Previous reports on the synthesis of "LEDC" involved nucleophilic addition of di-lithium ethylene glycolate ($LiOCH_2CH_2OLi$) to CO_2 in ethereal solvents.[37,39,41] The reaction of EG with excess lithiation agents (n-BuLi or LiH) was expected to yield the di-lithium ethylene glycolate intermediate that subsequently reacts with CO_2 in ethereal solutions. However, it appears that the mono-lithiated intermediate, $LiOCH_2CH_2OH$ (LiEG), is virtually insoluble in ethereal solvents and precipitates from solution before the second deprotonation can occur. We have found that addition of excess CO_2 (g) to the heterogeneous mixture results in an initial deactivation of the excess n-BuLi followed by a slower carbonate formation reaction with sparingly soluble $LiOCH_2CH_2OH$ to give LEMC as the exclusive product. The experimental and calculated powder XRD and FTIR data for the analytically-pure LEMC single crystals from our studies are perfect matches to all previously reported data for "LEDC", indicating that these studies actually characterized LEMC (see Supplementary Fig. 11 - 12). With this knowledge, we employed the more convenient synthesis of LEMC involving direct deprotonation of EG with n-BuLi at 0°C, as described above in Fig. 2a.

Upon recognizing the solubility issues associated with the lithium glycolate intermediates, we devised an alternative synthesis of LEDC from LEMC in DMSO solutions. White polycrystalline LEDC•2DMSO was conveniently prepared through the deprotonation of LEMC by lithium tert-butoxide in DMSO, followed by reaction with excess CO_2 (Fig. 2c). The powder precipitates from solution in high yield and is slightly soluble in rigorously dry DMSO. The solid and its solutions are sensitive to moisture and other protic sources and are also air sensitive. Spectroscopic and analytical data (FTIR, solution and solid-state NMR, elemental analysis, see Supplementary Fig. 5 - 8) reveal a composition of $LiOCO_2CH_2CH_2OCO_2Li$•2($OSMe_2$) or LEDC•2DMSO. To date, we have been unable to isolate single crystals of the compound and the precipitates give broad powder XRD profiles (Supplementary Fig. 1). Regardless, the analytical and spectroscopic data, specifically the NMR data (see below), unequivocally show that the compound is LEDC•2DMSO. Removal of DMSO solvates from the crystalline lattice of LEDC•2DMSO was accomplished by sonication in anhydrous THF at 50 °C, which generated amorphous LEDC as indicated by powder XRD and NMR studies (Supplementary Fig. 1 and 13).

Crystal structures of LEMC and LMC. The solid-state structures of LMC and LEMC were determined from single crystal X-ray studies of the respective crystals. Details of the refinements and crystallographic data are given in the supplementary information (crystallographic information file (CIF), Supplementary Table 2-3). LMC is monoclinic, space group $P2_1/c$, and contains two independent LMC molecules in the asymmetric unit that are partitioned into two different layers of the crystal lattice (see Fig. 3a and 3b). Layer A contains double sheets of LMC molecules with LiO_4 tetrahedra at the layer interior and the Me groups on the layer exterior. Each oxygen of the LiO_4 tetrahedra originates from a terminal carbonate oxygen of a different LMC molecule, two from each side of the layer, which links the structure into a two-dimensional network via edge-shared tetrahedra. While layer A is perfectly ordered, layer B has a 3:2 positional disorder in the y-z plane but is otherwise identical to A. The two layers alternately stack along the x-axis of the cell to give an unusual order - disorder - order layered structure of functionally identical

