

Microcalorimetric Study of the Reactivity of Lithiated HOPG with Organic Electrolytes

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For the first time, the reactivity of lithiated graphite (HOPG) with organic electrolytes has been followed by calorimetric measurements. The role of three different solvents, ethylene carbonate (EC), dimethyl carbonate (DMC), diethyl carbonate (DEC), and their binary and ternary mixtures, has been investigated, with or without LiPF_6 . The lithiated HOPG is shown to react totally with DEC, whereas with EC and DMC the reaction is only partial. This has been attributed to the formation of a passivating film on the surface of the lithiated HOPG. The importance of EC on the film composition and heat exchanged during its formation is demonstrated. LiPF_6 seems to enhance the reactivity with EC-based electrolytes whereas it lessens the heat exchanged with DMC or DMC–DEC. Reaction mechanisms have been considered, and the composition of the film has been discussed with regard to the calorimetric data.

1. Introduction

Lithium-ion batteries are excellent autonomous electrical power sources, because they provide a good combination of high energy and power and long cycle life.^{1,2} Typical lithium-ion cells consist of a graphite negative electrode, an organic electrolyte, and a metal oxide positive electrode made of LiCoO_2 , LiMn_2O_4 , or LiNiO_2 .³ Lithium-intercalated graphites are good alternatives to lithium metal as a negative electrode because of their advantages with regard to cycle life and safety, as lithium intercalation prevents dendritic growth of metallic lithium, which may lead to short circuits, and therefore constitutes a safety risk. In addition, graphite yields a high specific capacity, close to the theoretical (372 mAh/g), and shows a long cycle life.

Commonly used organic electrolytes, based on aliphatic or cyclic carbonates as ethylene carbonate (EC), diethyl carbonate (DEC), and dimethyl carbonate (DMC) or ethers, such as dimethoxyethane (DME), are not thermodynamically stable in contact with the lithiated graphite.^{4–7} The apparent stability is due to the formation of a passivating film, at a potential near 0.8 V vs Li/Li^+ , which prevents further reduction of solvent species by being ionically conductive for Li^+ ions but more or less impermeable to the solvent molecules (solid electrolyte interface, SEI).^{8,9}

During recent years, intensive work has been carried out in the search of new solvents, lithium salts, and additives toward which graphite electrodes behave reversibly because of the formation of a stable SEI film and in the study of the surface chemistry developed on graphite in a variety of electrolyte solutions. A remarkable stabilization of graphite electrodes is obtained by the use of EC as cosolvent. Even in cases where reversible lithium insertion cannot be obtained, such as in single solvent solutions based on DEC, DMC, or ethers, the addition of EC to these solvents leads to highly reversible behavior of

graphite.^{10–14} The formation of a passivating film may be connected to the fast reduction kinetics of EC to form insoluble compounds. It is commonly accepted that the film formed in EC-based electrolytes consists of so-called semicarbonates or alkyl carbonates (ROCO_2Li), besides lithium alkylates (ROLi), lithium carbonate (Li_2CO_3), lithium oxide (Li_2O), and lithium hydroxide (LiOH), coming from the reduction of the solvent.^{4,12,15} When LiPF_6 is used as supporting salt, the SEI also contains LiF and phosphorus-containing compounds of lower phosphorus valence (Li_xPF_y), coming from the reduction of LiPF_6 .^{16,17} The SEI is a very complex mixture of these compounds, either as nanocrystalline particles or in a multi-layered structure with an inorganic part (Li_2CO_3 , LiF) toward the surface and the organic part (ROCO_2Li) toward the solvent.^{18–20} The presence of polymeric compounds has been discussed too.^{21,22}

Reduction mechanisms were proposed for the formation of these compounds.^{4,23,24} Recently, Wang et al.²⁵ published a theoretical study on the reduction mechanisms of EC, based on density functional theory (DFT) calculations. They confirm the possible formation of the above-mentioned products but also suggest that the formation of a product with a Li-C bond, $\text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$, already mentioned by Aurbach et al.,²⁶ and an ester group-containing molecule, $\text{LiO}(\text{CH}_2)_2\text{CO}_2(\text{CH}_2)_2\text{OCO}_2\text{Li}$, should also take place.

Highly oriented pyrolytic graphite (HOPG) has a highly anisotropic structure with well-defined basal and edge planes. Thus, HOPG can be regarded as a typical model of highly graphitized carbonaceous materials. Understanding the influence of the solvents and salts on the formation of the passivating film is essential to further characterize the fundamental phenomena or processes that control the interfacial chemistry.

In the present study a comparison is made on the reactivity between lithiated HOPG and three different solvents: EC, DEC, and DMC, as well as LiPF_6 . Reaction mechanisms for the reduction of the solvents are reconsidered, reaction enthalpies for the reactions are established, and composition of the film for the different solvent/electrolyte systems is suggested.

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2. Experimental Section

HOPG, provided by Advanced Ceramics (Colorado, U.S.A.), was used for this study. Small pieces (7 mm × 7 mm × 0.3 mm) were dried under vacuum at 350 °C overnight and were then lithiated by immersion into molten lithium (contained in a stainless steel tube) at 270 °C for 3 weeks in an argon-containing glovebox (<1 ppm H₂O and O₂). Excess metallic lithium was removed mechanically, and the golden-colored lithiated graphite (LiC₆) was scraped into fine particles using a scalpel. The solvents used were EC, DMC, and DEC “battery grade” (<30 ppm H₂O) from Merck KGaA (Darmstadt). They were further dried over an activated molecular sieve (3 Å), and the water content was determined by Karl Fischer titration to below 5 ppm. The LiPF₆ “battery grade” obtained from Merck KGaA was stored as received in a glovebox. The electrolyte mixtures used were stored over freshly cut lithium metal for several days prior to use, so that the free water and HF contents were reduced still further and were very low at the reaction and did not need to be considered for the discussion of the surface reactions.

The calorimetric measurements (Setaram, C 80 microcalorimeter) were performed in a two compartment cell: a lower compartment, where approximately 20 mg of LiC₆ powder was placed, and an upper compartment, where typically 2 mL of the different electrolytes was introduced. The two compartments were separated by a poly(tetrafluoroethylene) (PTFE) membrane. A reference cell of the same type was used, the upper compartment also contained 2 mL of the same electrolyte, and the lower compartment was empty. The two cells were placed in the apparatus for temperature equilibration until the relative heat flow was below 50 μW. The Teflon membranes of the two cells were then pierced simultaneously by a movable steel needle, and the mixture of LiC₆ powder and electrolyte was stirred for a few seconds. The isothermal heat flow $q(t)$ (W/g) was recorded, and the reaction heat released or consumed was determined by the area under the heat flow vs time curve $\int_0^t q(t) dt = Q(t)$. The experiments were conducted at different temperatures in an isotherm mode, and for each composition of electrolyte and each temperature, separate experiments were carried out.

The specific area was determined by a Brunauer–Emmett–Teller (BET) technique on the reacted graphite powder, after delithiation in DEC/acetone in air. Lithiated HOPG itself could not be used, as it may react with the nitrogen used for BET measurements, and nonreacted HOPG could not be used because it could not be ground in the same manner.

