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Short communication

Aggressive electrolyte poisons and multifunctional fluids comprised of diols and diamines for emergency shutdown of lithium-ion batteries

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HIGHLIGHTS

- Aggressive poisons arrest short circuit joule heating to shutdown battery function.
- Diols increase electrolyte viscosity upon mixing to slow charge-carrying ion motion.
- Diamines polymerize electrolyte solvent to rapidly turn solution into a solid mass.
- Diverse poison selections enable development of novel battery safety features.

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ABSTRACT

Electrolyte poisons comprised of diols and diamines are investigated for the intended function of exacerbating internal resistance in lithium-ion batteries upon short circuit failure, to quickly arrest uncontrolled joule heat generation in the earliest stages. The competing dynamics of powerful short circuit currents and electrolyte poisoning interactions are evaluated via simultaneous nail penetration and poison injection of LIR2450 format $LiCoO_2$/graphite 120 mAh coin cells. To forcibly increase electrolyte impedance, diols serve to hinder charge-carrying ion mobility by raising solution viscosity, while diamines disrupt solvent permittivity by rapidly polymerizing the ethylene carbonate solvent. Diamines demonstrate great potency, and are suitable for integration into battery cells within chemically-inert, breakable containers, rigged for release upon mechanical activation. Mixtures of 1,2-ethanediol and 1,2-ethanediamine show synergistic poisoning effects, decreasing peak temperature accrued by 70% when introduced simultaneously upon nail penetration. With the innate presence and abundance of diols and diamines in electric vehicle heat exchangers, they may be employed for multifunctional applications.

1. Introduction

Short circuit hazards potentially leading to thermal runaway have plagued energy-dense, flammable lithium-ion battery (LIB) chemistries since their outset [1,2]. In 1978, a patent was awarded for over-temperature battery deactivation with thermally-activated blocking agent and reaction agent poisoning mechanisms, intended to shut down non-rechargeable lithium thionyl chloride batteries in an emergency [3]. Blocking agents, typically chemically-inert phase change materials serving to physically impede ion-transport pathways, and reaction agents, chemicals hostile to the LIB that interfere with electrolyte or electrode function, are employed to slow or halt short circuit discharge and heat generation. Depending on the nature of the poisons, they may be encapsulated in inert materials rigged for release upon thermal activation of the container, or remain inert below a certain threshold temperature; the latter enabling direct incorporation of the agent into the LIB cell.

Various renditions of this shutdown feature concept have emerged to address the dangers of modern, rechargeable LIB chemistries. Uncontained blocking agents have been incorporated in several designs [4–6], with the trilayer shutdown separator being the most prominent example [7]. Encapsulated poisons have also attracted some interest, with focus primarily given to fire retardants [8–10]. Conversely, encapsulated reaction agents which actively interfere with specific electrochemical components have received relatively little attention [11].

Severe LIB shorting failures are of particular concern for electric vehicles and portable electronics prone to physical abuse [1,12]. As such, it is highly desirable that shutdown mechanisms be mechanically-

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activated to address heat generation in the earliest stages of short circuit progression. Breakable capsules filled with poisons designed to rupture in an impact event, such as an automobile collision, could fill the gap between primary protection structures and thermally-triggered safety features. Liquid alkanes and amines encapsulated in breakable containers have demonstrated some success in impact testing [13,14], but further investigation is warranted to identify more aggressive poisons to arrest heat generation at lower temperatures with reduced loadings, and provide diverse selections for enabling novel shutdown feature designs.

This study seeks to identify aggressive and potent reaction agent poisons capable of exacerbating electrolyte resistance to safely shut down short circuit discharge, early in the joule heating regime. Upon determining the effective poisoning options for modern electrolyte chemistries, further development of advanced shutdown systems can proceed to impart greater safety in LIB devices.