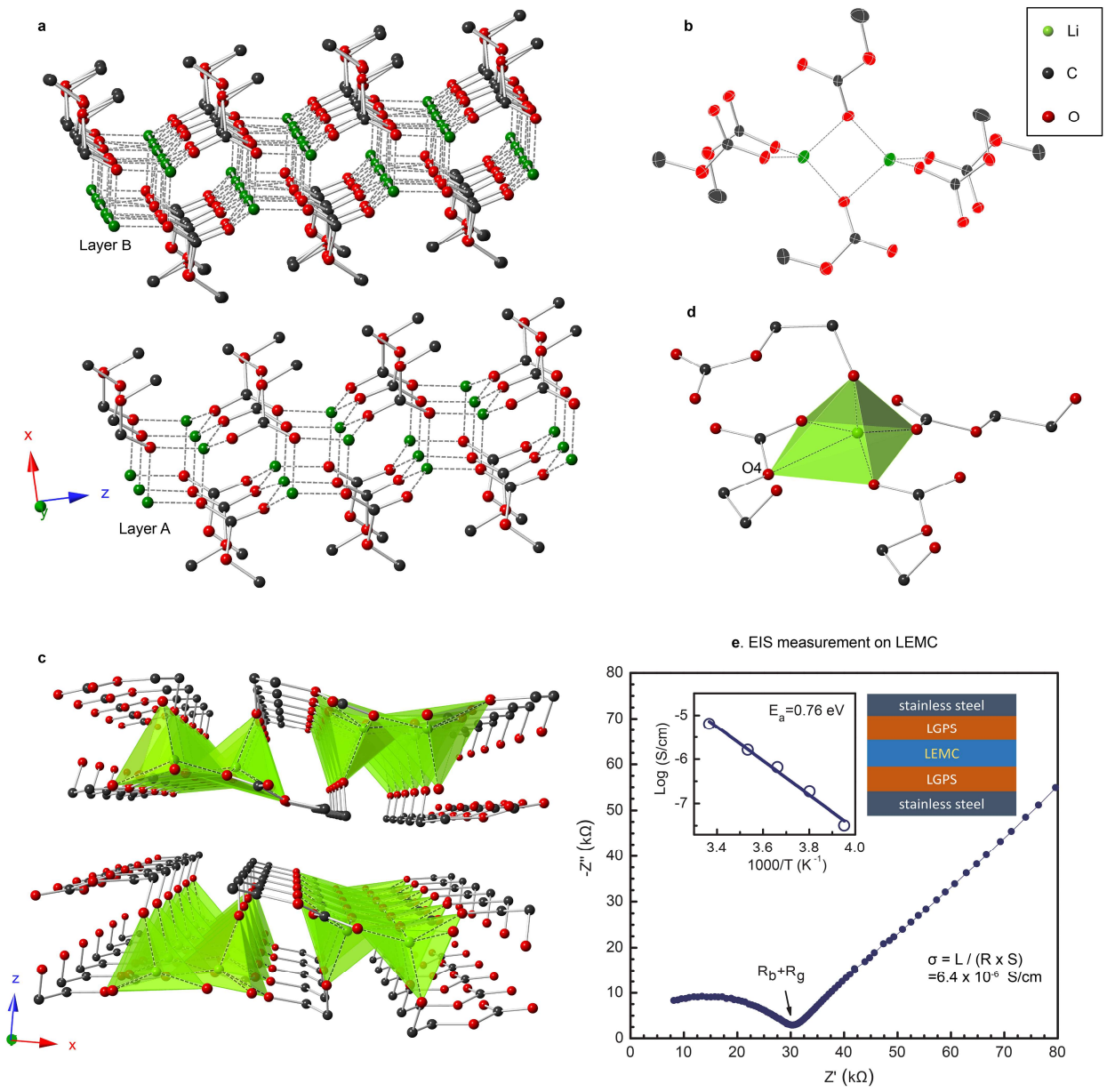


Figure 3. X-ray structures of LMC and LEMC, and EIS measurements on LEMC. Structures of LMC showing (**a**) the alternative packing of ordered Layer A and disordered Layer B and (**b**) the tetrahedral coordination of Li^+ by O atoms. Structures of LEMC showing (**c**) the layers of LEMC double sheets and (**d**) the distorted pentagonal pyramidal 5-coordinate Li^+ ion polyhedron. (**e**) shows the ionic conductivity of LEMC measured by EIS at 25 °C. The figure inset in (**e**) shows the linear fit used to calculate activation energy (E_a) for Li^+ conductivity. The scheme shows the electrochemical cell used for the EIS measurements, where the LEMC layer was sandwiched between LGPS layers to block proton transfer. The ionic conductivity, σ, was calculated from the thickness of LEMC film, L, the resistance measured by EIS ($R = R_b + R_g$) and the area of LEMC in the cell, S.

subunits. The LiO_4 tetrahedra are somewhat distorted with Li-O bond distances that vary from 1.922 (6) - 2.011 (6) Å (ave. 1.960 (2) Å) and O-Li-O angles that vary from 88.9 (3)° - 117.2 (3)°.

