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Studies on the thermal breakdown of common Li-ion battery electrolyte components

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Abstract

While much attention is paid to the impact of the active materials on the catastrophic failure of lithium ion batteries, much of the severity of a battery failure is also governed by the electrolytes used, which are typically flammable themselves and can decompose during battery failure. The use of $LiPF_6$ salt can be problematic as well, not only catalyzing electrolyte decomposition, but also providing a mechanism for HF production. This work evaluates the safety performance of the common components ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC), and ethyl methyl carbonate (EMC) in the context of the gasses produced during thermal decomposition, looking at both the quantity and composition of the vapor produced. EC and DEC were found to be the largest contributors to gas production, both producing upwards of 1.5 moles of gas/mole of electrolyte. DMC was found to be relatively stable, producing very little gas regardless of the presence of $LiPF_6$. EMC was stable on its own, but the addition of $LiPF_6$ catalyzed decomposition of the solvent. While gas analysis did not show evidence of significant quantities of any acutely toxic materials, the gasses themselves all contained enough flammable components to potentially ignite in air.

1. Introduction

Lithium ion batteries have long been used in consumer devices and are being fielded in emerging electric vehicles, including electric drive (EV), plug in hybrid (PHEV) and conventional hybrid vehicles (HEV). However, traditional safety studies have focused on the impact of a single small cell going into thermal runaway in an otherwise benign environment. This has led to a heavy focus on the onset temperatures and total energies of a thermal runaway, treating gas production as a secondary concern. These gasses can be flammable, and if produced in significant enough quantities can create a severe mechanical hazard from a resulting case rupture. Further, when cells rupture the escaping gas can aerosolize the flammable battery solvents. A full evaluation of the quantity, composition and possible acute health effects of the gasses produced by common electrolyte components would allow a more complete view of the safety of lithium ion batteries.

While other materials are being studied, lithium ion batteries still typically rely on $LiPF_6$ dissolved in carbonate solvents, typically ethylene carbonate (EC), diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC). While the carbonate solvents are relatively stable on their own, the addition of $LiPF_6$ has been demonstrated to catalyze thermal breakdown of the solvents into various volatile species. [1-15] Campion et al. [16, 17] demonstrated that battery electrolytes containing organic carbonates and $LiPF_6$ produced a variety of compounds, including CO_2, ethylene, alkyl fluorides, dialkyl ethers, fluorophosphates, fluorophosphoric acids, HF, LiF and oligoethylene oxides. They also found that the autocatalytic reactions were enhanced by protic impurities such as H_2O and ethanol, leading to reduced thermal stability. Additionally, the presence of water impurities has been shown to have an impact on the decomposition of battery electrolytes. Multiple researchers have argued that the presence of trace water or alcohol impurities allows for the formation of POF_3, which catalyzes further decomposition of the electrolyte. [5, 17] Potential instabilities leading to gas generation are magnified by use or misuse in the field and may include long cycle life, high depth of discharge, overcharge, or exposure to elevated temperature.

The thermal impact of electrolyte decomposition has also been observed to be highly dependent upon the composition of the electrolyte. Differential scanning calorimetry (DSC) work by Botte et al. [1] found that common solvents EC and EMC, including various mixtures of the two, saw both reduced onset temperatures and increased heat release with increased concentrations of $LiPF_6$. Eshetu et al. [18] took this a step further and evaluated the safety performance of various electrolyte solvents using combustion calorimetry. They based the evaluation on various physical and combustion parameters, and while results were somewhat varied generally concluded that the linear solvents (DEC, EMC, DMC) generally had poorer fire performance than cyclic solvents (EC).

Evaluating the safety performance of an electrolyte is a complex task that requires the evaluation of many factors. Flammability of lithium ion electrolytes has been widely studied, as a significant amount of the energy released during a battery fire event comes from the external combustion of the carbonate solvents that make up the bulk of the electrolyte. [3, 4, 17-20] Toxicity of battery gasses has been examined as well. [21, 22] However, a comparison of the total amount and composition of different electrolyte decomposition products has been limited. Even if the specific gasses released are relatively benign, the quick evolution of large quantities would itself pose a significant hazard, particularly if it were to occur in a confined space. Conversely, the release of toxic or flammable species may be mitigated if the normal quantities released are below the lower flammability limit (LFL) for flammable species or below threshold limit values (TLV) for toxic species. A full evaluation of the safety of the electrolyte should include the amount of gas released during decomposition, combined with the potential hazards that gas poses.

