



Short communication

A combustion chemistry analysis of carbonate solvents used in Li-ion batteries

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ABSTRACT

Under abusive conditions Li-ion cells can rupture, ejecting electrolyte and other flammable gases. In this paper we consider some of the thermochemical and combustion properties of these gases that determine whether they ignite and how energetically they burn. We find a significant variation among the carbonate solvents in the factors that are important to determining flammability, such as combustion enthalpy and vaporization enthalpy. We also show that flames of carbonate solvents are fundamentally less energetic than those of conventional hydrocarbons. An example of this contrast is given using a recently developed mechanism for dimethyl carbonate (DMC) combustion, where we show that a diffusion flame burning DMC has only half the peak heat release rate of an analogous propane flame. Interestingly, peak temperatures differ by only 25%. We argue that heat release rate is a more useful parameter than temperature when evaluating the likelihood that a flame in one cell will ignite a neighboring cell. Our results suggest that thermochemical and combustion property factors might well be considered when choosing solvent mixtures when flammability is a concern.

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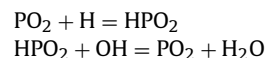
1. Introduction

Li-ion battery technology is used in many practical devices including cell phones and laptop computers, and it is now being contemplated for mass-produced hybrid and electric vehicles. Almost all Li-ion cells contain an electrolyte comprised of a mixture of linear and cyclic carbonate solvents and a dissolved lithium salt such as LiPF₆. These linear and cyclic carbonates are flammable. Occasionally abusive electrical, thermal, or mechanical conditions can cause cells to undergo self-heating and/or form ruptures in packaging, which can lead to incidents of thermal runaway [1–6].

Electrified portable devices and vehicles require batteries with both high power density and high energy density. For such systems, using a small number of large cells has an advantage over using a large number of small cells because of the reduced amount of cell packaging and fewer terminal connections with larger cells. However, large cells are more difficult to manage thermally, and they contain more electrolyte per individual unit.

There are a number of ways to mitigate the effects of flammability. One method isolates the individual cells and shields them from one another and from air exposure. Such an approach would be heavy, bulky and costly. Another approach addresses the issue at a chemical level. For example, one could choose an electrolyte solution that is relatively nonflammable [2]. Alternatively,

one could use a flame-retardant additive. Flame-retardants generally act by catalytically removing free radicals, especially atomic hydrogen, from the flame [7]. The additives that have been evaluated in the literature generally fall within one of two main categories, phosphorous-containing and halogen-containing compounds [8–13]. Phosphorous-containing compounds break down in the flame to form species such as PO₂, HOPO, and HOPO₂, which reduce H atom concentrations [14,15]. A typical catalytic cycle is



Note that the net result of the two reactions converts H and OH radicals into water, which tends to starve the flame of radicals: with lower radical concentrations, the flame cannot propagate. The cycle is catalytic because the PO₂ is regenerated and can therefore destroy more radicals on subsequent cycles. Similarly, halogens also catalytically scavenge H atoms [16,17].

When Li-ion batteries are abused by over charging, short-circuit, or puncture, electrolyte can be released into the air, generally in the form of aerosol droplets together with small amounts of partially reacted gases such as CO and H₂ [18]. Fig. 1 shows a cartoon depicting the combustion of evaporating aerosol droplets ejected from an abused cell [18]. Whether or not a flame actually ignites and propagates is determined by a variety of factors, including the local temperature, pressure, gas composition, and convection. Since materials do not easily burn as condensed phases, the aerosol droplets must evaporate before they can burn. In regions where the local concentration of electrolyte vapor is below the lean flamma-

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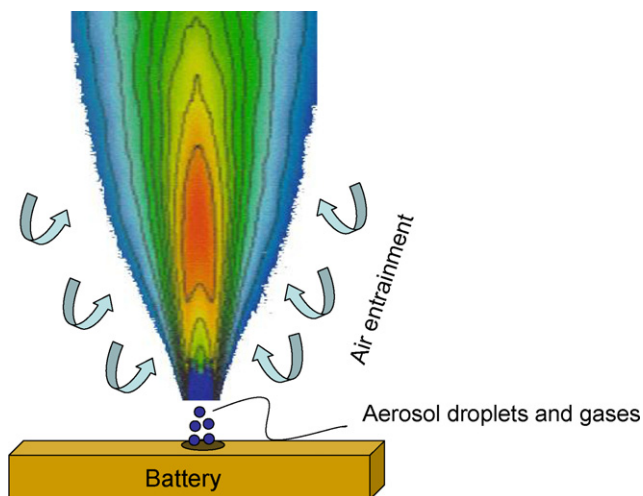