LEMC is orthorhombic, space group *Pbcn*, and contains a single unique molecule in the asymmetric unit. The structure contains double sheets of LEMC molecules stacked along the z-axis of the orthorhombic cell (Fig. 3c and 3d), but the Li^+ ions are in distorted 5-coordinate pentagonal prismatic environments defined by three terminal carbonate oxygens, one alkyl carbonate oxygen and an alcohol oxygen. Four of the Li-O bonds are typical (1.917 (8) - 2.027 (9) Å; ave. 1.996 (4) Å) with a longer 2.580 (9) Å contact to the alkyl carbonate oxygen O4. The pentagonal prisms share corners to form double ribbons running in the y-direction that are linked together in the x-direction by the spanning alcohol groups of the LEMC. Unlike the LMC structure, the Li^+ ions in LEMC reside in Li-O-Li-O lined crevices on the exterior of the layers. This unusual Li^+ coordination geometry and its position in the interlayer crevices of the layered lattice structure may play an important role in the Li^+-ion conductivity described below.

Li-ion conductivities. As both LMC and LEMC (reported as "LEDC" in prior publications) have been frequently reported as key organic components of the SEI on graphite electrodes, information on their Li^+ ion conductivities are thus of great importance and are measured here by electrochemical impedance spectroscopy (EIS). Cold-pressed LEMC pellets are sandwiched between two $Li_{10}GeP_2S_{12}$ (LGPS)[43,44] rectifiers to block any proton conductivity during the measurements (See Methods for details). The EIS data and the Arrhenius plot for Li^+ conductivity of LEMC are shown in Fig. 3e. LEMC has reasonably high Li-ion conductivity of 6.4 x 10^{-6} S/cm at 25 °C, which is slightly better than single-domain LiPON films ($S \approx 3 \times 10^{-6}$ S/cm),[45] The activation energy (E_a) for Li^+ conductivity calculated from an Arrhenius analysis is 0.76 eV (Fig. 3e inset and Supplementary Fig. 14), which is higher than common inorganic Li^+ conductors but similar to organic-based Li^+ ion conductors, such as $LiClO_4$/poly(ethylene oxide).[43,45,46] The influences of OH-rotation, Li^+ interstitials, Li^+ and H^+ vacancies on the Li^+ diffusion in LEMC were examined using Born Oppenheimer molecular dynamics (BOMD) simulations of the superheated LEMC (Supplementary Figure 15-16). Addition of Li^+ vacancy or Li^+ substitution for H in the O-H groups results in the fastest Li^+ diffusion, followed by Li^+ interstitial diffusion occurring via a "knock-off" mechanism[23] that is similar to Li_2CO_3, where the 5-fold Li-O coordination environment significantly decreases Li^+ diffusion barriers.[23] Measurements on the amorphous LEDC and LMC (pressed pellets) give resistances outside the measurable range, which we attribute to high resistivities (< 10^{-9} S/cm) of the two compounds. The high resistivity measured for LMC is consistent with previous studies.[47]

Solution properties and NMR Studies. In contrast to previous reports,[41,48] our studies show that LEMC and LMC, as well as LEDC·2DMSO, dissolve to give stable solutions in rigorously dry DMSO. However, all three compounds undergo aggregation in the solution that leads to concentration-dependent chemical shifts in the ^1H, ^{13}C and ^7Li NMR spectra. Moreover, the compounds are reactive towards water, residual solvent (MeOH, EG, EC or DMC) and are involved in complex equilibria and interconversions. Details of the solution chemistry and the spectroscopic properties are given in Fig. 4, Supplementary Fig. 17 - 20, and will be described in a subsequent publication. Only the pertinent properties are presented here.

Solution ^1H and ^{13}C {^1H} NMR spectra for LEDC•2DMSO in DMSO-d_6 are given in Fig. 4a and Supplementary Fig. 5. Solid-state 1D ^1H and ^7Li magic-angle spinning (MAS) NMR spectra, along with 2D ^1H (SQ)- ^1H (DQ) and ^7Li-^1H MAS NMR spectra are given in Supplementary Fig. 6 and 7. The 1D solid-state NMR spectra of LMC and LEMC simulated using the density-functional theory (DFT) gauge-including projector-augmented wave (GIPAW) approach[49,50] demonstrate high consistency with experimental data (Supplementary Fig. 6 and Supplementary Table 4 and 5). In DMSO-d_6 solution (saturated solution, ~ 20 mmol/L, 25 °C), the LEDC ethylene protons give rise to a singlet at 3.63 ppm with the ethylene and carbonate carbons appearing at 62.7 and 155.2 ppm, respectively, which is consistent with the symmetry of the compound. In the solid state, ^1H NMR resonances appear at 3.4 and 2.6 ppm, which are assigned to the ethylene protons and lattice DMSO, respectively.