This work evaluates the thermal decomposition of common electrolytes used in lithium ion batteries using Accelerating Rate Calorimetry (ARC) along with analysis of both the amount and substance of gaseous species produced during decomposition of the electrolyte. EC, DEC, EMC and DMC, as well as binary and ternary mixtures of these electrolytes are evaluated. The gas production during thermal decomposition is measured, and the products of individual solvents containing $LiPF_6$ are analyzed. This work ultimately hopes to provide a better understanding of the impact of electrolyte decomposition on the safety performance of lithium ion batteries.

2. Experimental

Battery electrolyte solutions were prepared from EC, DEC, EMC and DMC. These battery grade solvents were purchased from Kishida Chemical Co. Ltd., Japan. $LiPF_6$, when used, was added to a concentration of 1.2 M. The samples were prepared in a controlled environment to limit the impact of H_2O impurities. 500 mg of the prepared electrolyte solutions were added to a 10 mL stainless steel calorimetry bomb. All preparation of electrolyte solutions was performed inside an argon glove box. The bombs were sealed with a Swagelok fitting before removing from the glove box and transferring to the ARC. Air was purged from the ARC fixture using nitrogen. Loading onto the ARC fixture was performed by both removing the Swagelok fitting and attaching the bomb to the ARC fixture under a blanket of nitrogen.

ARC measurements were performed on a Thermal Hazard Technologies ES ARC system. [23] The electrolyte samples were heated from ambient temperature up to 405 °C. Heating was performed in 5 °C increments, after which the sample would be allowed to equilibrate. The sample was contained within a pressure tight system within the ARC. The “hot zone” of the ARC contained the calorimeter bomb holding the sample attached with ¼” stainless steel tubing. This led to the manifold outside the calorimeter itself which provided volume for gas expansion, as well as connections for pressure measurement, volume calibration and gas sampling. Pressure measurements were made using a Honeywell 3000 psi pressure transducer. The volume of the sample holder and attached manifolds were determined through the expansion of inert gas from an attached vessel of known volume into the manifold. A known volume was attached to the fixture and flooded with nitrogen gas. All of the fixture but the known volume was then evacuated. The volume was then opened to the fixture and the pressure from the resulting gas expansion measured. The volume of the fixture was then calculated as an ideal gas expansion.

Gas sampling was performed using the automatic sampler feature of the ES ARC system. 500 mL gas sample bottles were first evacuated using a vacuum pump. The sample bottles were then sealed and attached to the automatic sampler. Gas samples were taken at 400 °C to allow for complete decomposition of the electrolyte solution. The sampler was kept open for 5 minutes to allow the decomposition gas to fill the sample bottle. Gas sample bottles were then sealed and shipped off site for subsequent analysis. Fixed permanent gases and major constituents (CO_2, CO, CH_4, H_2, O_2, N_2) were analyzed using gas chromatography equipped with a thermal conductivity detector. Linear hydrocarbons (C_2-C_6) were analyzed using a gas chromatograph equipped with a flame ionization detector. Volatile compounds (generally < 1000 ppm) were analyzed with gas chromatography/mass spectroscopy (GC/MS).

