Tuning the Reactivity of Electrolyte Solvents on Lithium Metal by Vinylene Carbonate

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Abstract:

Organic solvents undergo degradation reactions when in contact with lithium metal. These reactions form a layer of decomposition products that partly prevents further electrolyte decomposition - passivation. Still, the chemical processes in this system are complex and have not yet been fully understood though it is of high relevance for lithium metal batteries. Scanning Electrochemical Microscopy (SECM) in feedback mode as well as GC-MS are used for analyzing the interface as well as soluble decomposition products. SECM data show that the native interface thickness on metallic lithium from ethylene carbonate (EC) and ethyl methyl carbonate (EMC) electrolyte solutions is reduced by approx. 98% by adding 5 wt% vinylene carbonate (VC) to the solution. The addition of VC changed significantly the dynamics of the growth of the deposition layer. GC-MS studies of the EC:EMC electrolyte solution proof an ongoing reaction of the metallic lithium with the electrolyte even after several days. In comparison, the addition of VC appears to stabilize the interface and no decomposition products could be identified. It is concluded that the addition of VC to the electrolyte solution from EC:EMC prevents the trans-esterification of EMC by surface passivation and not by scavenging alkoxides as claimed in literature.

Keywords: lithium metal, passivation, electrolyte additives, scanning electrochemical microscopy

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Introduction

Using highly reactive electrode materials like lithium metal or intercalated lithium in graphite at low voltages for electrochemical storage devices is challenging with respect to the long term stability of the electrolyte solvents. The solvents and even the salts are consumed by direct chemical reaction of with the electrode material [1]. In a unique fashion, a stabilization of carbonate solvents with intercalated lithium has been achieved for lithium ion batteries. A kinetically stabilized electrochemical system is reached by the so-called solid-electrolyte-interphase (SEI), which in contrast to continuously growing deposition layers, can be considered as stable functional passivation layer: It is electrically insulating in order to prevent further degradation of the electrolyte, but functions at the same time as ionic conductor allowing the reversible intercalation of lithium ions [2]. This remarkable success gave rise to battery cells with lifetimes of many years and up to thousands of charge-discharge cycles. It is not exaggerated claiming that the SEI enabled smartphones and electric vehicles. Granting the Nobel Prize for the lithium ion battery reflects well the magnitude of this technological breakthrough. Inspired by the concept of the SEI, researchers worldwide seek to apply similar concepts to metal based electrodes, which promise significantly higher energy densities and specific energies by using e.g. lithium (3860 mAh g^{-1} [3]) in its elemental form, but facing tough challenges due to electrolyte reactivity [4]. Establishing a long term stable solid-electrolyte functional passivation layer on lithium metal faces several major challenges including the fact that when stripping lithium during discharge, the structural support of the interphase is removed [5], which is a fundamental difference to intercalation based anodes. This renders it highly uncertain, if the SEI concept can be transferred from lithium ion to lithium metal. Besides this fundamental issue, the extreme reactivity of organic solvents on lithium metal surfaces results in a most complex chemistry of deposition products, which is an intriguing challenge for the scientific understanding and a systematic design approach. One way to overcome the challenges in stabilizing organic solvents in contact with lithium metal might be seen in powerful electrolyte additives, which have shown their potential already in lithium ion batteries [6, 7]. It is established that less than 5 wt% of compounds like vinylene carbonate or fluorethylene carbonate are well able to stabilize the solid electrolyte interface and prolong the lifetime of battery cells [8]. These beneficial effects have been studied in great detail in graphitic intercalation and silicon alloying systems [9-11], but to a much lesser degree with lithium metal

substrates. Previous studies of lithium metal batteries show that the addition of VC to the electrolyte enhances the cycling efficiency [12-14], leads to a thinner SEI at room temperature and above [12] with a different composition [14] and influences the lithium deposition [12-14]. Still, the effect of VC on the native deposition layer on metallic lithium that is formed without a current has not yet been studied. We attempt to provide new insights by combining results of scanning electrochemical microscopy as surface probe technique and GC-MS as bulk method for detecting potential soluble deposition products.