On account of its lower symmetry, the ethylene protons of LEMC appear as two triplets at 3.44 and 3.72 ppm with an *OH* resonance at 4.82 ppm (DMSO-d_6, initial concentration: 0.53 mol/L, 25 °C), with similar shifts in the solid state (Supplementary Fig. 6). The ethylene carbons and the carbonate carbon appear at 61.0, 65.8 and 156.9 ppm, respectively. However, LEMC quickly establishes an equilibrium with LEDC and EG in solution (K_c = 0.14), as illustrated in Fig. 4b and 4e. Adding EG or LEDC to the solutions shift the equilibria to the left, as expected. Likewise, adding EG to a pure solution of LEDC•2DMSO will generate LEMC according to the equilibrium expression (Supplementary Figure 18). These data not only establish that LEMC readily reaches equilibria in solution but also confirm the identity of LEDC through the equilibrium relationship.

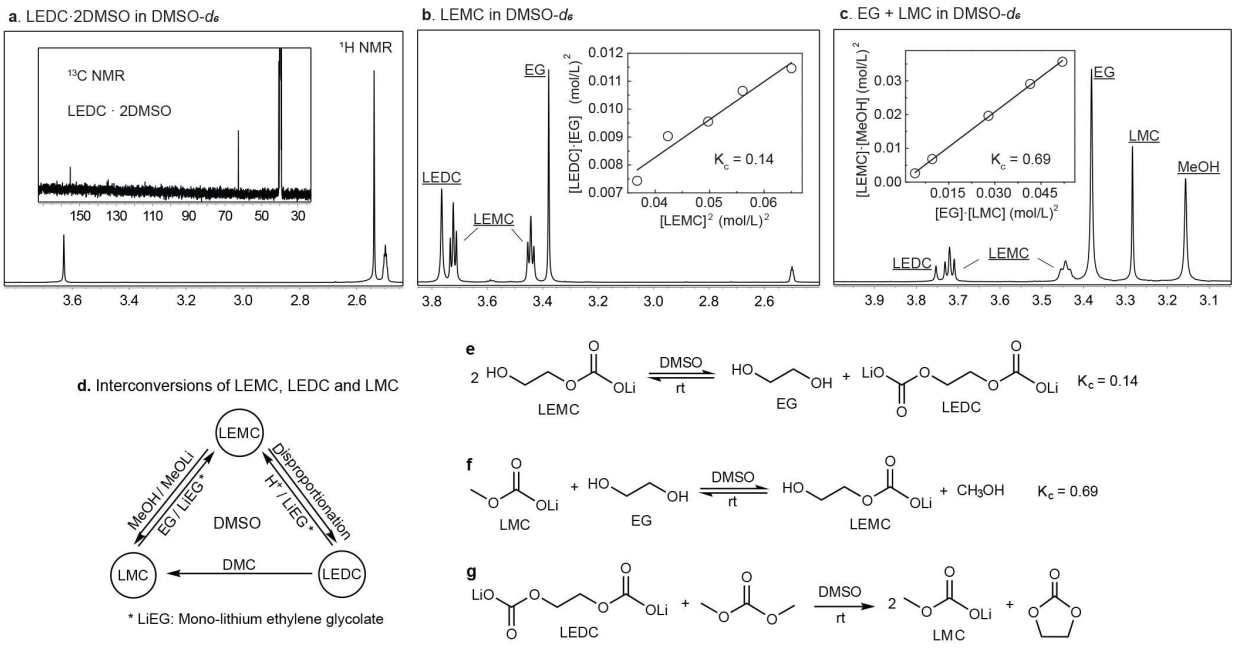


Figure 4. Solution NMR studies on LMC, LEMC and LEDC·2DMSO. NMR spectra (500 MHz, 25 °C) of (**a**) LEDC·2DMSO (saturated, *ca.* 0.02 mol/L), (**b**) LEMC (initial concentration: 0.53 mol/L) and (**c**) LMC + EG (initial concentration: LMC 0.34 mol/L + EG 0.41 mol/L) in DMSO-d_6 indicate complex equilibria. The insets in figures (**b**) and (**c**) show linear fittings used to calculate the equilibrium constants. (**d-g**) indicate the interconversions between these lithium organic carbonates, in reactions with alcohols and carbonate electrolytes in DMSO.