3. Results and Discussion

The gas production during the thermal decomposition of battery electrolytes was evaluated. Individual carbonate solvents that typically form the major constituents of lithium ion electrolytes were first evaluated in their pure, as-received form. The gas production for each carbonate solvent, expressed as a ratio of moles of gas produced to moles of solvent, is shown in Figure 1. As EC is typically always included as part of the electrolyte solution, some binary mixtures with EC were also examined. The data shows that pure EMC and DMC are fairly stable and produce very little gas over the temperatures studied. Relatively low levels of gas evolution are observed as the temperature increases up to ~130-140 °C, after which both attain a relatively stable liquid-vapor pressure equilibrium within the sealed apparatus and show no sign of additional gas evolution as the temperature is increased. DEC shows similar behavior at first, with the pressure increasing until liquid-vapor pressure equilibrium is observed at ~180 °C. However, the solvent then appears to undergo a thermal decomposition beginning at 305 °C, where the gas production can be seen to sharply increase until the liquid is fully consumed. EC shows evidence of thermal decomposition beginning at 190 °C, with steady gas evolution as the temperature is increased. When compared to the boiling points of the solvents, shown in Table 1, the lower boiling point solvents are EMC and DMC, while EC and DEC would appear at first to be more stable with higher boiling points. It is possible that the lower boiling points of EMC and DMC cause them to vaporize before any decomposition can occur, with the vaporization consuming the energy that would otherwise cause the solvents to break down.

Figure 2 shows the result of the addition of 1.2M $LiPF_6$ salt to the individual solvent species. It is well known that $LiPF_6$ can decompose to form the strong Lewis acid PF_5 according to the following equilibrium reaction[10]:

$$LiPF_6\,(s) \rightleftarrows LiF\,(s) + PF_5\,(g) \tag{1}$$

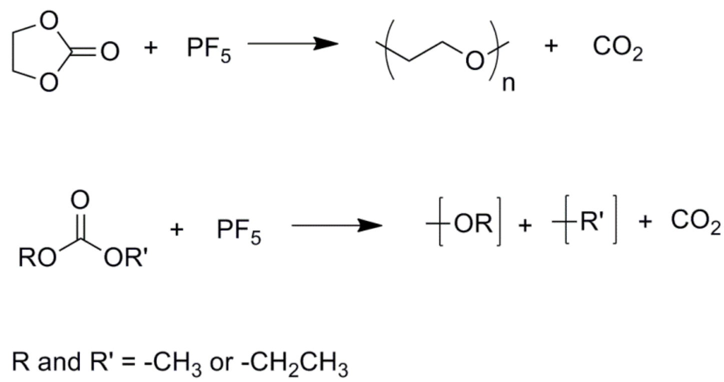
In addition, the presence of protic species such as water or alcohols can lead to further reaction resulting in additional highly reactive and catalytic species such as HF and POF_3:

$$PF_5(g) + H_2O(l) \rightarrow POF_3(g) + 2HF(g) \tag{2}$$

Water is a contaminant that can be present as an initial impurity in the electrolyte, introduced during processing of the cell components or result from other degradation reactions.

As shown in Figure 2, the salt catalyzed the decomposition of the electrolyte solution in most cases, with the exception of DMC, which behaves similarly with or without $LiPF_6$. Figure 1 shows for example that EMC and DMC both exhibit little to no evidence of thermal decomposition without the inclusion of $LiPF_6$ salt. However, when adding $LiPF_6$ (Figure 2)EMC shows evidence of thermal decomposition, seen as the sharp rise in pressure occurring at 175 °C, while DMC shows results very similar to those observed without $LiPF_6$, indicating that the stability of DMC is not affected by the presence of the salt. This is similar to previous work showing that electrolytes containing DMC were less reactive than electrolytes containing DEC.[20] The changes in the behavior of EC are largely kinetic. However, it undergoes a sharper transition with the addition of $LiPF_6$, with full decomposition occurring very rapidly after the electrolyte reaches its onset temperature. Sloop, et al. have shown that PF_5 and other catalysts can induce a ring-opening polymerization of EC resulting in PEO-like polymers and generation of CO_2.[24] The overall gas production of EC, while similar, was measurably reduced with the addition of $LiPF_6$. This indicates that the overall reactions taking place may be altered with the addition of the salt. DEC is more unstable and undergoes a more complete decomposition with the addition of $LiPF_6$, with the onset temperature reduced significantly (from ~300 °C down to 170 °C) and the maximum gas production observed increasing from 1.25 gas/electrolyte molar ratio to 1.55 gas/electrolyte molar ratio. EMC, while even with $LiPF_6$ does not produce as much gas as DEC, perhaps undergoes the most dramatic change with the salt addition. In Figure 1, no sign of decomposition of the pure solvent is observed, however Figure 2 shows that the addition of $LiPF_6$ allows for rapid decomposition occurring at ~170 °C.