The scanning electrochemical microscopy (SECM) is a promising method to analyze the formation and properties of the electrolyte-electrode interfaces. SECM is an *in-situ* method that uses platinum micro electrodes with a diameter in the micrometer range. This microscopic method allows to measure the electrochemical activity of any substrate [15-17]. In the so-called feedback mode, a redox mediator is added to the electrolyte solution to form a measurable current between the micro electrode and a counter electrode. The surface properties are investigated by moving the microelectrode into close proximity of the surface while applying a constant potential. The resulting current signal as a function of the distance to the surface forms the so-called approach curve. When approaching an insulating substrate, the current decreases. In contrast, the current increases when the micro electrode is in close proximity of a conducting substrate [18].

A powerful tool to evaluate the composition of electrolyte solutions is gas chromatography coupled to a mass spectrometer as detector (GC-MS). It can be used for both liquid [19, 20] and gaseous products [21]. Several groups have focused on the electrolyte decomposition during electrochemical cycling of LIBs [22]. However, according to our best knowledge, only very few investigations on chemical reactions between metallic lithium and electrolytes have been conducted.

In this study, the degradation process of electrolyte solutions in contact with lithium metal is investigated using SECM and GC-MS. Various approach curves were recorded on lithium metal immersed in electrolyte solutions (EC:EMC) with and without vinylene carbonate (VC). By fitting the approach curves to the analytical function by Cornut and Lefrou [23] changes in the electrolyte reactions on the metal surface could be tracked. Furthermore, *ex-situ* GC-MS experiments were conducted to identify the corresponding degradation products in the electrolyte. By comparing the *in-situ* SECM data with the *ex-situ* GC-MS data, new insights into the formation of the deposition of decomposition products in the context of SEI formation

and passivation on metallic lithium surfaces and the corresponding chemical reactions taking place were obtained.

Experimental Section

Experimental Methods

The baseline electrolyte (EC:EMC 1:1 v/v with 1M $LiPF_6$) and the electrolyte with 5% VC (EC:EMC 1:1 v/v 1M $LiPF_6$ + 5 wt% VC) were received from Tomiyama and used as received.

For the SECM experiments Li foil (Battery grade, 300 µm thickness, received from Albemarle) was covered with approx. 2 mL of the electrolyte with additional 5 mM ferrocene as redox mediator (99%, Alfa Aesar). Paraffin oil (Vaseline Oil, pure, pharma grade, PanReac AppliChem) with 9.5 mM ferrocene was placed on top of the electrolyte as a second liquid phase to prevent evaporation. The non-dissolution of electrolyte in the oil was proven by GC-MS analysis (Clarus 680, Perkin Elmer, Elite-5MS column, 60 m, inner diameter 0.32 mm; Clarus 600 C, Perkin Elmer).

A platinum disc microelectrode with a diameter of 25 µm (Sensolytics, Bochum, Germany) was used in the SECM Setup. The SECM device (Sensolytics, Bochum, Germany) was placed in an argon filled glovebox with H_2O and O_2 levels <0.1 ppm (MBraun, Garching, Germany) and was connected to a potentiostat (GSTAT30 with ECD module, Metrohm Autolab Utrecht, Netherlands) outside with gastight feedthroughs. The experiments were performed in a 2-electrode set-up with a platinum counter electrode (Sensolytics, Bochum, Germany). The polarization voltage of the electrode tip was set to 0.4 V and multiple approach curves were performed for each data point (speed 5 µm/s in steps of 1 µm, waiting time 20 ms). Each approach curve was stopped when the feedback current reached 50% of the bulk current. The tip was then retracted by 400 µm for the baseline electrolyte and by 300 µm for the VC containing electrolyte. Due to the fast growth of the layer in the baseline electrolyte, the approach curves started with current values that were expected to be present in the feedback regime. These approach curves were stopped, the tip retracted by another 400 µm and the measurement was restarted.

For the investigation of the electrolyte decomposition, 3 cm x 4 cm Li foil (Battery grade, 300 µm thickness, received from Albemarle) was cut into strips (0.5x3 cm) and placed in 20 mL

of electrolyte. The mixture was kept and stirred for 19 days under argon in a closed flask and electrolyte samples were taken approx. every 5 days. Samples were taken with a syringe equipped with a filter (pore size 0.20 µm) and mixed with iso-propanol (≥99.9%, Chemsolute) in a mixture 1:100 v/v before the analysis. Analysis was performed by gas chromatography (Clarus 680, Perkin Elmer, Elite-5MS column, 60 m, inner diameter 0.32 mm) coupled with a mass spectrometer (Clarus 600 C, Perkin Elmer). All species were identified by the help of TurboMass NIST 2008 Libraries, Version 2.2.0.