X-ray diffraction (XRD) measurements were performed on a Siemens D 5000 diffractometer using Cu K_α radiation ($\lambda = 1.5405$ Å). The lithiated HOPG sample was protected from air by a thin aluminum foil, which was fixed to the sample holder with vacuum grease, under argon atmosphere. To magnify weak peaks in the diffraction pattern, the intensity of the latter was expressed as $I^{1/4}$.

3. Results and Discussion

3.1. Lithiation of the Graphite. The HOPG powder is well-crystallized as shown in Figure 1a. It is composed mainly of hexagonal (2H) phase with traces of rhombohedral phase (3R). Because of the high crystallinity of the sample, also, weak reflections, resulting from the K_β radiation, are visible. The homogeneously golden-colored lithiated sample shows a high degree of lithiation, visible in the high intensity of the 001 reflection of stage 1 LiC₆ (Figure 1b), and lower intensity reflections coming from stage 2, stage 3, and graphite, present as impurities.

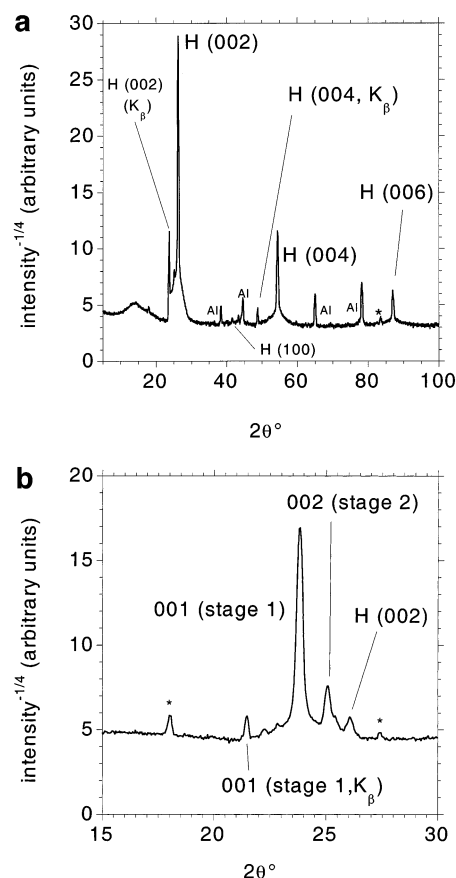


Figure 1. XRD patterns of HOPG (a) and lithiated HOPG (b). H denotes the hexagonal graphite phase (2H), stage 1 denotes the fully lithiated phase LiC₆, stage 2 denotes the partially lithiated phase (LiC_{12–18}), and K_β denotes the diffraction lines coming from the K_β radiation, which traverses the filter. The asterisk denotes diffraction lines, coming from unidentified products. The fourth square root of the intensity is plotted against the diffraction angle, which means that even very weak peaks are visible.

3.2. Calorimetric Study. **3.2.1. Calibration.** To overcome the difficulty of symmetrical manual piercing of the PTFE membrane, we carried out several blank tests with the reference and measurement cells, containing only ternary electrolyte (EC: DMC:DEC (2:2:1)–1 M LiPF₆). The values recorded for the heat flow lie between -5×10^{-3} and -10^{-3} J (exothermic phenomenon), which means that they are small and random. The overall experimental uncertainty was therefore estimated to be 0.05 J.

Pristine HOPG should not have any particular reactivity with an electrolyte (organic solvent, lithium salt), except for adsorption phenomena. This measurement is, to some extent, useful as reference as it will make it possible to withdraw the adsorption phenomena from the reactivity of the electrolyte with LiC₆. A 100 mg amount of unlithiated HOPG powder was put in the cell and reacted with EC:DMC:DEC (2:2:1)–1 M LiPF₆. A heat release $Q(t)$ of -0.8 J/g of HOPG was measured at $T = 30$ °C. This exothermic reaction can be attributed to electrolyte adsorption on the surface of the graphite powder. The amount of heat for this reaction is much less than for each of the following reactions (ΔH approximately 50–200 J/g), so that this phenomenon could be separated from the heat released from the chemical reaction of LiC₆ with the electrolyte.

We also measured the thermal inertia of the calorimeter by carrying out an instantaneous perturbation, i.e., the passage of a liquid from the upper compartment of the cell toward the lower

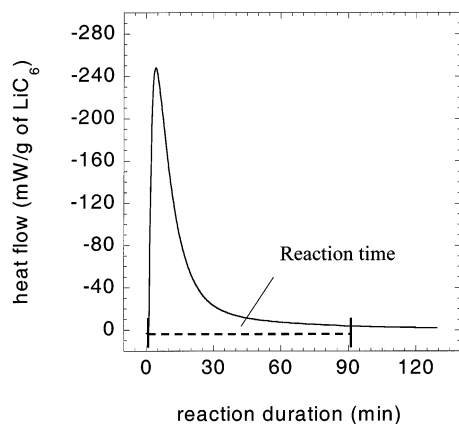


Figure 2. Thermogram for the reaction of lithiated HOPG powder with EC–1 M LiPF₆.

compartment. We obtained a return of the flow signal to the baseline in 1000–1500 s. The calorimeter can thus give information only on kinetics of slow reactions, typically of durations of several hours.

In this study, the reactivity of LiC₆ with the three solvents EC, DMC, and DEC, their binary mixtures (1:1 in vol), and the ternary mixture (2:2:1 in vol) has been carried out, with or without addition of 1 M LiPF₆, at different temperatures (30, 40, 60, and 80 °C).

3.2.2. Single Solvent. A typical thermogram is shown in Figure 2, in the case of the reaction of LiC₆ with EC–LiPF₆. An exothermic signal appears starting from the beginning of the reaction after piercing the membrane, whose maximum is reached after 3–4 min. The heat flow returned to the baseline only after about 90 min. This is due to a prolonged reaction between the LiC₆ and the electrolyte but may also reflect the slow response of the microcalorimeter.

Figure 3a depicts the heat evolved during the reaction of LiC₆ with the three different solvents EC, DMC, and DEC, with and without LiPF₆ salt at different temperatures. The corresponding reaction durations are shown in Figure 3b.

A large difference is observed between DEC and the other solvents. For DEC, a heat of approximately –2600 J/g of LiC₆ is released independently from the presence or not of LiPF₆ and the reaction temperature. Nevertheless, the reaction time becomes much shorter with increased temperature.

The heat released for DMC and EC is much lower as compared to DEC (in the range of –50 to –250 J/g) but increases with temperature. However, the reaction time was not significantly affected by the reaction temperature.

When LiPF₆ is present, the quantity of heat released triples for EC and lessens remarkably for DMC, so that the energy liberated in the two cases is comparable. Therefore, it seems that the presence of LiPF₆, in the case of DMC as solvent, enhances the protective role of the SEI in reducing the heat released upon its formation. For EC, LiPF₆ participates readily in the film formation too, but the heat exchanged is nonetheless quite small, and the film formed in this case is protecting. At higher temperatures, the heat exchanged rises significantly for EC–LiPF₆, as the quality of the film diminishes, but a certain protective ability is still there. One could assume that the film porosity increases, which means that more electrolyte would be reduced before the film becomes impermeable to the electrolyte. It is also possible that differences in the respective reduction rates of EC, DMC, and LiPF₆ account for the effect of LiPF₆ stated for the two electrolytes.