For the purposes of this analysis, gas volume and decomposition onset temperature can be used as metrics of electrolyte/$LiPF_6$ reactivity; where greater gas volume and lower onset temperature represent greater reactivity. The relative reactivity of these carbonate components with $LiFP_6$ at elevated temperature follows EC > DEC > EMC > DMC. In these experiments, the EC decomposition follows the PF_5 Lewis acid catalyzed ring opening polymerization of EC described by Soga et al. and Sloop et al. to for form poly(ethylene oxide) and liberate CO_2. [24, 25] Assuming the decomposition reaction of the linear carbonate solvents follows the same initial steps in the mechanism as the ring opening polymerization of EC to liberate CO_2 and methoxy ($-OCH_3$) or ethoxy ($-OCH_2CH_3$) intermediates, then this order of relative reactivity of carbonates is consistent with what is expected for the PF_5/carbonate reaction.



In this mechanism, ring opening EC is the most energetically favorable, followed by ethoxy leaving group intermediates, followed by methoxy leaving group intermediates, based on the ring strain of cyclic EC and relative stability of longer chain aliphatic groups to stabilize charged or radical intermediates.

Battery electrolytes typically require some content of EC to provide good conductivity of lithium ions during charge and discharge, as well as help the SEI layer develop on the anode during formation. [26, 27] Tests of the pure component, however, show that it is also one of the largest individual contributors to decomposition gas generation, regardless of the role of $LiPF_6$. Figures 3 and 4 examine binary mixtures of EC with DEC (Figure 3) and EMC (Figure 4). Mixtures of EC and DEC with $LiPF_6$, shown in Figure 3 (A), show little difference between varying solvent mixtures, as the gas production of EC and DEC when $LiPF_6$ is present are relatively similar. Without $LiPF_{6,}$ shown in in Figure 3 (B), the addition of EC does appear to increase the amount of gas production, however the onset temperature is increased slightly from pure DEC, from 110 °C to 120 °C.

Mixtures of EC and EMC, shown in Figure 4 show a fairly linear impact of mixtures. When the mixtures contain $LiPF_6$, the gas production generally increases with increasing EC content. The exception to this was the mixture of 5% EC, 95% DEC, where the gas production was slightly, but measurably, reduced. At the same time, the addition of $LiPF_6$ makes the decomposition much faster kinetically for all mixtures, where decomposition of all mixtures is largely complete at 250 °C, while solvents without $LiPF_6$ require temperatures of 300 °C and higher to reach completion. At low concentrations of EC, it is possible thermal breakdown of the EC in solution is difficult and serves only to dilute the EMC present. Without the salt, as shown in Figure 4 (B), EMC remains stable even when mixed with EC and gas generation is kinetically much slower for the EC:EMC mixture without $LiPF_6$. Evidence of decomposition of EC is still present in the mixture, however the presence of EMC has served to limit its effect, increasing the onset of decomposition from 195 °C to 240 °C and reducing the gas production to 0.25 moles gas/moles electrolyte. It was also observed that at very high temperatures, the apparent gas production of some $LiPF_6$ containing EC/DEC mixtures and DEC actually decreased with increasing temperature above 300 °C. This may indicate the development of condensable materials at extreme temperatures. It should also be considered, however, that the gas calculations used became less viable at the increasing pressure after significant gas production had occurred.

