BLEVE, or no BLEVE, that is the question – On the superheat limits of solvents commonly used in Li-ion batteries

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Abstract

The thermodynamic superheat limits of five solvents commonly used in Li-ion batteries are calculated using the Peng-Robinson equation of state. The superheat limit of a two-component solvent mixture is also estimated using the generalized corresponding states principle. The superheat limit theory is used to disuss potential occurrence of BLEVE (boiling liquid expanding vapor explosion) during a thermal runaway of a Li-ion battery.

Keywords: BLEVE, equation of state, Li-ion battery, superheat limit, thermodynamics

Introduction

Nowadays, high-energy-density Li-ion batteries are ubiquitously used as rechargeable power sources in portable electronic devices, personal e-mobility devices, power tools, small appliances, other electronic gadgets, electric vehicles, and energy storage systems. Electrolytes commonly used in Li-ion batteries are non-aqueous solutions in which lithium hexafluorophosphate salt ($LiPF_6$) dissolved in combinations of linear (dimethyl carbonate DMC, ethyl methyl carbonate EMC, diethyl carbonate DEC) and cyclic (ethylene carbonate EC, propylene carbonate PC) alkyl carbonates [1]. These organic electrolytes are flammable. Under abusive conditions, be it mechanical (e.g., impact, puncture), electrical (e.g., short circuit or overcharge), or thermal (e.g., heat exposure), or due to manufacturing defects, Li-ion batteries can be damaged and overheated, leading to thermal runaway and subsequently causing fire/explosion and emission of toxic combustion gases [2].

In a series of full-scale fire experiments using large-format Li-ion battery modules conducted in an ISO 9705 Fire Test Room by Huang et al. [3], explosion of the modules was observed during thermal runaways and

was alluded to the so-called BLEVE (boiling liquid expanding vapor explosion) event in passing without further discussion.

The purpose of this work is to explore the application of the concept of superheated liquid to try to answer the question whether BLEVE could potentially occur or not during a thermal runaway event of a Li-ion battery.

Superheat limit

Superheated liquid theory has been postulated to explain a BLEVE event in a series of articles by Reid [4−9]. A superheated liquid is a metastable liquid exists at temperatures beyond its saturation boiling point at the same pressure. The metastable state can be attained from isobaric heating or isothermal decompression. When the metastable state is reached, rapid phase transition occurs from liquid to vapor in this case.

From classical thermodynamic stability theory [10], the metastable state is defined on a $P - V$ phase diagram as

$$\frac{\partial P}{\partial V}\bigg|_{T,n} = 0 \qquad \text{(Eq. 1)}$$

where P, V, T, and n are pressure, volume, absolute temperature, and amount of substance, respectively. If an equation of state (EOS) for

the fluid is available, the *thermodynamic* superheat limit (T_{sl}), defined as the temperature at which Eq. (1) is satisfied, can be calculated. Alternately, one can estimate the so-called *kinetic* superheat limit based on kinetic theory models [9]. The superheat limit can also be measured using various techniques as described in [11]. Since the thermodynamic superheat limit is based on intrinsic thermodynamic stability criteria, it can only be approached but not be attained. Therefore, superheat limits measured experimentally or calculated using kinetic theory models are lower than their thermodynamic counterparts [9,11]. For our discussion, it suffices to use the thermodynamic superheat limit to elucidate the potential occurrence of BLEVE because they can be easily calculated using an EOS.

Since the Peng-Robinson EOS [12] has been used to correlate vapor-liquid equilibria for alkyl carbonate systems [13], we use the Peng-Robinson EOS to calculate the thermodynamic superheat limits of the five aforementioned pure solvents (DMC, EMC, DEC, EC, and PC). The Peng-Robinson equation of state is in the form of

$$P = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)} \qquad \text{(Eq. 2)}$$

where $a(T) = a(T_c)\alpha(T_r,\omega)$, $b(T) = b(T_c)$, $a(T_c) = 0.45724R^2 T_c^2 / P_c$

, $b(T_c) = 0.07780RT / P_c$, $\sqrt{\alpha} = 1 + \kappa(1 - \sqrt{T_r})$,

$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2$, $T_r = T / T_c$, $v = V / n$ is the

molar volume, R is the universal gas constant, T_c is the critical temperature, and ω is the acentric factor.

Table 1 summarizes the thermophysical properties of DMC, EMC, DEC, EC, and PC. The properties of DMC, DEC, EC, and PC are obtained from DIPPR [14], those of EMC are from NIST TRC [15], and the acentric factor is taken from Ref. [13]. Table 2 summarizes the thermodynamic superheat limits of DMC, EMC, DEC, EC, and PC calculated using Eq. (1) and Eq. (2).