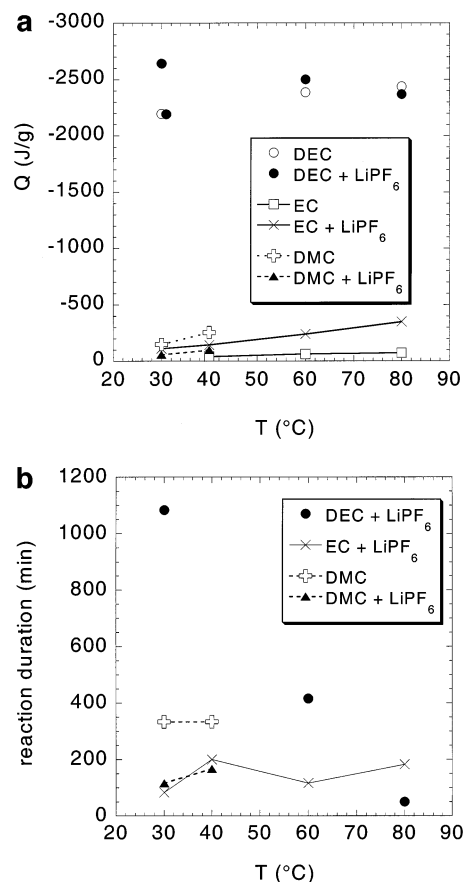


Figure 3. Reaction heat (a) and duration (b) of LiC₆ powder in the single solvent systems EC, DMC, and DEC (without LiPF₆ and with 1 M LiPF₆) at different temperatures. To enhance the clarity of the representation, EC and DEC (without LiPF₆) have been omitted in panel b.

Basically, the chemical reactions expected to take place for DEC and DMC are of the same type; hence, the reaction energies should be in the same range. The differences in the heat release may result from the fact that the reaction products, in the case of DMC, form a SEI that protects the sample from total reaction, whereas in the case of DEC the major part of LiC₆ reacts with the solvent, probably because the reaction products are soluble or do not form a sufficiently protective SEI. Indeed, for DEC, the powder turned to a black color after reaction, whereas for EC and DMC (with or without LiPF₆) it retained its golden coloring, which indicates that the surface of the LiC₆ is actually protected from oxidation by a passivation film. In the absence of LiPF₆, EC does liberate much less heat than DMC (about 50 J/g as compared to about 200 J/g), which reflects the superior ability of EC to form a highly protective passivation film, preventing the solvent from further reaction with LiC₆. Moreover, the reaction time of the LiC₆ with DMC is longer (6 h as compared to 3 h for EC and EC–LiPF₆).

The fact that the reaction time in the case of DEC is significantly shorter with increased temperature can be understood if one takes into account the diffusion of the Li⁺ ions within the graphite as the rate-limiting process. This seems quite logical, as the reduction reaction, above all when soluble species are formed, is quite fast. For EC and DMC, nearly no temperature dependence of the reaction time or at least one that is negligible as compared to the response of the calorimeter can be found. As in this case only the surface of the graphite reacts, Li⁺ diffusion should not play a rate-limiting effect, so

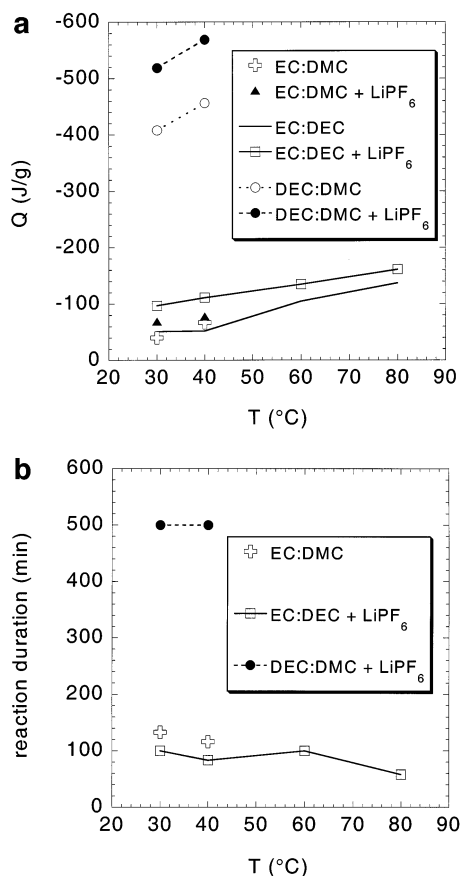


Figure 4. Reaction heat (a) and duration (b) of LiC_6 powder in the binary solvent systems EC:DMC, EC:DEC, and DEC:DEC (without LiPF_6 and with 1 M LiPF_6) at different temperatures. In panel b, only three significant mixtures are shown.

that the reduction process remains relatively fast, even at low temperatures.

3.2.3. Binary Solvent Mixture. Figure 4a,b, respectively, shows the heat and the reaction durations for the three binary systems, with and without 1 M LiPF_6 . They clearly show that the presence of EC in these systems plays an important role: whereas only a small difference in the reaction heat is observed between EC:DEC and EC:DMC, a larger one is observed between these two systems and DEC:DMC. The reactivity of the LiC_6 in the presence of EC:DEC and EC:DMC mixtures is relatively low, as well in heat released as in reaction time. The reaction in the presence of EC:DMC releases a little less heat, which could be due to the lower reactivity of DMC as compared to DEC. The results obtained for the mixtures in the presence of EC are relatively close to those obtained for EC alone, which seems to indicate the prevalence of EC in the formation of a more protective passivation layer. For these mixtures as for EC, the presence of LiPF_6 slightly increases the quantity of released heat. These results are in agreement with published studies^{4,13,14,17,27,29} that proposed the predominant role of EC in the formation of an efficient SEI and the contribution of LiPF_6 in the reaction heat yield.

For DEC:DMC, the presence of DMC decreases the heat released as compared to DEC alone, indicating the formation of a protective passivation layer. Nevertheless, the formation of the latter is slower in this system than in DMC as both released heat and reaction time are higher. By comparing the results obtained with DEC:DMC ($\Delta H = 400\text{--}450$ J/g; $t = 8$ h) to those observed with DMC alone ($\Delta H = 200\text{--}250$ J/g; $t = 2$ h), the presence of DEC seems to delay the formation of

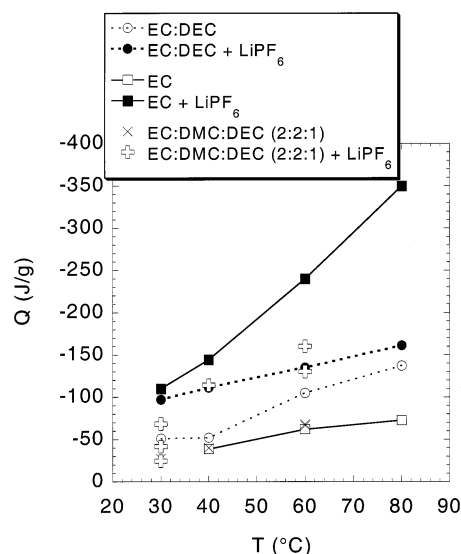


Figure 5. Reaction heat for the reaction of LiC_6 powder in the ternary solvent system EC:DMC:DEC = 2:2:1–1 M LiPF_6 in comparison with EC:DEC and EC (without LiPF_6 and with 1 M LiPF_6) at different temperatures.

a protective passivation layer. Two explanations can be given, (i) the reaction products with DMC:DEC are partially soluble¹⁶ and (ii) the formation of an inhomogeneous and/or porous film would require a thicker film to guarantee a real protection.