A significant observation is that the linear solvent species with ethyl groups (DEC and EMC) are more unstable than solvents with methyl groups (DMC). Work by Kawamura et al.[20] has shown that DEC containing electrolytes were more reactive than DMC containing electrolytes. An argument was made that the strong Lewis acid PF_5 attacks the C-O bond and that a stronger electron density on the oxygen increases the reaction. The presence of the C_2H_5- group gives a higher electron density on the oxygen than CH_3- and thus decreases the stability of these ethyl group based solvents.[5, 10, 20, 28, 29]

Figure 5 shows the results of gas analysis performed on samples taken from the decomposition gas of solvents with 1.2 M $LiPF_6$. This shows that not only is the gas production of DMC low, but that the decomposition products are relatively inert. 80mol% of the gas produced was CO_2, with the remainder H_2 and C_2H_6 vapor. Slightly more flammable products were observed from the decomposition of EMC and EC. Both had a CO_2 composition of 72-73mol%. EMC produced a higher fraction of linear carbonates, in particular C_2H_6 (11mol%) and C_3H_8 (5mol%), while the primary flammable product of EC was H_2, with ~18v% measured.

DEC had by far the highest fraction of flammable gas products. Only 37v% of CO_2 was produced, while H_2 (9mol%), C_2H_6 (33mol%) and C_3H_8 (11mol%) were all produced in significant quantities. Campion et al. [17] saw evidence of a variety of C_2 based compounds during the decomposition of liquid DEC held at 85 °C, and proposed a decomposition mechanism where $LiPF_6$ is able to react with trace alcohol or water impurities to form POF_3. This in turned catalyzed the decomposition of DEC to form ethanol over time at elevated temperatures. The work here further accelerates the process by elevating the temperature to the point where the solvents are no longer stable. While all of the gas products observed here were in high enough quantities to be flammable, and considering that a battery under thermal runaway often provides ample heat sources for ignition, high quantities of DEC in the electrolyte may pose a particular safety hazard beyond that of other electrolyte components.

The trace components of the gasses analyzed are listed in Table 2. While several organic compounds are identified, no acutely toxic chemicals were found in this analysis. While HF has been predicted elsewhere [30], and observed in some cases [31, 32], it was not detected in any measurable quantities here. It should be noted that because an ex-situ technique was used that highly reactive compounds, such as HF, or condensable species, such as solvent vapors, may not have been detected even though they were present immediately after the decomposition of the electrolyte.

4. Conclusions

The potential safety performance of common lithium ion battery electrolyte materials was evaluated by looking at both the total gas production as well as the constituents of the gas products. EC and DEC were found to be the most significant contributors to total gas production, EC in particular was found to be prone to significant gas production even in absence of $LiPF_6$. EC and DEC also were shown to interact with each other in a negative manner. The total gas production is equivalent to the pure solvents, however all mixtures of EC and DEC take on the lower onset temperature of DEC. As well, when the $LiPF_6$ salt was not present, the breakdown of EC was able to accelerate the decomposition of DEC, resulting in overall gas production that was similar to the production when $LiPF_6$ was present. The data shows that to at least some degree the solvents themselves are problematic when it comes to safety performance, and the use of less active salts will not be a perfect solution. There is some room for improved performance even with traditional solvents. EMC, while responding somewhat to the presence of $LiPF_6$, was shown to have little interaction with EC, with both the total gas production and onset temperatures simply shifting relatively with mixture composition. DMC as well was found to be fairly stable in all cases, showing very little gas production even when mixed with $LiPF_6$. In general, methyl based solvents (DMC) were more stable than the ethyl based solvents (DEC and EMC).

Eshetu et al. [18] similarly found that DEC had poor safety performance when evaluating electrolytes using combustion calorimetry. However, by most measures they showed a fairly strong performance of EC; here we show that while EC may perform well from a combustion standpoint, it contributes significantly to the overall gas production during the breakdown of electrolyte, and remains prone to decomposition even without other more active components.

The constituents of the gasses produced were evaluated as well, examining the potential hazards of the gasses produced. All tests showed production of flammable gasses in significant enough quantities to make the resulting mixture flammable in air. Of particular note were the gas products of DEC, which showed significant production of both hydrogen as well as various hydrocarbons. The relatively large amount of gas produced along with the high concentrations of flammable gasses make DEC a dangerous contributor in a thermal runaway situation, as hot surfaces, electrical arcing or incandescent particles present during a thermal runaway could easily ignite the gasses produced. Carbon monoxide was detected in measurable quantities as well, in particular from the decomposition of EC. In large enough quantities this may be significant enough to make the product gas acutely toxic, however it is worth noting that the trace gas analysis did not detect any associated gasses that are highly toxic in small quantities (notably HF was not detected).