At the end of each experiment 100 µL of aged electrolytes were taken with a filter (pore size 0.20 µm), additionally 100 µL samples of the as received electrolytes were taken. These samples were added to 10 mL aqua regia and boiled for 30 minutes. Afterwards the solutions were filled up to 100 mL with distilled water and the lithium concentration was measured using inductive coupled plasma (ICP-OES, Varian 725-ES). By this procedure we determined the concentration of lithium in solution.

Fitting of Approach Curves

To analyze the changes of the lithium surface, SECM feedback data were evaluated. During the immersion of lithium metal in the electrolyte, several approach curves at different times were recorded. The approach curves were fitted according the theory of Cornut and Lefrou [23]. They have proposed a function that can be used for a wide range of parameters as tip radius, substrate-tip distance and surrounding insulator thickness around the platinum wire. From the fitted approach curves the distance of the microelectrode from the lithium surface is received. With the known travelled distance of the microelectrode from the position of the stepper motors of the SECM device the changes in height of the sample can be directly received according to the used equation [23]. The ratio of the conducting part of the tip and the insulating glass area R_g and the radius of the active tip r were fitted for the first approach curve only and were then kept constant. The measurement of the baseline electrolyte after 1.5 hours shows a sudden change in the measured current in the bulk current regime. Therefore, only the values from the surface to this point in time were used for fitting. In all other measurements the entire range was used for fitting.

Results and Discussion

The recorded approach curves for the baseline electrolyte are depicted in figure 1. The zero tick of the x-axis is set according to the position of the surface that was calculated from the first approach curve at t=0 hours. The current of each approach curve is divided by the bulk current that was received by fitting to the used equation [23] at this specific approach curve. With increasing reaction time of the metallic lithium with the electrolyte the cut-off of the approach curves is shifted to larger distances from the initial surface. The position of the surface at each approach curve was calculated according to the equations from Cornut and Lefrou [23]. A comparison of the SECM results of the baseline electrolyte and the one with 5 wt% VC is shown in figure 2. The position of the surface changes and is calculated at greater distances from the initial surface with increasing reaction time. We assume that these changes are because of a surface layer of reaction products that builds-up on top of the lithium.

In the baseline electrolyte consisting of EC, EMC and $LiPF_6$, within four hours a surface layer of approx. 1500 µm has formed. This is several orders of magnitude thicker than that reported by other groups only measuring practical layer heights in the nanometer range [5]. However, it is unlikely that our results correspond to any sort of dense solid layer that may form on the lithium surface. More likely the measured insulating properties originate from diffuse decomposition products that attach loosely to the surface. Still, the measurements indicate changes close to the surface when lithium metal is immersed in the electrolyte. Since the layer height shows a linear trend with time, the surface reaction is not suppressed or slowed down in the observed timespan of four hours – in other words, an electrolyte protecting passivation layer is not built. We conclude that the surface reaction between the electrolyte and the lithium does not form a stable layer on the surface that prevents the diffusion of fresh electrolyte to the metal. Hence, the shielding of the deposition products cannot be considered as passivation layer. Adding 5 wt% vinylene carbonate to the electrolyte leads to a decreased layer growth rate. The surface layer grew to a total thickness of 25 µm in the observed 3.5 hours. The layer growth is reduced by about 98% compared to the baseline electrolyte. This indicates that in contrast to EC:EMC, VC is able to form a stable surface layer on lithium metal that successfully prevents the electrolyte from being further decomposed at the lithium surface.