The alkyl carbonates are quite reactive towards protic solvents such as water, alcohols and the carbonate solvents EC and DMC. For example, hydrolysis of LEDC gives rise to LEMC, in both DMSO-d_6 solutions and the solid state (monitored by NMR and FT-IR spectroscopies, respectively. Supplementary Fig. 21-22). LEMC and LMC show much higher stability towards moisture than LEDC, but all three compounds will be hydrolyzed eventually to give corresponding alcoholic species (FTIR and simulation studies, Supplementary Fig. 23-25). In addition, the alkyl carbonates can be interconverted in DMSO solutions through the addition of complementary carbonates or alcohols. The interconversions of LMC and LEMC through the addition of EG and MeOH are illustrated in Fig. 4c and 4f with an equilibrium constant of 0.69, while the conversion of LEDC to LMC through reaction with DMC is given in Fig. 4g and NMR spectra in Supplementary Fig. 17. Dissolving LEMC and DMC together in DMSO-d_6 instantly results in multiple equilibria (Fig. 4 e-g) and products such as EG, LMC, LEDC and MeOH (Supplementary Fig. 20). An overview of

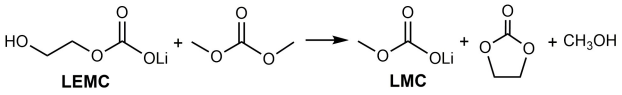
the interconversion chemistries that occur with LMC, LEMC and LEDC is highlighted in Fig. 4d with supporting spectra given in the Supplementary Information (Supplementary Fig. 17). The interconversions *only* occur in DMSO solutions (as DMSO solvates the species) and do not occur (or only occur slowly at the liquid-solid interface) when insoluble LEDC, LEMC or LMC are in contact with pure EC/DMC solvents in a battery environment. Analysis of the reactions where LEDC or LEMC is suspended in DMC or EC/DMC solutions (without DMSO) is presented in the supplementary information (Supplementary Fig. 26).

Chemical compositions of SEI layers on graphite electrodes. Because SEI layers are only 10 - 50 nm thick, isolating enough material to evaluate by traditional spectroscopic methods (*e.g*. NMR) is a challenge. To overcome this problem, we fabricated large and thoroughly dried electrodes containing at least 400 mg graphite (TIMREX KS44) coated on Cu current collectors (~ 200 cm^2). The electrodes were cycled three times from 0.7 to 2.0 V vs. Li/Li^+ to generate SEI layers. Three types of electrolytes, 1M $LiPF_6$ in EC/DMC (v: v = 1: 1), 1M $LiPF_6$ in DMC and 1M $LiPF_6$ in EC, were used (mixing 1.52 g $LiPF_6$ and 13 g EC forms a liquid solution at 27 ^oC). The electrochemical performances of the three systems are shown in Supplementary Fig. 27. When EC is included in the electrolyte solutions, a plateau at ~ 0.8 V is observed in the first cycle but disappears in subsequent ones, indicating the formation of SEI layers. However, when only DMC is used, no such plateau is observed. These data are consistent with literature studies indicating that SEI layers are formed in the first discharge cycle and originate from EC. Previous works have demonstrated continuous evolution of SEI layers during battery cycling,[21,22] but we only focus on the initial step in SEI formation here (the 0.8 V plateau in the 1st discharge process

The SEI films were extracted into both DMSO-d_6 and 0.1 M DCl in D_2O for solution NMR analysis. Representative 1D and 2D spectra are given in Fig. 5, Supplementary Fig. 28 and 29. Both the aqueous and DMSO extracts show significant quantities of ethylene glycol bis(methyl carbonate), EGBMC, originating from catalytic reactions of EC/DMC with oxides (*e.g*. surface oxide layer on Cu current collector or methoxide), which is well documented in the literature.[38,51] The 0.1 M DCl extraction method instantly hydrolyzes possible SEI candidates (*e.g.*, LEMC, LMC and LEDC) to give methanol and EG (Fig. 5b). Control experiments (Supplementary Fig. 30 and 31) show that the complex equilibria and secondary chemical reactions described above are averted and the observed EG: MeOH ratio provides an accurate measure of the EC-derived SEI products (*e.g.* LEMC+LEDC) : DMC-derived SEI products (*e.g.* LMC) ratio present in the SEI film. The DMSO-d_6 extracts of SEI layers formed in 1M $LiPF_6$/EC/DMC electrolytes contain LEMC, LEDC, EG, LMC and MeOH, as well as residual EC and DMC. NMR spectra in Fig. 5d collected on SEI layers grown in the EC-only cell, where DMC, as well as DMC-related equilibria/interconversions are excluded, indicate the presence of LEMC. Solid-state ^1H MAS NMR characterizations of the SEI layers coated on graphite powders, unfortunately, give very broad peaks, possibly due to the presence of paramagnetic impurities in the electrodes (Supplementary Fig. 32).