Fig. 1. Schematic drawing showing aerosol droplets, electrolyte vapor, and decomposition products exiting a puncture in the battery and entraining air to burn as a diffusion flame. Lines in the flame are contours of constant temperature.

bility limit or above the rich flammability limit, the mixture will not burn. The result is that combustion is possible only on a relatively thin (perhaps 1 mm thick or less) surface or surfaces where the air-fuel mixture ratio is between the flammability limits. An ignition source such as a spark or hot surface must then be present in or near that thin region in order to ignite the mixture.

These fundamental physical and chemical phenomena must be understood in order to find electrolyte solutions that maximize abuse tolerance without compromising other aspects of the technology. Detailed chemical kinetics models can be used for this purpose, and over the years they have evolved to the point that they are extremely successful in predicting flame speeds, temperature profiles, heat release rates, flame inhibition, and other properties. However, since electrolyte solvents and additives are not common fuel components, the chemistry of their combustion is usually not well understood and needs to be investigated. Researchers at Lawrence Livermore National Laboratory have developed detailed chemical kinetics models for many hydrocarbons and other compounds [19–21], including dimethyl carbonate (DMC) [22], which is a common electrolyte solvent for Li-ion batteries. Their chemical kinetics models have been used to address important issues such as flammability [23,24]. In addition, they have been used to study flame inhibition through the development of detailed chemical kinetics models for organophosphorus flame inhibitors such as dimethyl methyl phosphonate (DMMP) and trimethylphosphate (TMP) [14,15]. These compounds, among others, have been considered as additives to electrolyte solvents to improve safety [7,8,25–27]. In this paper, we provide initial calculations that show that the flammability of carbonate solvents in general differs fundamentally and substantially from that of comparable hydrocarbons. In addition, we will see that

there are significant flammability differences among the carbonate solvents.

The purpose of this paper is to identify key combustion properties that will allow evaluation of electrolyte solvents in terms of their relative flammability and combustion intensity. We are not at this point trying to predict, for example, thermal runaway in a full Li-ion cell. However, by using the sort of analysis shown below, we can quickly evaluate electrolyte solvents in terms of their relative suitability for use when flammability is critical.

2. Analysis

A model describing the flame shown in Fig. 1 requires thermochemical properties such as the heat of formation, heat of vaporization, and heat capacity of the relevant species (solvents, electrolytes, additives, combustion intermediates), as well as their transport properties. In addition, a mechanism that includes all of the important chemical reactions together with their associated rate constants is necessary. The required chemical kinetics and thermochemical databases have been provided by the work of Glaude et al. [22] for dimethyl carbonate and are available at the LLNL chemical kinetic mechanism website [19].

The analysis then predicts a number of processes that are associated with the physical and chemical nature of such a flame. These processes include:

1. Heat and free radical transport: Transport of heat and free radicals produced by the flame into the unburned gas region initiates combustion reactions just ahead of the flame.
2. Laminar flame speeds: A flame will extinguish if its flame speed is too low, perhaps less than 5 cm per second [30], because heat and free radicals in the unburned gases ahead of the flame have time to diffuse away.
3. Adiabatic flame temperature: Because of the exponential dependence of reaction rate on temperature, a high adiabatic flame temperature (a theoretical temperature that ignores heat losses) leads to a much faster heat release rate.
4. Ignition energy: High minimum ignition energy can inhibit or prevent a flame from forming.
5. Heat release rate: The rate at which heat is released from a flame can control whether neighboring cells will ignite.
6. Flame inhibition: Flame inhibitors work by catalytically destroying H atoms and OH radicals in the flame. Their effectiveness depends sensitively on the local chemical environment.

Let us consider how some of the thermochemical properties of typical carbonate solvents compare to those of analogous hydrocarbons. Pentane and diethyl carbonate (DEC) each have five carbon atoms, but three of the carbon atoms of DEC are already partially oxidized. As a result, the amount of energy released by the complete oxidation (combustion) of DEC is substantially lower than that of pentane. Table 1 compares the heats of formation [28,29], of four carbonates (EC, DMC, PC, and DEC) with hydrocarbon analogs

Table 1
Thermochemical properties of carbonate solvents compared to those of hydrocarbons with similar numbers of carbon atoms.