From the approach curve fits the dimensionless substrate reaction parameter κ can also be derived. According to Cornut and Lefrou, κ is defined by the kinetic reaction constant of the

mediator at the substrate k, the radius of the platinum wire inside the tip a and the diffusion coefficient of the solution D as [23]

$$\kappa = \frac{ka}{D}. \quad (1)$$

The substrate kinetics parameter describes the kinetics of the reduction of the redox mediator at the surface and, therefore, serves as a parameter to evaluate the passivation of the substrate surface. The change of κ over time is depicted in figure 3. Immediately after exposing the electrolyte to lithium metal, κ shows a value of approx. 10^{-3} for both electrolytes. For the baseline electrolyte κ increases during four hours to $2x10^{-2}$. As will be discussed, the tip radius might be reduced due to accumulating decomposition products. This would result in a decreased value of κ. Since κ is increasing over time in both experiments, any changes need to originate either from a change of the substrate reaction kinetics k or a change of the diffusion coefficient D. This diffusion coefficient describes the diffusion of the redox mediator in the solution. According to equation (1), an increasing κ can be attributed to an increase of k or a decrease of D. An increase of the substrate kinetics k would indicate a decreased shielding of the lithium metal from the electrolyte. This would indicate a less efficient passivation layer. A decrease of the diffusion coefficient D may occur due to the decomposition of the electrolyte. From our measurements it is not possible to separate these two effects. Which of the processes is dominant for the increase of κ needs to be investigated in further experiments. Regardless of the cause, the increase of κ indicates an ongoing change of the surface properties.

For the baseline electrolyte with 5 wt% VC, κ is also increasing during the timespan of the experiment, but only to approx. $5x10^{-3}$, which is 25% of the value of the baseline electrolyte (see figure 3). The changes in k and D are therefore assumed to be significantly less severe than in the baseline electrolyte. It is hypothesized that the smaller changes indicate an efficient passivation of the lithium caused by VC. As discussed above, the exact reasons for the change in κ cannot be evaluated with this measurement since a differentiation of the two parameters k and D is not possible. Furthermore, the proposed equations of Cornut and Lefrou [23] used for the fitting assume a flat and dense surface as substrate. With the decomposition products accumulating on the lithium surface it cannot be ensured that this assumption is valid for the system of lithium metal immersed in reactive electrolyte. With increasing layer heights this assumption becomes more inaccurate and accordingly the results from the fits are less precise.

However, we conclude that the increasing κ values indicate a reaction of the lithium metal with the electrolyte. The addition of VC inhibits the reaction and, therefore, has passivating properties with respect to the lithium electrolyte interface.

The bulk current in SECM feedback experiments depends on several parameters of the set-up: the concentration of the redox mediator, the diffusion coefficient and the radius of the active area of the micro electrode [15]. The bulk current during the experiments decreases by approx. 25% in both electrolytes in the observed timespan of four hours. Accumulation of deposition products on the micro electrode might lead to a reduced active area of the micro electrode. A related reduction of radius of active area (a) results in a decrease of the dimensionless substrate reaction parameter that is introduced in equation (1). Since this parameter is increasing in both experiments, the reduction of the active area of the micro electrode appears to be unlikely. The decrease in current can also originate from a change of the diffusion coefficient. As already discussed, a reducing diffusion coefficient can neither be confirmed nor excluded. A partial decomposition of the redox mediator and the associated reduced bulk current seems also possible. By examining the SECM approach curves during fitting in normalized units [23], this has no effect on the approach curves [18]. It is therefore concluded that the stability of the experimental set-up is sufficient for data interpretation.

Further chemical analysis was carried out to improve the understanding of the reactions between metallic lithium and the electrolyte. Lithium metal was placed into the electrolyte and the solution was stirred for several days.

Figure 4 shows the gas chromatography results of the baseline electrolyte and the baseline electrolyte with 5 wt% VC at different reaction times. In the initial gas chromatogram as well as in the gas chromatogram after 0.8 days the pure electrolyte (EMC/EC) with no contaminants can be recognized: In these two gas chromatograms only EMC (t_R=10 min) and EC (t_R=20 min) are present. The signal at t_R=0 minutes is only an artefact of the measurement independent of the sample being injected. In the measurements after t=13.9 days and t=18.8 days additional signals arise, which can be assigned to dimethyl carbonate (DMC, t_R=7 min) and diethyl carbonate (DEC, t_R=15 min). These signals also already appear in the gas chromatogram after 8 days when they are too small to be quantified. The increase of the new signals shows that the decomposition of the electrolyte does occur over a time span of several days, which is long compared to the presented SECM measurements. This supports our hypothesis from the

interpretation of the SECM measurements that the reaction of the baseline electrolyte with lithium does not result in an efficient passivation of the lithium electrode and electrolyte decomposition does continue. From lithium ion battery research it is established that the presence of DEC and DMC originates from the trans-esterification of EMC at the anode during formation steps [10, 24] (see figure 5). This effect was also shown for lithium metal batteries after 100 cycles [25]. It is suggested that the trans-esterification is catalyzed by lithium alkoxides that are formed during the reduction of the electrolyte [24, 26].