2. Experimental

Diol poisons: 1,2-ethanediol, 1,3-propanediol, 1,5-pentanediol; diamine poisons: 1,2-ethanediamine, 1,3-propanediamine; and carbonate solvent components: ethylene carbonate (EC), ethyl methyl carbonate (EMC) were obtained from Sigma Aldrich in their highest available purity. Pristine electrolyte, 1 M $LiPF_6$ EC:EMC (1:1 w:w), was obtained from BASF with Product Code Selectilyte LP50.

Viscosities of pristine electrolyte, diols, and electrolyte/diol mixtures were evaluated over the temperature range of 23 °C and 63 °C, using an NDJ-9S Digital Rotary Viscometer with #0 and #1 rotors. Temperature was controlled using a water bath on a hot plate. Ionic conductivity of pristine electrolyte, electrolyte/diol mixtures, and electrolyte/diamine mixtures were determined using a Yoke DDS-307A Conductivity Meter. Solutions of predetermined compositions were vigorously mixed, and conductivity measurements were taken via probe immersion exactly 1 min after mixing initiation. Reaction temperature for mixtures of EMC, EC:EMC (1:1 w:w), or pristine electrolyte solutions with 1,2-ethanediamine was monitored using a type-K gage-40 thermocouple immersed in the mixture, contained within a polypropylene test tube. Tested liquid volume was 2 mL.

Simultaneous nail penetration and poison injection tests were performed on LIR2450 format $LiCoO_2$/graphite 120 mAh coin cells, obtained from Xiamen TOB New Energy Technology. Closely following the procedure described in Ref. [14], the cells were cycled twice at 12 mA, fully charged to 4.2 V, disassembled in an argon filled MBraun LABStar glovebox, and reassembled into modified LIR2450 coin cell cases. The modified coin cell cases had 2 holes oriented on opposite sides. Poison volumes of 65 μL or 400 μL were injected through the holes into the cell, and nail penetration was subsequently performed within 1 s. Prior to shorting, the cells were outfitted with a thermocouple for measuring temperature, and affixed to a drill press assembly to initiate the event, as recounted in Ref. [15]. The reference nail penetration experiments followed identical reassembling procedure, but no fluid was injected.

The effective short circuit resistance dynamics (R_{eff}) in the poison injection experiments were compared with the internal resistance dynamics of the reference nail penetration scenario (R_{ref}), based on the measured heat generation rates ($\dot{q}_{\mathrm{gen,x}}$ where x= eff or ref). Details of the heat transfer evaluation methods and specific parameters characteristic of this cell testing system are enumerated in Ref. [15]. For both R_{eff} and R_{ref},

$$R_{\mathrm{x}} \propto \dot{q}_{\mathrm{gen,x}}^{-1} \tag{1}$$

3. Results and discussion

Modern-day, commercialized LIB electrolyte consists of a conductive inorganic lithium salt, most commonly $LiPF_6$, dissolved in a solution of cyclic carbonates, such as EC, and linear alkyl carbonates, such as EMC. To achieve high ionic conductivity and low resistance, the salt concentration is optimized for abundance and mobility within solution, characterized by high solvent permittivity and low viscosity. Efforts to manipulate the permittivity or viscosity of electrolyte through reaction agent poisoning, intended to subdue joule heating by disrupting ionic conductivity to forcibly exacerbate internal resistance, are discussed as follows.

Diols and diamines are proposed here for examination as reaction agent LIB electrolyte poisons. Diols are high viscosity fluids miscible with linear alkyl carbonates. Mixing them with electrolyte would hamper charge-carrying ion mobility, thus increasing resistivity. Primary and secondary amines have known poisonous character in electrolyte, reacting with the high dielectric constant EC electrolyte component via ring-opening mechanism [16]. This reaction mechanism has also been discussed as a synthesis route for polyurethane [17]. As low molecular weight primary diamines comprise a particularly high density of reactive, EC-passivating amine functional groups, they are expected to be potent poisons, serving to rapidly turn the liquid electrolyte into a nonconductive solid mass.