	ΔH_{form} (kcal mol ⁻¹)	ΔH_{vap} (kcal mol ⁻¹)	ρ (g cm ⁻³)	ΔH_{comb} (kcal ml ⁻¹)	ΔH_{vap} (kcal ml ⁻¹)
Ethylene carbonate	-128	14	1.3	-4.1	0.21
Dimethyl carbonate	-138	9	1.1	-3.8	0.11
Propylene carbonate	-137	14	1.2	-4.8	0.16
Diethyl carbonate	-154	10	1	-5.0	0.08
Propane	-25	4.5*	0.6*	-6.7	0.06
Butane	-30	5.4	0.6	-6.3	0.06
Pentane	-35	6	0.6	-6.5	0.05

* At its boiling point.

(propane, butane, and pentane). There is a substantial difference between the heats of formation of compounds in the two groups, amounting to about $100 \text{ kcal mol}^{-1}$. As a result, carbonates typically have only about 2/3 as much combustion energy per milliliter as hydrocarbons. Perhaps more interesting is the variation among the carbonate solvents. For example, DEC has almost 30% more combustion energy per milliliter than DMC, primarily because of its two additional un-oxidized carbon atoms.

The fact that carbonates are strongly polar, while the analogous hydrocarbons are non-polar, also affects their relative flammability because polar molecules generally have a higher heat of vaporization.

Table 1 [28,29] shows that carbonates require typically 2–4 times as much energy per milliliter to vaporize as hydrocarbons. The vaporization of the aerosol droplets in effect extracts this energy from the system, cooling it and reducing the energy available to create a flame. Moreover, there is a substantial difference in vaporization enthalpy among the carbonate solvents. EC has twice the vaporization enthalpy per milliliter as DMC and more than twice the vaporization enthalpy per milliliter as DEC. In fact, the vaporization enthalpy for EC is 5% of the combustion enthalpy. A consequence of the increased energy associated with vaporizing EC as compared to ethyl methyl carbonate (EMC) has been observed in thermal abuse experiments of cells containing these solvents [18]. When the solvent was EC/EMC, EMC was reported in the gases vented from the abused cell, while EC was not.

Because carbonate solvents have lower combustion energies and higher heats of vaporization than analogous hydrocarbons, their heat release rates are substantially lower. We compared the heat release rates of carbonate solvents and analogous hydrocarbons in a counter flow diffusion flame. This flame mimics the mixing behavior that could be realized when carbonate solvent escapes from an abused battery into the surrounding air. In a counter flow flame, a flow of fuel is directed at a flow of oxidizer (N_2/O_2) and a flame forms in the region between the two flows. The flame properties can be calculated using a one-dimensional reacting flow code that solves the conservation of mass, momentum and species. The code that we used was the Chemkin opposed-flow flame simulator (OPPFS) [31]. To compute the flame properties, a database containing the relevant chemical reactions and their associated reaction rate constants are needed. Also, thermodynamic and transport properties of each species involved in the chemical reactions are required. For this purpose, we used the previously developed and validated databases for propane [32,33] and DMC [22]. The parameters in the calculation were set to match experimental conditions in [22]. Both fuel and oxidizer inlet streams were set at velocity of 10 cm s^{-1} and a temperature of 315 K. The molar composition of the fuel stream was 8% fuel and 92% N_2 and the oxidizer stream contained 39% O_2 and 61% N_2 . The fuel and oxidizer ports were set at 2 cm apart. To start the calculation, the OPPFS code provided an initial guess for the temperature, species and velocity profiles across the flame. Then the OPPFS steady-state solver iterated to find the final solution. The conservation equations were solved, including the energy equation, and the heat release and temperature profiles were computed. Fig. 2a shows the predicted heat release rate profiles for the propane and DMC flames, while Fig. 2b compares the predicted temperature profiles.