Our measurements show that with lithium metal the inherent chemical potential is sufficient for the trans-esterification of the EMC electrolyte and no current or externally applied potential is required. The signals at a retention time of 22 minutes could not be identified with sufficient certainty, since the MS signals are complex and a variety of chemical species are arising at similar retention times. Still, by analyzing the MS signals, the development of oxygen containing oligomers, both linear and cyclic, appears likely. From graphite based batteries with an EC:EMC electrolyte it is known that during cycling a total of 38 decomposition products may be formed [27]. We assume that due to the low electrochemical potential of metallic lithium a similar complex reaction situation is to be expected at lithium metal electrodes.

The sample with 5 wt% VC added to the electrolyte does only show the signals of the pristine electrolyte: EC (t_R=20 min), EMC (t_R=10 min) and VC (t_R=12 min). During the 19 days of the experiment the electrolyte does not exhibit the development of DEC and DMC signals. It is therefore concluded that VC effectively shields the electrolyte from the lithium metal. Literature suggests that the suppression of the trans-esterification occurs either due to VC consuming lithium alkoxides [28, 29], or the alkoxide production is limited due to the formation of a VC based surface layer as observed on graphite anodes [29]. Our GC-MS data show no further species that may be assigned to soluble reaction products of VC with any part of the electrolyte, which contradicts the hypothesis from literature that VC neutralizes alkoxides [28, 29]. In contrast, the SECM data show a growing accumulation of decomposition products on the metallic lithium in the VC containing electrolyte. Still, the height of the layer is two orders of magnitude smaller than without VC, but even VC does not lead to a perfectly passivated surface. We assume that the decomposition products form a similar layer on the metallic lithium as it is known from graphite anodes [29] and conclude that the formation of an effective passivating layer is the predominant effect.

The passivating effects of VC were also observable after the 19 days of stirring the electrolyte lithium mixture. The lithium metal immersed in baseline electrolyte had deteriorated into small particles whereas from the initial pieces with a size of approx. 5x30 mm none were left (figure 6 a). The lithium particles had no metallic appearance anymore and had turned dark. Additionally, the former colorless and transparent electrolyte had become dark black. In comparison, the electrolyte after 19 days with 5 wt% VC is depicted in figure 6 b). The remaining lithium particles were significantly bigger than in the baseline electrolyte. Most particles still had the shape similar to the pristine ones that were used in the experiment. The surface still appeared metallic and had only darkened slightly during the experiment. Still, some very small particles could be found in the electrolyte. However, in contrast to the particles in the baseline electrolyte, these particles do not appear completely black, but had also a rather metallic appearance. The electrolyte itself had changed from colorless and transparent to grey/brown. In direct comparison with the baseline electrolyte, the electrolyte with 5 wt% VC appears lighter and still transparent. These results indicate a stronger reaction of the baseline electrolyte with the lithium metal than of the VC containing electrolyte with lithium.

ICP measurements did not show an increased lithium concentration after 4 weeks, indicating that the formation of soluble lithium containing compounds is unlikely.

Conclusions

The reaction of metallic lithium with a baseline electrolyte made from EC, EMC and $LiPF_6$ and with an advanced electrolyte made from EC, EMC, $LiPF_6$ and 5 wt% VC was studied. The reactions that were observed without VC lead to a decomposition of the electrolyte. The decomposition occurs without any current and potential being applied to the lithium unlike in lithium metal batteries. SECM measurements showed that the chemical reaction of baseline electrolyte (EC:EMC w/o VC) with lithium metal does not lead to a dimensionally stable surface layer. We showed that the electrolyte decomposition does not stop within 4 h using SECM and even within 19 days using GC-MS measurements. GC-MS data proofed the trans-esterification of the EMC to DEC and DMC still proceeds after several days. This effect is known from literature at low electrochemical potentials at an unpassivated anode in lithium ion batteries, but has not been reported at bare lithium metal.