The equilibrated DMSO-d_6 SEI extracts show that the primary SEI candidates (LEMC, LEDC and LMC) are indeed present, but the complex equilibria and secondary reactions described above prohibit the determination of their origin (*i.e.* were they present in the SEI). The hydrolyzed SEI extracts suggest that the ratio between EC-derived SEI products (*e.g.* LEMC and LEDC) and DMC-derived SEI products (*e.g.* LMC) is *ca.* 5: 1 in all the repeated measurements. However, electrodes cycled in 1M $LiPF_6$ in pure DMC result in no LMC formation and no 0.8 V SEI plateau in the first discharge cycle. These findings suggest that a significant LMC component is present in SEI films but that it results from a secondary chemical reaction with LEMC or LEDC. Control experiments of insoluble LEMC powders suspended in pure DMC (and EC/DMC mixture) for several weeks indicate a slow surface reaction at the solid-liquid interface that transforms LEMC into LMC and EG (equation (2) and Supplementary Fig. 26). However, the

suspended powders are primarily LEMC after several weeks at room temperature suggesting that the particles contain a core of LEMC surrounded by a thin shell of LMC. Similar chemical transformations occur with LEDC as well (Supplementary Fig. 26).



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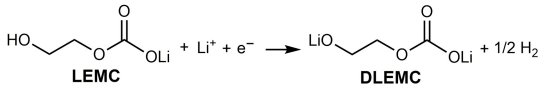

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While we cannot unequivocally determine whether LEDC or LEMC (or both) are the initial and primary components of the SEI, our hypothesis is that LEMC is the major SEI constituent and LEDC does not exist (or does not persist) in the typical LIB environment. This proposal is based on the following observations: 1) A number of previous studies have linked the organic SEI component to the "LEDC" standard,[28,39,41] which was actually LEMC. 2) LEDC is highly reactive toward residual protons, which are ubiquitous in all cell assemblies, from trace moisture in bulk electrolytes to surface functionalities on graphite. The presence of EG (or LiEG) in the EC-only control cell (which was rigorously dried) is a direct measure of the protio impurities in battery components. The protio impurities would likely convert any LEDC into LEMC. Thus, even if LEDC were formed through the single electron reduction pathway (equation (1)), it is likely converted to LEMC and LMC through reactions with protons and DMC, respectively, due to its inability to "survive" in the LIB environment.

Formation and evolution of LEMC on graphite electrode. While LEMC is likely a key component in the graphite SEIs, the precise mechanism of its formation is still unclear. It is possible that LEDC is generated as the first step,[10,15] but a subsequent hydrolysis/protonation transforms it to LEMC, as suggested by our model chemical and computational studies (Supplementary Fig. 21-22). In addition, we have discovered two alternate pathways for LEMC formation involving nucleophilic addition of OH^- (See Supplementary Fig. 33) and MeO^- to EC (See Supplementary Fig. 34). LiOH is a well-known component of the inorganic SEI layer[7,24] and can be converted to LEMC in a heterogeneous transformation. LiOMe is known to exist in DMC-derived SEIs[7,24,27] and its participation in electrolyte degradation through nucleophilic reactions has been thoroughly investigated.[51]

The evolution of the SEI layer with battery cycling is well known[21,22] and reactions of LEMC are likely part of that process. For example, the heterogeneous reaction of LEMC with DMC (eq. 2) forms an "LMC-capped LEMC organic layer", which should self-terminating in a dense layered structure (*i.e.* DMC cannot access the LEMC beneath the LMC surface). We believe that LEMC persists in a well-functioning SEI and facilitates Li^+ ion transfer. The well-established need for EC as the indispensable component in carbonate-based electrolytes[6,52] strongly implicates an active EC-derived compound in an effective SEI, which we attribute to LEMC. The relatively high Li^+ conductivity of LEMC likely benefits SEI function, in contrast to LMC which is a bulk insulator. The alcoholic proton (R-OH) on LEMC may well be subject to electrochemical reduction, generating partially di-lithiated ethylene mono-carbonate (DLEMC) and H_2 (eq. 3). Our computational studies suggest that DLEMC has equivalent or better Li^+ ion conductivity than LEMC (Supplementary Information, Section 1.7). However, we always detect a significant fraction of the protonated LEMC in the electrode analyses.