Table 1. Thermophysical properties of the solvents.

	MW (kg/mol)	T_{nb} (K)	T_c (K)	P_c (Pa)	ω
DMC	0.0901	363	548	4.50 x 10^6	0.385
EMC	0.104	381	560	4.00 x 10^6	0.429
DEC	0.118	400	576	3.39 x 10^6	0.486
EC	0.0881	521	806	6.77 x 10^6	0.442
PC	0.102	515	778	5.41 x 10^6	0.450

Table 2. Calculated thermodynamic superheat limits at 0.101 MPa.

DMC	507 K
EMC	519 k
DEC	536 K
EC	748 K
PC	722 K

In addition to the thermodynamic superheat limits of the pure solvents, the superheat limits of various solvent mixtures also need to be examined since solvent mixtures are normally used in Li-ion batteries. If the binary interaction coefficients are available, the Peng-Robinson EOS can, in principle, be used to estimate the thermodynamic superheat limits of solvent mixtures. Instead, the method based on the generalized corresponding states principle (GCSP) and developed by Avedisian and Sullivan [16] is used to calculate the thermodynamic superheat limit of the mixtures. The method only requires the thermodynamic superheat limits of individual mixture components, and the thermodynamic

superheat limit of a mixture ($T_{sl,m}$) can be estimated using the following equation.

$$\frac{T_{sl,m}}{T_{c,m}} = \sum_i x_i \frac{T_{sl,i}}{T_{c,i}}$$ (Eq. 3)

In Eq. (3), the thermodynamic superheat limit ($T_{sl,i}$) of component i with the mole fraction x_i in the mixture is evaluated at the *same* reduced pressure ($P / P_{c,m}$) of the mixture, $T_{c,m}$ is the mixture critical temperature, and $P_{c,m}$ is the mixture critical pressure.

For illustration, the EC-DEC binary combinations are used as a representative solvent mixture used in Li-ion batteries. Table 3 summarizes the mixture superheat limits at various component concentrations and the critical properties of the mixtures at various concentrations of its components that were used to calculate the mixture superheat limits using the GCSP. The methods of Li [17]. Schick and Prausnitz [17], and Kreglewski and Kay [17] were used to estimate mixture critical temperaures, mixture critical molar volumes, and mixture critical pressures, respectively.

Table 3. Critical properties and superheat limits at 0.101 MPa of EC-DEC mixtures at various mole fraction x_i.

x_{EC}	x_{DEC}	$T_{c,m}$ (K)	$v_{c,m}$ (m³/mol)	$P_{c,m}$ (Pa)	$T_{sl,m}$ (K)
0.0	1.0	576	3.56 x 10⁻⁴	3.39 x 10⁶	536
0.1	0.9	589	3.31 x 10⁻⁴	3.52 x 10⁶	548
0.2	0.8	603	3.06 x 10⁻⁴	3.64 x 10⁶	561
0.3	0.7	619	2.82 x 10⁻⁴	3.80 x 10⁶	576
0.4	0.6	637	2.60 x 10⁻⁴	3.98 x 10⁶	592
0.5	0.5	657	2.39 x 10⁻⁴	4.20 x 10⁶	611
0.6	0.4	679	2.20 x 10⁻⁴	4.44 x 10⁶	631
0.7	0.3	704	2.05 x 10⁻⁴	4.77 x 10⁶	654
0.8	0.2	733	1.94 x 10⁻⁴	5.23 x 10⁶	680
0.9	0.1	767	1.90 x 10⁻⁴	5.90 x 10⁶	712
1.0	0.0	806	1.93 x 10⁻⁴	6.77 x 10⁶	748

BLEVE or no BLEVE

During a thermal runaway, the temperature and pressure inside a Li-ion battery will increase rapidly, causing sudden rupture of the battery or activation of the pressure relief valve that comes with the battery. According to the hypothesis proposed by Reid [8] and supported by very few small-scale experiments, for BLEVE to occur two conditions have to be met: (1) the depressurization of the hot liquid must be very rapid and (2) the temperature of the hot liquid must be above its superheat limit at 0.101 MPa.