Mixing pristine electrolyte in equal volumes with α,ω-polymethylenediols $HO\text{-}(CH_2)_n\text{-}OH$ of n = 2, 3, and 5 methylene bridges increases viscosity by 1.7-fold, 2.4-fold, and 4-fold, respectively at room temperature (see Fig. 1). Simultaneously, the charge-carrier concentration is diluted. However, the degree of thickening incurred by addition of diols is reduced as temperature increases, both in terms of absolute viscosity and relative increase with respect to the pristine electrolyte reference at equivalent temperature. As such, employing diols as electrolyte poisons is likely to be most effective at low temperatures, but offer diminishing returns as shorting progresses and the generated joule heat accrues.

Upon mixing EC:EMC (1:1 w:w) solution with 20 vol% 1,2-ethanediamine, notable reaction heat is generated, compounding to gradually increase temperature over several minutes, suggesting ring-opening polymerization occurs. When mixed with pristine electrolyte, the reaction is more aggressive, resulting in a faster temperature increase. This suggests that $LiPF_6$ either participates in or catalyzes the EC/diamine reaction, also potentially interacting through competing solvation [18]. The diamine reaction also rapidly increases solution viscosity as higher molecular weight products are formed, in addition to starving the electrolyte of its solvent's permittivity (see Table 1). The reaction amasses an almost completely solid reaction product within 10 min.

As hypothesized, the introduction of diols and diamines suppresses the ionic conductivity of pristine electrolyte (see Fig. 2). Larger, more viscous diol species employed in high loadings have a greater degree of influence, with 1,5-pentanediol reducing ionic conductivity by 80% within 1 min when added at 50 vol%. In addition to increased viscosity, reduced salt concentration and lower permittivity imparted by mixing the lower dielectric constant poison also influences the resultant ionic conductivity. Conversely, 1,2-ethanediol increases the ionic conductivity of the mixture when added at less than 20 vol%, despite moderately raising viscosity and reducing ion concentration, likely due to moderate increase in permittivity by the higher dielectric constant poison. However, as 1,2-ethanediol loading further increases, viscous contributions and charge-carrier concentration reductions overwhelm conductive gains experienced at low diol loadings, hindering electrolyte performance. Upon introduction of the diamines, a large reduction in ionic conductivity of 95% is realized within 1 min when added at only 20 vol%, demonstrating the high potency of the EC/low molecular weight primary diamine poisoning interaction.

The competing short circuit discharge and reaction agent poisoning dynamics of these fluids are evaluated via simultaneous nail penetration and injection testing of LIR2450 cells (see Fig. 3). Upon diol injection, quick mixing dilutes the native electrolyte, increasing its viscosity to slow the ion transport between electrodes, thus suppressing the