The presence of LiPF_6 in the mixture increases the reaction heat and does not seem to enhance the protective character of the film as was observed for DMC. These results are in agreement with the XRD study,³⁰ which shows little influence of the presence of LiPF_6 on the stability of the lithiated HOPG for the DMC:DEC mixture.

3.2.4. Ternary Solvent Mixture. The ternary mixture behaves in the presence of lithiated HOPG similarly to the binary mixtures with EC, i.e., weak released heat, which increases with temperature and in the presence of LiPF_6 (Figure 5). The reaction time cannot be compared, all reactions being fast compared to the inertia of the microcalorimeter. Several measurements on the reactivity of the ternary mixture, at identical temperature, were carried out. The amounts of released heat show some dispersion. These variations are not due to experimental error but rather to an irreproducibility of the surface of HOPG per gram of powder, the powder being obtained by a manual scraping. Moreover, taking into account the strong reactivity of the lithiated HOPG, a partial passivation of its surface in the glovebox cannot be excluded. The experiments carried out with DEC are much more reproducible, which comes from the fact that mainly the bulk of the HOPG is concerned and not only its surface. Considering the difficulty in obtaining reproducible measurements, a fine comparison study of the reactivity of the ternary mixture with that of the binary mixtures based on EC is not possible.

4. General Discussion

4.1. Reaction Mechanisms and Discussion of the Heat Balances. To explain the results obtained by microcalorimetry and to relate them to the chemistry of film formation, the reactions likely to happen as well as their enthalpies will be developed in this section. This should be understood only as a first and partial approach, but it seems interesting to relate the reactions proposed in ref 25 and the products observed^{13,31–33} on the surface of metallic lithium or lithiated graphite. Lithiated HOPG, due to its potential of approximately 100 mV vs Li/

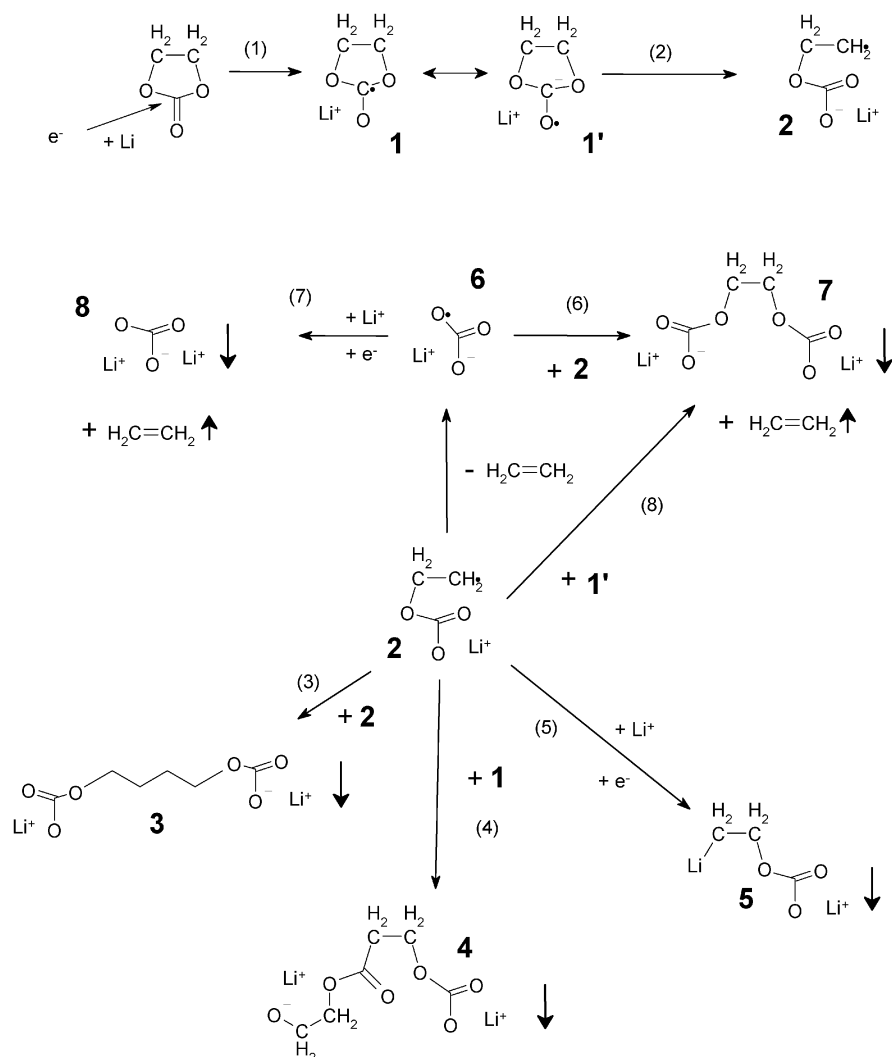


Figure 6. Possible reaction mechanisms of EC reduction leading to the different products supposed to be presented in the formation of the passivation film.

Li^+ , presents a reactivity toward the electrolyte that resembles more the one of metallic lithium than the one of graphite at electrochemical lithiation (reduction of the electrolyte species between approximately 1500 and 600 mV vs Li/Li^+). We develop our concept until an approximate calculation of the composition of the passivation film is obtained with different solvents or electrolytes. This study demands, of course, to be completed by X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) measurements, but it allows us to shed light on the question of the composition of the passivation film in an original manner and seems thus worth being communicated.

Despite the numerous work done in differential scanning calorimetry and ARC,^{34–44} only few studies have been attributed to the calculation of the enthalpy associated to the reactions of the solvent molecules upon reduction.^{25,45,46} To the authors knowledge, no calorimetric data for the determination of the heat released upon film formation have been published.

4.1.1. EC Reduction. We propose, in Figure 6, a tentative mechanism of the reduction of an EC molecule. In a first step, one electron transfer occurs, leading to the formation of the radical anion $1/1'$, with $1'$ thermodynamically less favorable than 1 (reaction 1). This compound $1/1'$ opens, and the radical anion 2 is formed (reaction 2). Radical anion 2 may either react with itself to give $(\text{CH}_2\text{CH}_2\text{OCO}_2\text{Li})_2$ (3, reaction 3) or react with

the radical anion 1 to give $\text{LiO}(\text{CH}_2)_2\text{OCO}(\text{CH}_2)_2\text{OCO}_2\text{Li}$ (4, reaction 4). The radical anion 2 may also be further reduced to give $\text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$ (5, reaction 5) or may expulse ethylene under formation of LiCO_3^\bullet radical (6), which reacts further to either under further one electron transfer, Li_2CO_3 (7, reaction 6), or under attack on radical anion 2, to $(\text{CH}_2\text{OCO}_2\text{Li})_2$ (8, reaction 7). The radical anion 2 could also attack the radical anion $1'$ to give $(\text{CH}_2\text{OCO}_2\text{Li})_2$ directly (reaction 8). From thermodynamics data in Table 1, the formation of lithium butylene dicarbonate (3) seems to be the most favorable, followed by the formation of the ester group-containing product (4). The formation of lithium ethylene dicarbonate (8), lithium carbonate (7), and $\text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$ (5) is the less favorable. The proposed mechanism goes along with the results of Wang et al. and is in good accordance with several of the products characterized experimentally, such as $(\text{CH}_2\text{OCO}_2\text{Li})_2$, Li_2CO_3 , $\text{LiCH}_2\text{CH}_2\text{OCO}_2\text{Li}$, and C_2H_4 .^{28,31–33}

We do not take into account the complexation of EC by lithium as suggested by Wang et al.²⁵ based on DFT calculations. It is given for a more general case, without LiPF_6 salt and without using theoretical calculations.