Adding 5 wt% vinylene carbonate (VC) to the electrolyte successfully shields the lithium metal from the electrolyte. According to our SECM experiments, the layer growth could be reduced

by 98%. GC-MS gave impressive evidence that the electrolyte decomposition, hence the trans-esterification reaction is suppressed by VC as electrolyte additive. The products of the trans-esterification could not be found in any sample and the formed surface layer therefore appears to be stable and functional with respect to the passivation. We conclude that adding vinylene carbonate successfully increases the stability of the metal electrolyte interface. One of several consequences with respect to battery applications is that the addition of VC presumably leads to an increased calendrical lifetime of lithium metal batteries. In perspective of the presented experimental evidence we finally conclude that the large impact of VC in stabilizing lithium based batteries is dominantly caused by its passivating properties rather than by scavenging alkoxides.

Literature

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Notes

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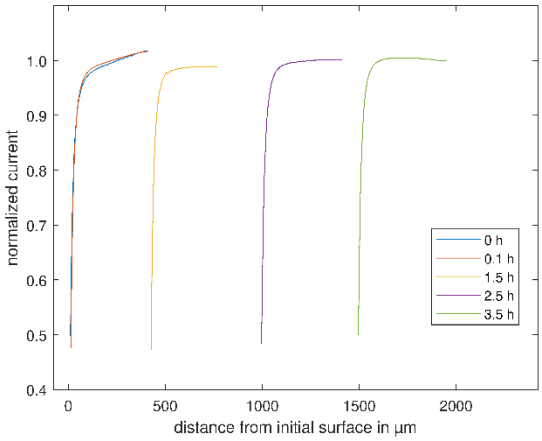

Figure 1: Approach curves at different reaction times of metallic lithium immersed in the baseline electrolyte. The position of the initial surface was calculated from the first approach curve according to [23]. The current of each approach curve is normalized by dividing it through the bulk current of each approach curve.

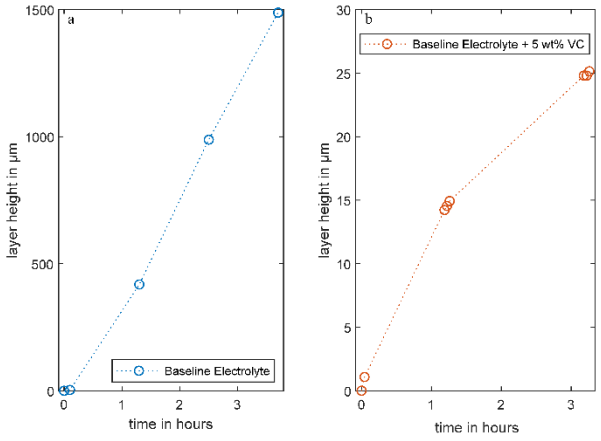

Figure 2: Layer height on lithium during immersion in electrolyte. The values were fitted using SECM approach curves and the equations from Cornut and Lefrou[23]. Links between the data points are only a guide to the eye. a) Layer height of lithium in the baseline electrolyte b) Layer height of lithium in the baseline electrolyte with 5 wt% VC.

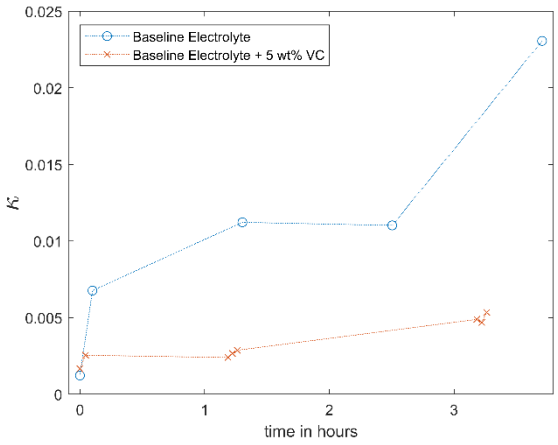

Figure 3: Dimensionless substrate reaction parameter κ fitted according to [23] from SECM approach curves on lithium metal at different immersion times in the baseline electrolyte and in the baseline electrolyte with 5 wt% VC as additive. The dashed lines are only a guide to the eye.