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Figures

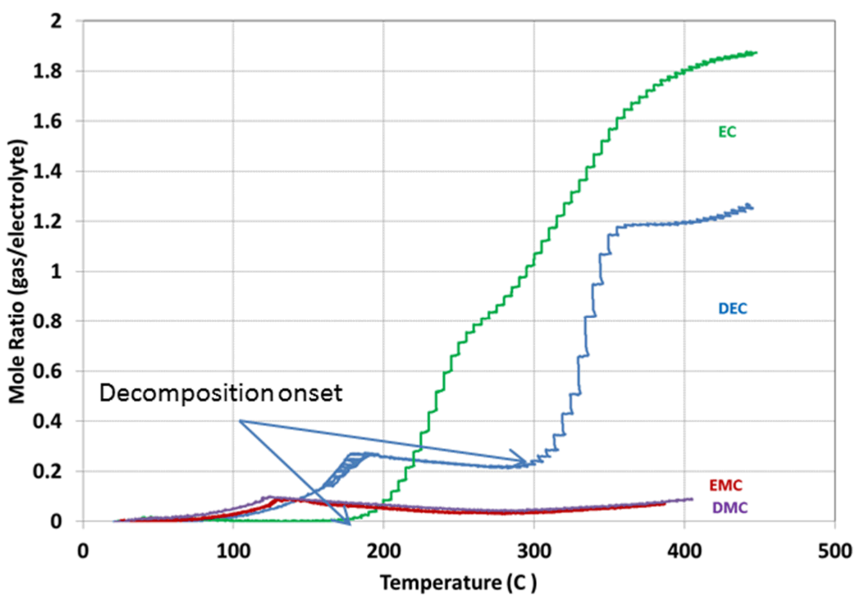

Figure 1 Gas production during thermal decomposition of typical Li-ion electrolyte solvents.

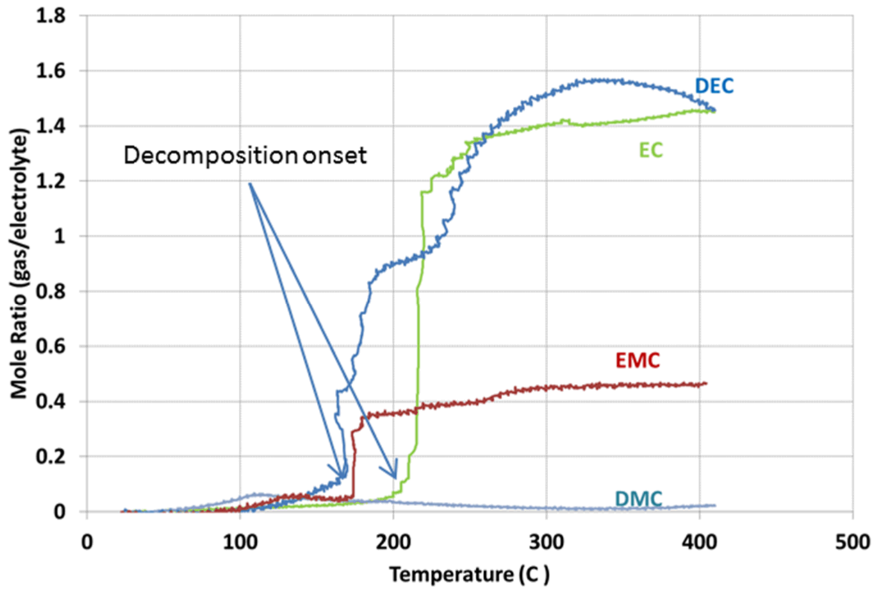

Figure 2 Gas production during thermal decomposition of typical Li-ion electrolyte solvents with 1.2 M $LiPF_6$