4.1.2. DMC and DEC Reduction. In Figure 7, we propose a tentative mechanism for the reduction pathway for DMC (and for DEC by replacing methyl for ethyl), which is based on comparable considerations as for the EC reduction.

TABLE 1: Standard Formation Enthalpies of Different Products of Interest in the Reduction of EC, DEC, DMC, and LiPF₆^a

product	ΔH_f^0 (kJ/mol)	origin of the values
Li	0	A
LiC ₆	-18.4	A
DMC	-619	B
DEC	-694	B
EC	-552	C
LiPF ₆	-2274	A
((CH ₂)OCO ₂ Li) ₂	-1873	C
((C ₂ H ₄)OCO ₂ Li) ₂	-1920	C
LiO(CH ₂) ₂ OCO(CH ₂) ₂ OCO ₂ Li	-1686	C
LiCH ₂ CH ₂ OCO ₂ Li	-1234	C
CH ₃ OCO ₂ Li	-932	C
C ₂ H ₅ OCO ₂ Li	-961	C
CH ₃ OLi	-439	C
C ₂ H ₅ OLi	-477	C
CO ₂	-393	A
CO	-109	A
C ₂ H ₄	+52	A
C ₂ H ₆	-84	A
C ₄ H ₁₀	-125	A
LiF	-610	A
PF ₃	-936	A
POF ₃	-1229	A

^a The standard enthalpy values are determined at the theoretical standard state of the compounds: 101.3 hPa and 298.15 K. A, value taken from refs 49–51; B, value calculated from the combustion enthalpies given in ref 49; C, values obtained from given (A) or calculated (B) values^{49,50} by replacing existing bonds by other bonds, for which the enthalpy is known, and calculation of the formation enthalpies of the so obtained compounds or by replacing a group in the molecule by another group of known enthalpy and calculation of the formation enthalpy of the so obtained compound. Example for C: the formation enthalpies of acetic acid and methyl acetate are -485 and -447 kJ/mol, respectively. The difference of the replacement of an H atom by a CH₃ group (on a oxygen bound to a highly oxidized carbon) is therefore +38 kJ/mol. Starting from the formation enthalpy of lithium hydrogenocarbonate (LiOCO₂H), which is -970 kJ/mol, we can now calculate the approximate formation enthalpy of lithium methyl carbonate CH₃OCO₂Li by adding +38 kJ/mol, and we obtain a value of -932 kJ/mol.

In a first step, one electron transfer leads to the formation of the radical anion 9/9' (reaction 9). This compound can form lithium methylate 10 and the radical 11 (reaction 10), which can be further reduced to form anion 12 (reaction 11). The latter can liberate CO under formation of lithium methylate 10 (reaction 12). Another possible reaction for the anion 12 to react is to liberate CO₂ under formation of a methyl radical (reaction 13).

The radical anion 9 can also undergo reaction 14, which forms a methyl radical and lithium methyl carbonate (13). Some of the lithium methyl carbonate may be further reduced to form 14, which finally gives a methyl radical and Li₂CO₃ (8) (reaction 15). The methyl radicals finally recombine to produce ethane (reaction 16). However, because this radical has a low stability, reactions 13 and 14, producing it, are less probable than reaction 12, and the film should be composed of a major part of lithium methylate.

In the case of DEC, as the ethyl radical is more stable, the reactions involving this product are more probable than in DMC reduction. The scenario proposed is in good agreement with what has been proposed in the literature.^{31,32,47,48}

In Table 1, we give the formation enthalpies of the solvents, LiPF₆, and the different products likely to be formed at their reduction (except for polymeric compounds). These values have

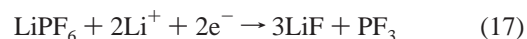
TABLE 2: Enthalpies ΔH_R for the Formation of the Different EC, DMC, and DEC Reduction Products Calculated from the Reactions Presented in Figures 6 and 7 and the Data of Table 1

product formed	enthalpy (kJ/formula unit)	enthalpy (kJ/g of lithium salt formed)
Reduction of EC		
Li ₂ CO ₃	-760	-10.3
(CH ₂)OCO ₂ Li) ₂	-850	-5.3
((C ₂ H ₄)OCO ₂ Li) ₂	-820	-4.4
Li(CH ₂) ₂ OCO(CH ₂) ₂ OCO ₂ Li	-581	-3.1
LiCH ₂ CH ₂ OCO ₂ Li	-682	-7.2
Reduction of DMC		
CH ₃ OLi + CO	-370	-4.9
CH ₃ OCO ₂ Li + C ₂ H ₆	-720	-4.4
Li ₂ CO ₃ + C ₂ H ₆	-680	-9.2
CH ₃ OLi + CO ₂ + 1/2 C ₂ H ₆	-260	-6.8
Reduction of DEC		
C ₂ H ₅ OLi + CO	-367	(-3.5)
C ₂ H ₅ OCO ₂ Li + C ₂ H ₆	-660	(-3.4)
Li ₂ CO ₃ + C ₄ H ₁₀	-640	-8.7
C ₂ H ₅ OLi + CO ₂ + 1/2 C ₄ H ₁₀	-250	(-4.8)

been taken from literature or calculated from the data given in the literature.^{49–51} The reaction enthalpies associated with the formation of the different products, using the reaction mechanisms developed in Figures 6 and 7, are given in Table 2.

For comparison, the enthalpies according to Wang et al.²⁵ for the reactions starting from both the Li⁺(EC) complex and the EC alone are given in Table 3. The different determination, either estimation of the formation enthalpies of the compounds involved or DFT calculation of the reaction enthalpies, gives slightly different, but nevertheless comparable, values.

4.1.3. LiPF₆ Reduction. The reduction of LiPF₆ is supposed to proceed as follows:



LiPF₆ dissociates as the following



It does not proceed homogeneously along the thickness of the film:^{17,36,52–54} the reduction seems to be more complete near the graphite surface, eventually with formation of P(0), whereas it is only partial near the electrolyte with the presence of fluorine-rich phosphorus compounds.

If one takes into account the formation of PF₃, according to eq 17, the reduction of LiPF₆ liberates -493 kJ, which is -247 kJ/mol of lithium involved. Assuming a complete reduction to P(0), according to eqs 18 and 19, -1388 kJ is liberated, which means -278 kJ/mol of lithium involved. A calorimetric study is thus not capable of distinguishing between the different possibilities of reduction of this salt. The heat released per gram of LiF formed is between -6.2 kJ (for reaction 17) and -8.9 kJ (for reactions 18 and 19).