For better illustration of BLEVE using the superheat limit theory, a single component solvent, say DEC, is assumed. The superheat limit of DEC at 0.101 MPa is 536 K from Table 2. Based on Reid's hypothesis [8], BLEVE or no BLEVE can be explained using Fig. 1, which shows the vapor pressure of DEC as a function of tmeperature obtained from DIPPR [14] and the superheat limit locus of DEC calculated using Eq. (1) and Eq. (2).
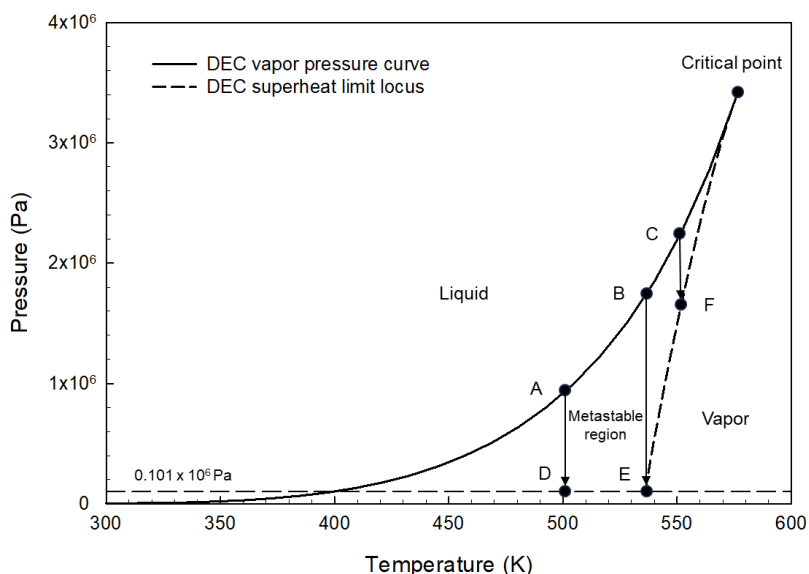

Fig. 1. Vapor pressure and superheat limit curves for DEC.

As the battery is being heated, the vapor pressure of DEC will increase thus causing pressure rise inside the battery. This heating process follows the vapor pressure curve in Fig. 1. If the internal pressure rise is high enough to cause sudden rupture of the battery, say point A, rapid isothermal depressurization to 0.101 MPa (point D) would not trigger BLEVE because the temperature of the hot DEC is below its superheat limit at 0.101 MPa. On the other hand, if rupture occurs at point B followed by rapid isothermal depressurization to point E, BLEVE is likely to occur.

If rupture occurs at point C, rapid isothermal depressurization to the pressure at point F, without reaching 0.101 MPa, would trigger potential BLEVE since the superheat limit locus which demarcates the meta-stable state of the superheated liquid has been attained. Beyond point F, rapid phase transition from liquid to vapor will occur. As pointed out by Reid [8], the transition from point B to point E results in higher intensity potential of BLEVE than that from point C to point F.

Similar reasoning about the potential occurrence of BLEVE, in principle, can be applied to solvent mixtures. In this case, the superheat limit of mixture, which is a function of mixture component concentrations, needs be considered (as illustrated in Table 3). Explantion of the BLEVE potential occurrence using plot similar to Fig. 1 becomes more challenging and less straightforward due to the complexity of mixture phase diagram, which now includes the mixture component concentrations.

The above discussion does not take into account the role of the $LiPF_6$ salt in the electrolyte solution. Although the dissolved salt in the solvent mixture would change the superheat limit of the neat solvent mixture, the same reasoning, rapid depressurization of the hot electrolyte solution with temperature above its superheat limit at 0.101 MPa, should still hold.

Another likely scenrio

During thermal abuse and runaway, sudden rupture of the battery or activation of the pressure relief valve that comes with the battery could eject flammable gases and aerosolize the liquid electrolyte solution to liquid droplets. Since the electrolyte solution is flammable and if the environment near the aerosol is hot enough, the droplets could be ignited and burned as a spray flame.

For solvent mixtures, another likely scenario which may give rise to the appearance of a mini-explosive event is also postulated. If the ejected mixture electrolyte droplets are ignited and burned, a phenomenon, known and observed in the combustion of multi-component droplets under certain conditions, is micro-explosion [18,19]. The superheat limit theory has also been used adequately to explain why liquid droplets with certain mixture concentration do or do not micro-explode during combustion; this could potentially provide a means to tailor the selection of solvent mixture concentrations to lessen fire hazards by suppressing droplet micro-explosion. However, there could also be potential trade-offs since it may be possible that solvent mixture concentrations optimized for mitigating micro-explosion may not be optimized for battery performance.

Conclusions

So, go back to the question, BLEVE or no BLEVE. If the superheat limit theory holds true, then the answer is "it all depends on when the battery

ruptures (i.e., how hot the electrolyte solution gets before rupture) and how fast the hot liquid depressurizes." Like any other theories, they need experimental validation.

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