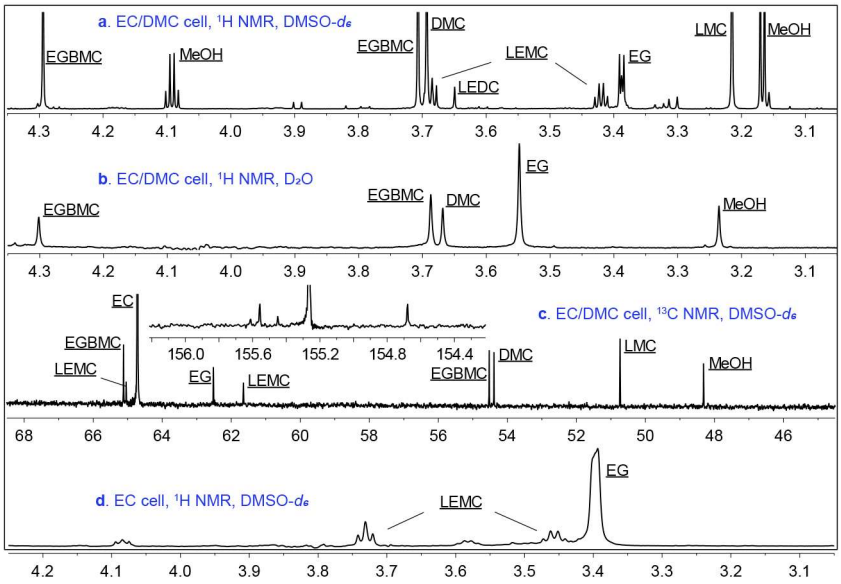

Figure 5. Solution NMR characterizations of the graphite SEI layer. Spectra (**a**) ^{1}H NMR, DMSO-d_6, (**b**) ^{1}H NMR, 0.1 M DCl in D_2O and (**c**) ^{13}C {^{1}H} NMR, DMSO-d_6 were collected from SEIs generated in electrolyte solutions of 1M $LiPF_6$ in EC/DMC, while (**d**) shows ^{1}H NMR spectra in DMSO-d_6 of SEI layers generated in the electrolyte solution of $LiPF_6$/EC. NMR spectra (**a**)(**c**) and (**b**)(**d**) were collected at 25 ^{o}C with an 800 MHz and 500 MHz spectrometer, respectively.

In conclusion, we have demonstrated, through rigorous and comprehensive characterizations including single crystal and powder XRD, FTIR, elemental analysis, solid-state and liquid 1D and 2D NMR spectroscopy, that the previously synthesized chemical standards, "LEDC", is actually LEMC. NMR studies on the SEI layers grown on graphite electrodes in typical LIBs with 1M $LiPF_6$ in EC/DMC electrolyte indicate that it is highly *likely* that LEMC, instead of LEDC, prevails as the major organic component in the SEI layers. These lithium organic carbonates, including LMC, LEMC and LEDC, show complex interconversions/equilibria in DMSO solutions. In a battery environment, these compounds (*i.e.*, LEMC and LMC) appear to be formed through secondary chemical reactions and are not generated through direct electrochemical reduction. The identification of LEMC and its properties (ionic conductivity, chemical reactivity) provide insight into Li^{+} ion transport across solid–electrolyte interphases and pave the way for future engineering of artificial interphases with superior properties.

Methods

General. Details on chemical synthesis, chemical / electrochemical characterizations and SEI extractions are described in the Supplementary Information.

Synthesis of LMC. All the synthetic procedures were carried out under inert atmospheres unless otherwise stated. To a Schlenk flask of magnetically stirred anhydrous methanol (20 ml) at 0 ^{o}C was added 2.5 M n-BuLi/hexane (10 ml, 25 mmol) dropwise. The reaction was warmed to room temperature and further stirred for 30 min. Afterwards CO_2 gas dried over a $CaSO_4$ column was bubbled through the solution for 2 h at room temperature. The solvents were removed *in vacuo*, leaving a white powder that was further rinsed with anhydrous diethyl ether. The resulting white powder was dried under vacuum for 12 h to afford LMC (1.8 g, 88% yield). Large needle crystals suitable for single-crystal XRD studies were obtained from a methanol/diethyl ether solvent mixture.