4.1.4. About the Presence of Oligomers and Polymers in the Passivation Film. In the mechanisms mentioned so far, reactions leading to polymeric compounds were not considered. Numerous authors consider the formation of either poly(ethylene ether carbonate) by direct polymerization of EC or of polyethylene by polymerization of the ethylene formed at the reduction of EC.^{22,32,35,52,54–57} These considerations are mostly based on spectroscopic observations as infrared spectroscopy and XPS,³⁶ which are quite delicate. Recently, however, Peled et al. proved

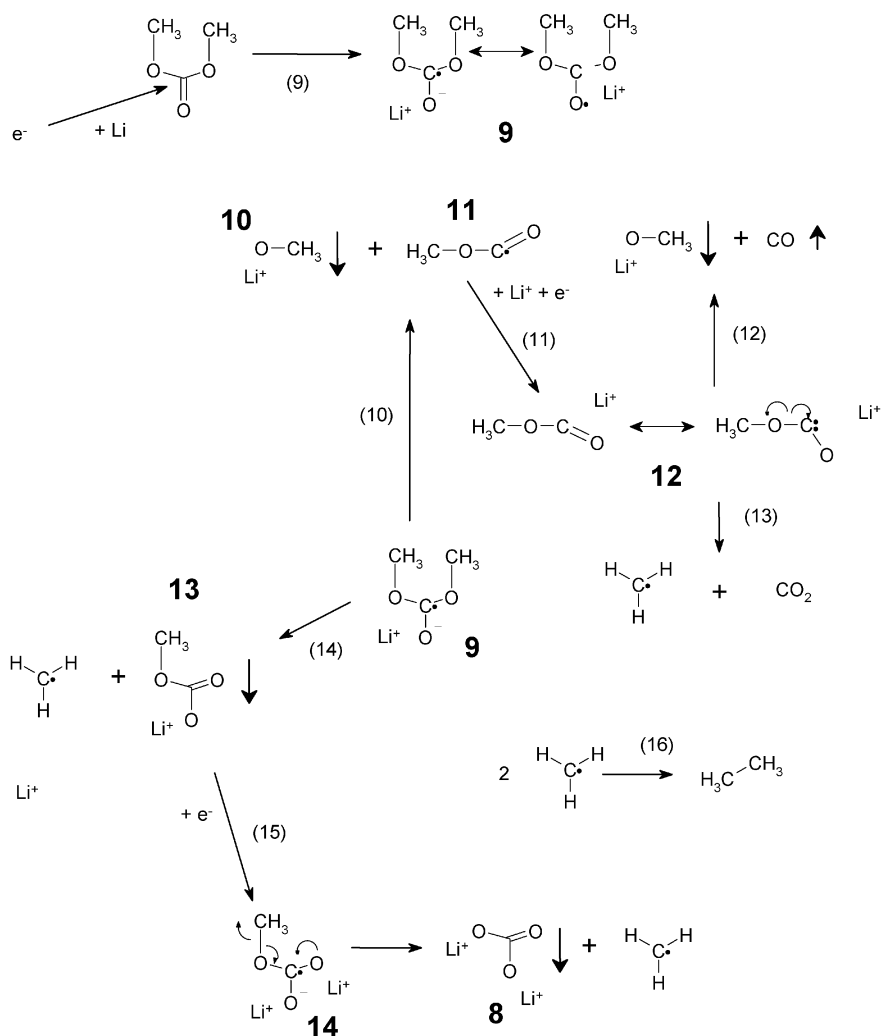


Figure 7. Possible reaction mechanisms of DMC reduction leading to the different products supposed to be present in the formation of the passivation film.

TABLE 3: Formation Enthalpies ΔH_R of the Different EC Reduction Products from EC and Li(EC), Respectively (According to Wang et al.²⁵)

product formed	enthalpy, starting from EC (kJ/formula unit)	enthalpy (kJ/g of Li salt formed)	enthalpy, starting from Li(EC) (kJ/formula unit)	enthalpy (kJ/g of Li salt formed)
(CH ₂ OCO ₂ Li) ₂	-1708	-10.5	-1286	-7.9
(CH ₂ CH ₂ OCO ₂ Li) ₂	-1778	-9.4	-1356	-7.1
LiO(CH ₂) ₂ OCO(CH ₂) ₂ OCO ₂ Li	-1640	-8.6	-1218	-6.4
LiCH ₂ CH ₂ OCO ₂ Li	-1512	-15.9	-1090	-11.5
Li ₂ CO ₃	-1728	-23.3	-1304	-17.6

by time-of-flight secondary ion mass spectrometry (TOF-SIMS) the existence of ethylene oligomers with a mass of less than 400 g/mol on the basal plane of HOPG.⁵⁸ We discuss here the probability of polymer formation on the surface of lithiated graphite on the basis of the experimental conditions necessary for their formation.

EC can polymerize to form poly(ethylene ether carbonate) under elimination of CO₂ by anionic-, cationic-, or coordination-catalyzed reaction.^{59–61} The polymerization proceeds under ring opening and thus under loss of entropy, which requires a temperature of 170 °C.⁵⁹ However, the reaction is favored by the elimination of CO₂, which diminishes the polymerization temperature. For a coordination-catalyzed reaction, the conditions are 170 °C and several hours, and for an anionic pathway, using butyllithium as initiator, the temperature required is above 100 °C. Cationic polymerization, however, proceeds already for temperatures as low as 70 °C with 30% yield.⁶²

At the lithiated graphite/electrolyte interface, anionic and cationic initiators are present, i.e., lithiated graphite and PF₅, but the experimental conditions, such as temperature and reaction time, are not fulfilled. It is therefore difficult to understand how polymerization could proceed, in particular at the surface of the lithiated graphite.

To check this, we carried out anionic polymerization of EC with naphthalene lithium at ambient temperature. With a very poor yield of less than 1% after 5 days of reaction, some polymer was obtained. As the formation of the passivation film proceeds in a few minutes and takes place in a heterogeneous medium, it is clear that the yield of such polymer in the passivation film will be very weak and can therefore be neglected in the following discussion. The characterization of this polymer will be published elsewhere.

Ethylene polymerization can proceed via a radical or a Ziegler–Natta pathway. Radical polymerization of ethylene is

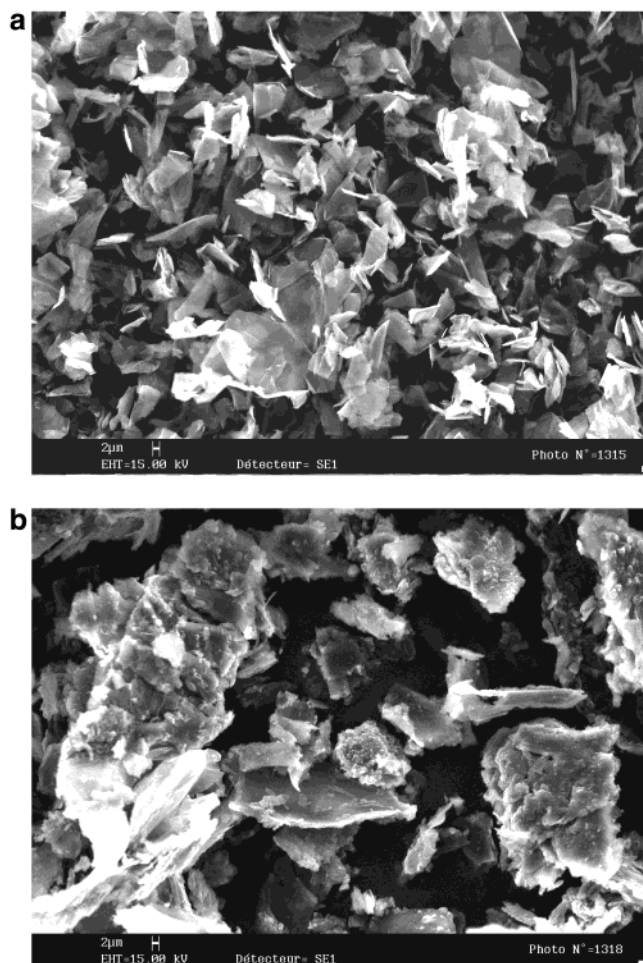


Figure 8. SEM photos of (a) commercial graphite powder (Thermopure, Superior Graphite) with a BET surface of 4.9 m²/g and (b) the lithiated HOPG powder used for our experiments.