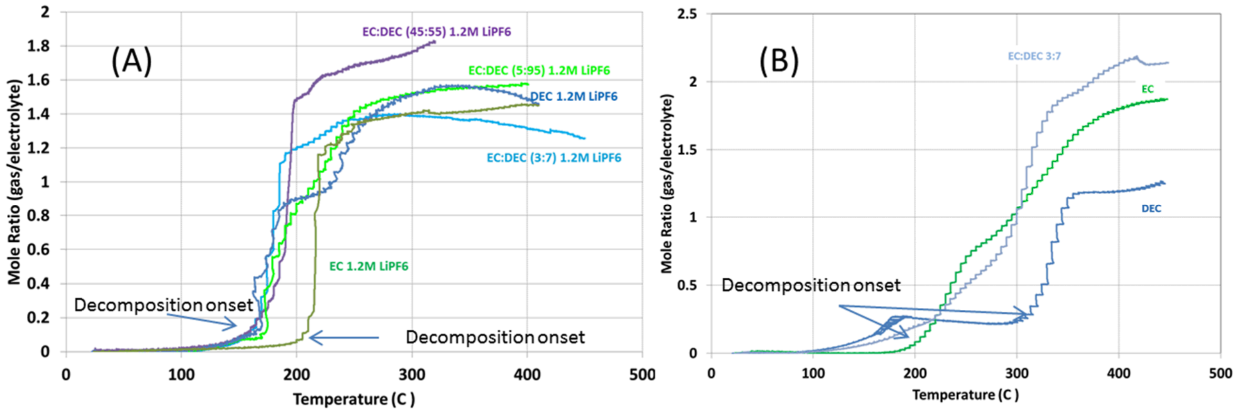

Figure 3 Gas production during thermal decomposition of binary mixtures of EC and DECwith (A) and without (B) 1.2 M concentration of $LiPF_6$

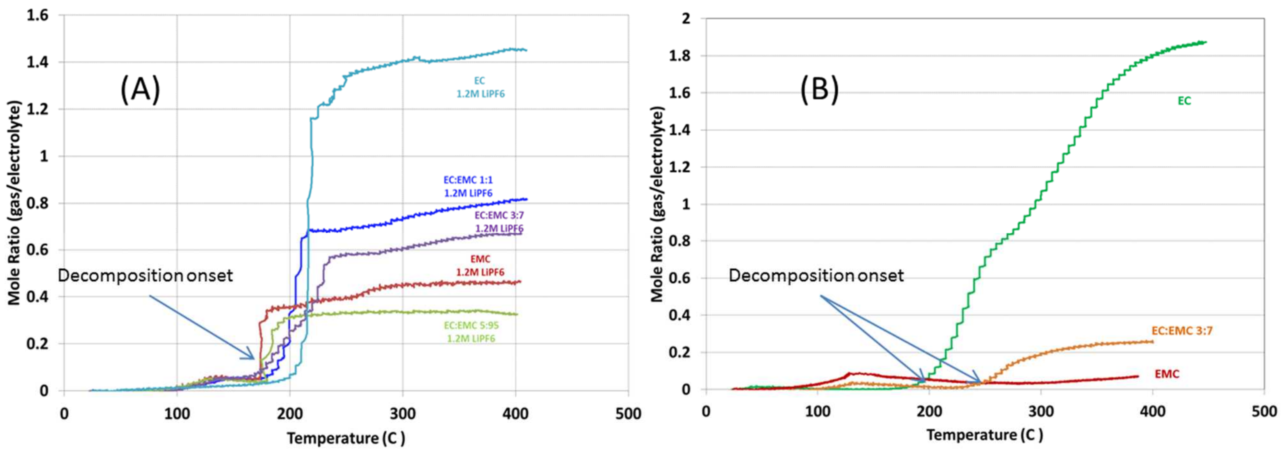

Figure 4 Gas production during thermal decomposition of binary mixtures of EC and EMCwith (A) and without (B) 1.2M concentration of $LiPF_6$