Synthesis of LEMC. To a Schlenk flask of magnetically stirred anhydrous EG (20 ml) at 0 ^{o}C was added 1.6 M MeLi/diethyl ether (25 ml, 40 mmol), or 2.5 M n-BuLi/hexane (16 ml, 40 mmol) dropwise. The reaction was warmed to room temperature and further stirred for 30 min. The diethyl ether (or hexane) was removed *in vacuo*, leaving a suspension of LiEG in EG. Dry CO_2 was bubbled through the suspension for 2 h under fast stirring, upon which the solid precipitates gradually dissolved and a clear but viscous solution was obtained. Afterwards, anhydrous pyridine (50 ml) was added to the solution. The EG/pyridine solution was stored at room temperature for 2 days under an inert atmosphere, during which time copious amounts of white powder precipitated from solution. The precipitates were collected through centrifugation, rinsed with anhydrous DMF and anhydrous diethyl ether, and further dried under vacuum for 12 h to afford LEMC (1.6 g, 36% yield). Large crystals suitable for single-crystal X-ray studies were obtained from the solvent mixture of EG/pyridine.

Synthesis of LEDC·2DMSO. To a Schlenk flask charged with a stirred solution of LEMC (224 mg, 2 mmol) dissolved in anhydrous DMSO (20 ml) was added lithium tert-butoxide (240 mg, 3.0 mmol, 1.5 equiv.) at room temperature. All powders dissolved and the clear solution was stirred for 30 min. Dry CO_2 was bubbled through the stirred solution for 3 h, during which time a white powder precipitated from solution. The white powder was collected through centrifugation, rinsed with anhydrous diethyl ether and dried *in vacuo* for 12 h to afford white microcrystalline LEDC·2DMSO (440 mg, 68% yield).

EIS measurement. To preclude contributions from the hydroxyl protons in LEMC that may contribute to the total ionic conductivities, we measured the impedance of analytically-pure LEMC pressed pellets sandwiched between two LGPS rectifiers. LGPS has very high Li^+ ionic conductivity (> 10^{-2} S/cm) but does not transport protons and,[43,44] as such, all measured transport is due to Li^+-ion conduction. A proton-blocking cell stainless steel/LGPS/LEMC/LGPS/stainless steel was assembled to measure the Li ion conductivity of LEMC. The cell was prepared by cold-pressing 20 mg LGPS, 140 mg LEMC, and 20 mg LGPS powders together under 360 MPa for 3 minutes. The electrochemical impedance spectrum of the cell was measured from 1Mhz to 0.1Hz using an electrochemical workstation (Solartron 1287/1260). The intercept with Z' axis is attributed to the resistance (R) from the bulk electrolyte and grain boundaries. The ionic conductivity (σ) is determined by L/RS, where L and S are the thickness and area of the electrolyte, respectively. The ionic conductivity of LMC and LEDC was also measured with the same method but without LGPS as proton-blocking media.

Data availability. Crystallographic data for the structures reported in this work have been deposited at the Cambridge Crystallographic Data Centre (CCDC) under deposition nos. CCDC 1847784 (LEMC) and CCDC 1847785 (LMC). Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/structures. Data supporting the findings of this study are available within this paper and its Supplementary Information, and are available from the corresponding author upon reasonable request. The MAS NMR experimental and GIPAW calculated data for this study are provided as a supporting dataset from WRAP, the Warwick Research Archive Portal at http://wrap.warwick.ac.uk/***.

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Additional information

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Author contributions

B.W.E., K.X. and C.W. designed and conceived the study. L.W. directed the project and contributed chemical synthesis, battery/electrode tests, FTIR and solution NMR studies. F.H. and C.W. performed ionic conductivity experiments and analysis. A.M., S.P.B. and D.I. contributed solid-state NMR measurements and analysis. P.Y.Z. and Y.W. contributed single crystal growth and crystallographic studies. K.G. performed XPS experiments and analysis. O.B. conducted quantum chemistry calculations. B.W.E. supervised the project. All authors contributed to discussions and preparation of the manuscript.

Competing financial interests

The authors declare no completing financial interests.