generally achieved using peroxide, mostly at high temperature and high pressure to ensure a homogeneous polymerization.⁶³ As the enthalpy and entropy for polymerization are -101 kJ/mol and -160 J/K·mol, respectively,⁶⁴ and the activation energy is quite low (34.3 kJ/mol),⁶⁵ ethylene polymerization should be relatively easy.

The formation of radicals during the reduction of the solvents has been evidenced by Endo et al.⁶⁶ Hence, the polymerization of ethylene on the surface of lithiated graphite, induced by these radicals during the formation of the passivation film, should be possible. As all of the reactions occur at the interface, the growing chains are very near to each other, which should favor the recombination of the radicals and therefore lead to the formation of oligomers rather than polymers. This would be consistent with the results of Peled et al.⁵⁸ Nevertheless, it must be noted that ethylene is a gas and can volatilize easily before chain growth takes place. It is therefore difficult to take into account ethylene polymerization in our calculations that should be understood, hence, only as a first approximation.

4.2. Correlation between the Experimental Data and the Reaction Mechanisms Suggested. *4.2.1. Reaction with DEC.* The reduction of DEC by the lithiated HOPG powder liberates -2600 J/g of LiC₆, which corresponds to -205 kJ/mol of LiC₆, and knowing that the formation of LiC₆ is exothermic by -18.4 kJ/mol,⁵¹ the enthalpy associated with DEC reduction should be -223 kJ/mol of lithium. This value is coherent with the two reactions 9–12 and 9, 14, and 16 for which the two calculated

energy values are -330 kJ/mol of lithium and -184 kJ/mol of lithium (Table 2). It seems that both reactions participate in the reduction of DEC and that with approximately the same rates, as the heat obtained experimentally is between the two values calculated for the production of either C₂H₅OCO₂Li or C₂H₅OLi. If one takes into account the formation of Li₂CO₃ (reactions 9 and 14–16), for which -640 kJ is exchanged, which corresponds to -320 kJ/mol of Li, it can be stated that this reaction cannot be discerned by calorimetry from the two other reactions.

As the energy for the reduction of LiPF₆ is comprised between -246 and -278 kJ/mol of Li, it cannot be discerned from the reduction of solvent. Thus, the presence of LiPF₆ does not influence the heat released, as a mole of lithium, reacting with LiPF₆ or with DEC, releases the heat of the same order (Table 3). The electrolyte reduction is limited by the amount of lithium. No contribution of LiPF₆ reduction can be made from calorimetry alone, nevertheless XRD data signal³⁰ that an acceleration of the reaction occurs in the presence of LiPF₆ suggesting an active participation of its reduction.

4.2.2. Film Composition for EC- and DMC-Based Electrolytes. This part deals with the determination of the film composition formed in the presence of different electrolytes, using the experimental data, the reaction mechanisms discussed, and the data from Table 2. By using the energies liberated per gram of insoluble matter and the densities of the compounds, the quantity of product necessary to form a stable passivation film could be calculated. It would be interesting to determine also the thickness of the passivation film formed from the knowledge of the active surface of the lithiated HOPG powder used. However, for several reasons, this is not done here. (i) It is not sure that the surface determined by BET technique is the same as the reactive one for solvent reduction. (ii) Standard BET measurements on the material itself were not possible, as LiC₆ may react with N₂. (iii) The delithiated product instead used (see Experimental Section) gave a value of 11 m²/g, which seems much too high. It is most likely that a partial exfoliation occurs during delithiation,⁶⁷ which increases much the active surface.

4.2.2a. EC. The formation of (C₂H₄OCO₂Li)₂ and LiO(CH₂)₂OCO(CH₂)₂OCO₂Li seems to be thermodynamically most favorable. Nevertheless, (CH₂OCO₂Li)₂ seems to be predominant in the film.^{12,32} This may result from the greater solubility of (C₂H₄OCO₂Li)₂ and LiO(CH₂)₂OCO(CH₂)₂OCO₂Li in the electrolyte, with respect to (CH₂OCO₂Li)₂.²⁵ It must, however, be pointed out that the two lithium alkylene carbonates can only with difficulty be distinguished by the spectroscopic techniques mostly employed to characterize the composition of the passivation film and that it is difficult to understand why (CH₂OCO₂Li)₂ should be less soluble than (C₂H₄OCO₂Li)₂.

As the reaction enthalpies do not differ in magnitude, it is not possible to determine the composition of the film and only calculations can be made to determine the quantity of product for the cases that one product is formed in majority over the other products, supposing that only this product be formed and that it be insoluble in the electrolyte.

The density of Li₂CO₃ is 2.11 g/cm³, and the ones of (CH₂OCO₂Li)₂ and (C₂H₄OCO₂Li)₂, LiO(CH₂)₂OCO(CH₂)₂OCO₂Li, and LiCH₂CH₂OCO₂Li are not documented but should be quite similar to the one of an organic lithium salt as lithium acetate, which means 1.2 g/cm³.⁶⁸ The heat released for EC at 40 °C is -40 J/g. The heat exchanged for the simple delithiation of the surface-near parts of the graphite is of the order of $+2.3$ J/g for $\Delta x = 0.01$ (18.4 kJ/mol LiC₆), endothermic in nature.

TABLE 4: Relative Quantities of the Different EC Reduction Products Per Gram of Lithiated HOPG, from EC and Li(EC), Respectively (According to Wang et al.²⁵)

EC reduction	mg of product per g of lithiated HOPG
product formed (using data from Table 2)	
Li ₂ CO ₃	4
(CH ₂)OCO ₂ Li ₂	8
((C ₂ H ₄)OCO ₂ Li) ₂	9
Li(CH ₂) ₂ OCO(CH ₂) ₂ OCO ₂ Li	13
LiCH ₂ CH ₂ OCO ₂ Li	5.5
product formed (using data from Wang et al.; from EC, Table 3)	
(CH ₂)OCO ₂ Li ₂	4
(CH ₂ CH ₂ OCO ₂ Li) ₂	4.2
LiO(CH ₂) ₂ OCO(CH ₂) ₂ OCO ₂ Li	4.6
LiCH ₂ CH ₂ OCO ₂ Li	2.5
Li ₂ CO ₃	0.8

As the amount of deintercalated lithium varies from case to case, no correction is made for the delithiation, but one should take into account that the values for the heat released for reduction of solvents and salts are somewhat higher than the values given. Table 4 summarizes the results for all of the products with the enthalpy values from our estimation of the formation enthalpies. We give also the results calculated from the DFT calculations by Wang et al.,²⁵ for comparison. The formation of (CH₂OCO₂-Li)₂ shall be presented here as an example: By using a heat exchange of -5.3 kJ/g of product, we obtain 7.5 mg of product per gram of LiC₆, which corresponds to 6.3×10^{-3} cm³.