3. Results and discussion

In Fig. 2a, the peak heat release rate in the propane flame is about twice that in the analogous DMC flame, while the temperature profiles differ by only about 25%. This apparent anomaly comes about because temperature depends not only on the rate of heat release, but also on local chemical conditions. In this case, for example, the extra enthalpy generated by the propane flame is consumed

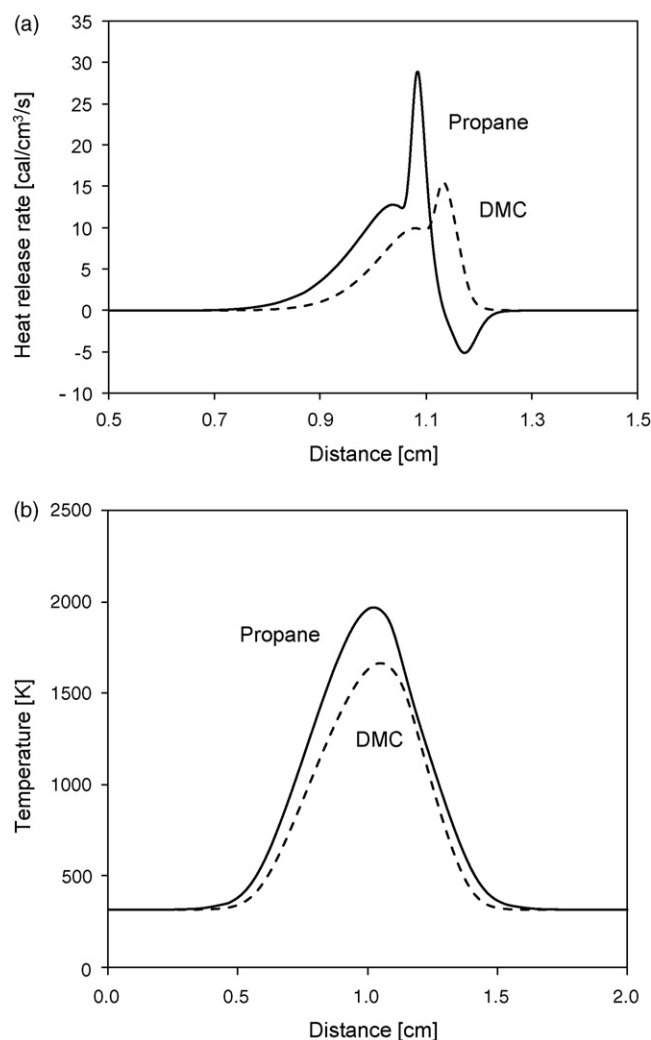


Fig. 2. (a) Heat release profiles across a counter flow diffusion flame. Fuel enters from the right-hand boundary and the oxidizer (O_2 and N_2) from the left-hand boundary. The calculations were performed at the experimental conditions of [22]. For the propane case, the DMC in the fuel flow was replaced by propane. (b) Temperature profiles for the same flame.

primarily in creating high energy radical species rather than in heating the gases. Thus, temperature is not a good measure of the *total* energy—temperature plus “chemical energy”—available to ignite a neighboring cell. (A gas of cold hydrogen atoms will more readily cause ignition than a gas of hot argon atoms.) In the case of Fig. 2, we see that a propane flame would be much more likely to ignite a neighboring Li-ion cell than an analogous DMC flame.

There have been a number of experiments carried out to determine the overall flammability of particular cell chemistries and geometries. In some cases cells are heated until they rupture, and the gases expelled are subjected to one or more sparks to determine if they ignite [18]. Based on the picture in Fig. 1, we see that if the sparks happen to physically overlap only regions that are above the rich flammability limit or below the lean flammability limit, the gases will not ignite, even if they are intrinsically highly flammable. On the other hand, if the sparks happen to physically overlap regions where the fuel–air mixture is flammable, the gases will likely ignite. (In fact, ignition should probably be treated as an intrinsically statistical event [34].) If the gases do ignite, the flame may extinguish if the local gas velocity is too great (e.g. in a highly turbulent environment.) Thus, proper interpretation of such experiments requires an understanding of the interaction between the chemical kinetics and

the physical mixing process of the expelled gases with the ambient air.

4. Conclusions

From the analysis provided here we make three observations.

1. Carbonate solvents have fundamentally and substantially lower heat release rates per unit volume than hydrocarbons.
2. There is a significant difference in the combustion energies and heats of vaporization among carbonate solvents. We would expect to find similar differences in other properties related to their flammability. Flame speed, ignition energy, and heat release rate should play a role when choosing solvents if flammability is of concern.
3. Heat release rate profiles that can be obtained from calculations are more useful than temperature profiles in comparing electrolyte solvents for their ability to ignite neighboring cells.

We expect that future fundamental combustion studies will lead to predictions of the ignition energy, flame speed, and heat release rate of various electrolyte mixtures as well as the effectiveness of flame-suppressing additives.

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