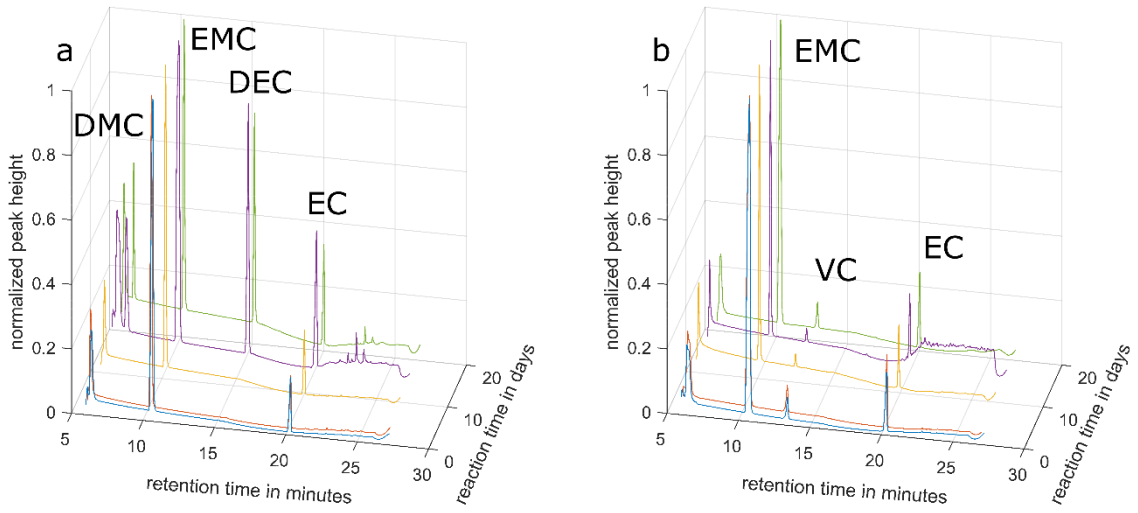

Figure 4: a) Gas chromatography of the baseline electrolyte exposed to lithium, normalized to the highest signal b) Gas chromatography of the baseline electrolyte with 5 wt% VC mixed with lithium normalized to the highest signal.

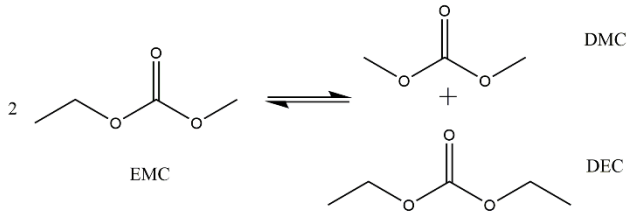

Figure 5: Trans-esterification of EMC to DMC and DEC according to [30].

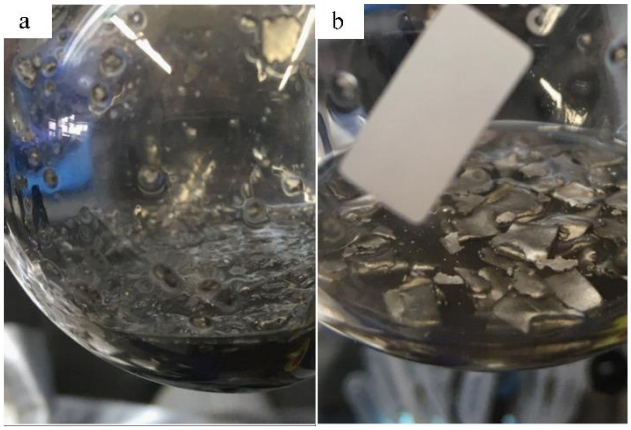

Figure 6: a) Lithium metal after 19 days in EC:EMC (1:1 wt:wt) 1 M $LiPF_6$ electrolyte. b) Lithium metal after 19 days in EC:EMC (1:1 wt:wt) 1 M $LiPF_6$ electrolyte with 5 wt% VC.