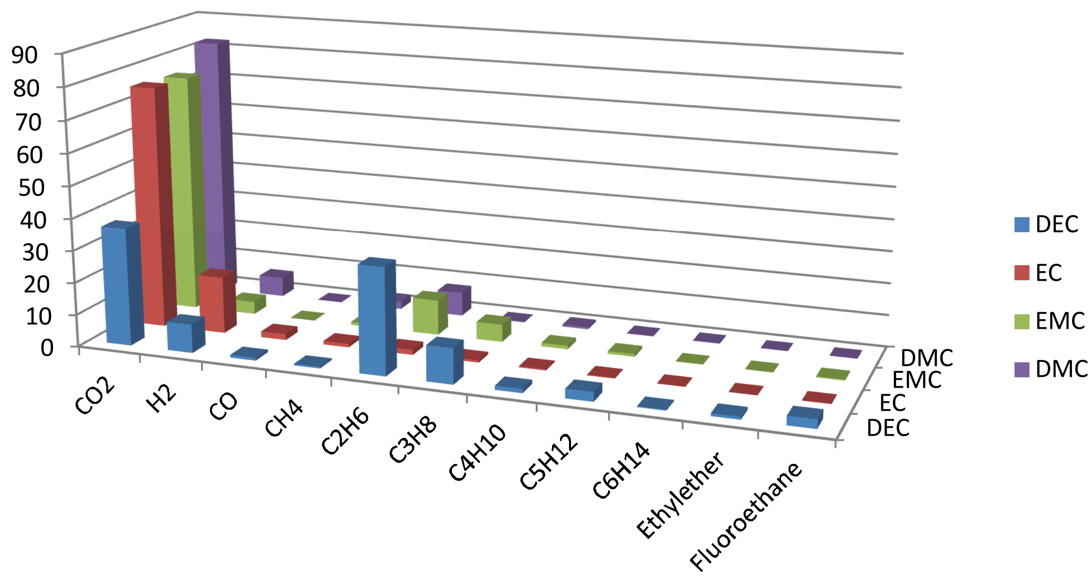

Figure 5 Molar percentage of major gas constituents of solvents studied all containing 1.2M $LiPF_6$

Tables

Table 1 Boiling points of solvents studied.

EC	517 K
DEC	400 K
DMC	364 K
EMC	380 K

Table 2 Molar percentage of trace compounds found within gas samples shown in Figure 5.

Compound	EC	DEC	EMC	DMC
Propene	2.35E-02	9.37E-02	3.29E-02	5.37E-03
1,3-Butadiene	2.43E-03	ND	ND	ND
Chloroethane	ND*	3.21E-03	1.17E-03	ND
EtOH	1.07E-02	1.14E+00	1.31E-02	1.24E-02
Ethyl acetate	2.56E-02	ND	ND	ND
n-Hexane	7.76E-03	ND	1.71E-03	ND
Benzene	1.93E-02	3.28E-02	1.93E-03	6.97E-04
1,4-Dioxane	ND	ND	4.78E-03	3.40E-03
n-Heptane	2.30E-03	1.90E-03	3.60E-04	ND
Toluene	4.30E-03	ND	ND	ND
n-Octane	5.63E-04	1.06E-03	ND	ND
ethylbenzene	9.56E-04	ND	ND	ND
Fluoroethane	1.43E-01	1.17E+00	3.40E-01	9.07E-02
Dimethyl ether	ND	ND	4.24E-01	ND
Ethylmethyl Ether	ND	ND	3.75E-01	1.65E-02
Isobutene	1.50E-02	7.03E-02	ND	ND
Ethylether	ND	4.08E-01	1.01E-01	6.61E-03
2-fluoropropane	2.83E-02	ND	ND	ND
1,2-difluoroethane	1.28E-02	ND	ND	ND
Isobutane	1.41E-01	ND	2.48E-01	2.06E-01
C4H8 Alkene	3.66E-02	ND	ND	ND
Isopentane	6.52E-02	ND	1.58E-01	4.53E-02
2-methylpentane	1.69E-02	ND	2.72E-02	ND
3-methylpentane	1.12E-02	ND	1.57E-02	ND
Dimethyl carbonate	ND	ND	4.01E-02	ND
Ethylmethyl carbonate	ND	ND	3.18E-02	ND

*ND – Compound not detected in gas sample.

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