The values obtained lie mostly in the range of 4–9 mg/g (for the organic salts), whereas for Li₂CO₃ the values are smaller (1.5–4 mg/g). The values obtained from the DFT²⁵ are by a factor of 2 smaller than those obtained from our estimation of the formation enthalpies (Tables 1 and 2), which lies in the fact that the energies used for their calculation differ by the same factor.

It is interesting to compare these values to the thickness of the passivation film that has been reported in the literature: 10–50 Å in ref 69, 40 Å in ref 70, 23 Å in ref 71, 20 Å for the «nonpolymer part» in ref 36, and 20–100 Å in ref 72.

If one takes a mean value of 25 Å for the thickness of the film, an average of 3–6 mg product per g of lithiated HOPG would give a specific surface of our lithiated HOPG of about 1.2–2.5 m²/g, using the given densities of the products. This seems to be coherent with SEM photos (Figure 8) performed on the lithiated HOPG powder and compared to a commercial graphite with a known BET surface of 4.9 m²/g (Thermopure, Superior Graphite). For EC–DEC and EC–DMC, the values of the film thickness can be assumed to be in the same range, as the energies liberated are close to the ones in the case of EC.

4.2.2b. EC–LiPF₆. In the case of EC–LiPF₆ electrolyte, the heat evolved is about -110 J/g, 70 J/g higher than for pure EC. Assuming that the LiPF₆ reduction goes along with the EC reduction but that the amount of EC reduction is not altered by LiPF₆ reduction, the difference of -70 J/g can be attributed to the reduction of LiPF₆. The reason for the enhanced reactivity of EC in the presence of LiPF₆ can be the formation of Li(EC)_n complexes (cf. ref 25) that ease EC reduction by a stronger polarization of the EC molecule due to the electrophilic effect of Li⁺. EC reduction can be supposed to be more rapid and the surface covering to be less homogeneous, which could favor the reduction of LiPF₆. The reactions considered for the reduction mechanisms of LiPF₆ (17–19) gave a heat of -247 kJ/mol of lithium liberated in the case of the formation of PF₃ and -278 kJ/mol of lithium liberated in the case of P(O)

formation. We can, as in the previous section, calculate the amount of LiF formed from this reaction (phosphorus-containing compounds are not considered, as their nature is actually not clear). We take a value of -8 kJ/g of LiF formed, which is an intermediate of -6.2 kJ/g of LiF (for PF₃ formation) and -8.9 kJ/g of LiF (for P(O) formation) and obtained 11 mg of LiF/g of LiC₆. Taking the gravimetric density of LiF as 2.65 g/cm³,⁶⁸ the corresponding volume is 4.17×10^{-3} cm³. The molar ratios of organic salt vs LiF are, as an example for (CH₂OCO₂Li)₂, 0.03–0.05 mmol of organic salt (CH₂OCO₂Li)₂ vs 0.4 mmol of LiF. For the other products that are formed, the molar amounts formed are in the same range. That means that the film, in the case of EC–LiPF₆ electrolyte, consists mainly of LiF.

One should take into account the fact that the amounts of the product formed should vary slightly when the enthalpy values from Wang et al.²⁵ are taken for their determination, as in this case the EC reduction starts from Li(EC)_n supramolecules and the enthalpy values for this reaction must be taken into account. They are higher as the ones when starting from noncomplexed EC molecules as the complexation of Li⁺ is exothermic. This slightly alters the heat release that could be attributed to LiPF₆ reduction (cf. Tables 2 and 3). A slight effect of HF can also be expected to occur, as HF reacts readily with ROCO₂Li to form LiF, ROH, and CO₂, which would also ease the reduction of LiPF₆. However, the content of HF can be supposed to be sufficiently low not to intervene in an important manner.

4.2.2c. DMC and DMC–LiPF₆. The DMC reduction products are, as for EC reduction, various, and the composition of the film is unknown. As for EC, we can only calculate the approximate amount of product formed for a film mainly composed of one reaction product, in the case of one reduction reaction being major over the others. Assuming that the formation of CH₃OLi is the most probable (cf. reactions 9–12), one can consider that approximately 25 mg of products is formed on the surface of 1 g of LiC₆ in the case of DMC, assuming the products to be insoluble.

The presence of LiPF₆ diminishes very much the reaction enthalpies, so that it is not possible to determine the amounts of either product, organic salt and LiF, that are formed on the LiC₆ electrode in contact with DMC–LiPF₆. Assuming the reduction products of DMC insoluble, one can conclude that the film formed must be much more homogeneous as in the case of DMC alone. If one supposes that DMC reduction products are somewhat soluble, the difference between DMC and DMC–LiPF₆ may come from the fact that LiF formation makes the DMC-based film protection rapidly and that much less DMC is reduced until the film is formed. Again, traces of HF would easily transform CH₃OLi to LiF and CH₃OH, which would slightly alter the surface covering by DMC reduction and ease the reduction of LiPF₆.

4.2.2d. DMC–DEC. For DMC–DEC, the situation is even more complex as the heat evolved is three times higher than that liberated for DMC alone. As the reduction mechanism for DEC is similar to the one for DMC, the formation of C₂H₅OLi and of C₂H₅OCO₂Li can be supposed to be predominant, although the formation of Li₂CO₃ may be somewhat more likely in the case of DEC than in the case of DMC. The high value of the heat evolved can be understood, as already discussed, by some dissolution of the film by DEC or by its adverse effect on the film homogeneity. The formation of LiF alone does not protect the surface of LiC₆, when the organic products are dissolved, so that even in the presence of LiPF₆ the heat

evolution is not much diminished as it is for DMC. The reaction time supports this, as it is significantly higher than the one observed for the EC-based mixtures.

Conclusion

Calorimetric measurements allowed us for the first time to measure accurately the enthalpy associated with the reactivity of lithiated HOPG with various components of a selected electrolyte. The energies obtained are well in agreement with the literature data. Of particular interest is the importance of the presence of EC on the composition of the passivation film and on the heat exchanged during its formation. Moreover, this study highlights the significant role of the LiPF_6 electrolyte salt. LiPF_6 limits the heat exchanged with DMC, increases it with the electrolytes containing EC, and does not have an effect on the reactivity of the HOPG, at least in terms of released heat, with DEC:DMC (1:1) and DEC. We tentatively discussed the possible reduction mechanisms for the three solvents and LiPF_6 , and this took into account the recent results on EC reduction by DFT calculations obtained by Wang et al.,²⁵ as well as the possibilities of polymer formation during the formation of the film. Approximate calculations were presented, which gave an idea of the quantity of insoluble products and the composition of the film for the different electrolytes. The strongly inorganic character of the film, with >80 mol % of LiF, was revealed for the electrolytes containing LiPF_6 .

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