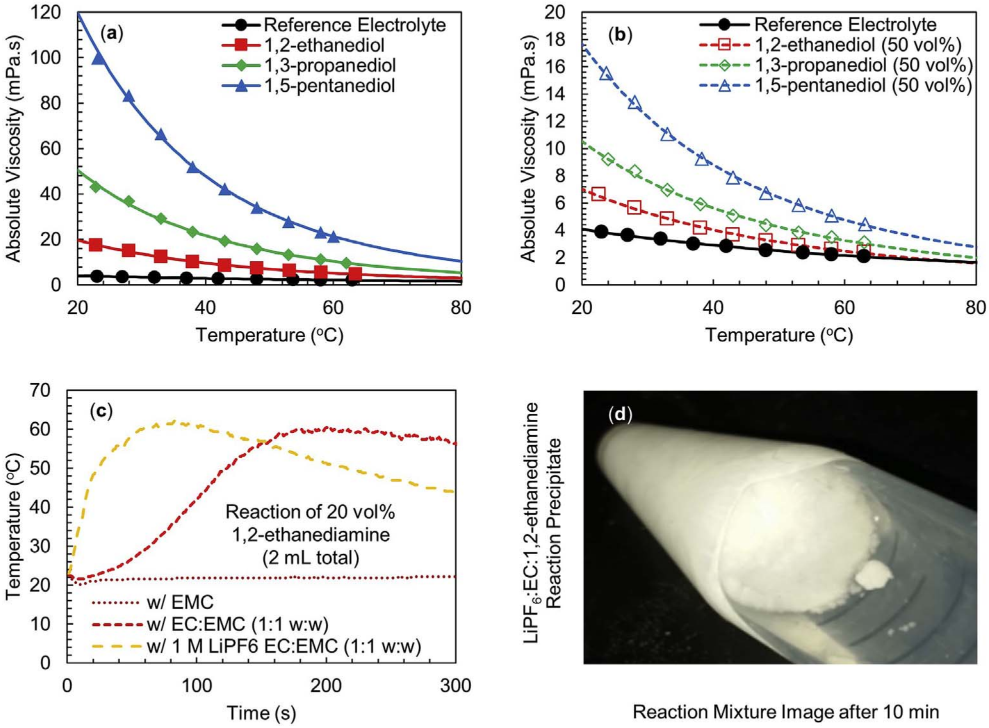

Fig. 1. (**a**) Viscosity of pristine electrolyte, diols, and (**b**) electrolyte/diol mixtures. (**c**) Reaction temperature of 2 mL mixture of electrolyte components with 20 vol% 1,2-ethanediamine and (**d**) image of solid reaction product after 10 min.

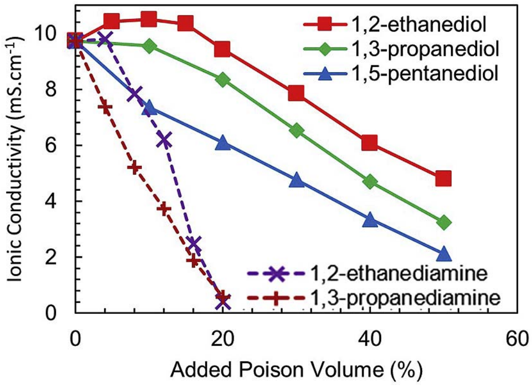

Fig. 2. Ionic conductivity of pristine electrolyte poisoned by diols and diamines of different volume ratios measured 1 min after mixing initiation.

discharge current and joule heating rates. The results show the influence of the tested diols increases sequentially with molecular size, as expected based on the viscosity and conductivity analyses. The 400 μL injection volume is about 15 wt% of all LIB cell components, excluding the cell case. This poison content produces an effective resistance increase to joule heating averaged over the first 3 min of shorting by 1.9-fold, 2.2-fold, and 2.7-fold for 1,2-ethanediol, 1,3-propanediol, and 1,5-pentanediol, respectively. For 1,5-pentanediol, active poisoning reduces the peak temperature accrued by 58% compared to the unmitigated reference nail penetration scenario.

For diamine poison injection, the effective resistance increase manifests slower than it does for the diols, but the ultimate magnitude is more significant once it takes full effect. The EC poisoning reaction proceeds gradually over time, decreasing permittivity and increasing the viscosity with the extent of reaction. The EC/diamine reaction also generates heat, which contributes to the observed temperature response. These inherent characteristics of diamine poison/electrolyte mixing delay the resistive contributions, but after the first 3 min of shorting, the effective resistance to joule heating is nearly 10-fold that of the reference event, essentially shutting down electrochemical function thereafter. Both tested diamines are potent, with little discernable difference observed in the nail penetration temperature response. The 65 μL diamine injection volumes, about 2.5 wt% cell mass, excluding the cell case, reduces peak temperature accrued by 62% with respect to the unmitigated shorting reference on average.

Diamines are effective reaction agent poisons in small loadings and could be considered for mechanically-breakable vessel encapsulation, without compromising a LIB cell's performance. Successful encapsulation of poisons in chemically-inert polyethylene/aluminum/polyester mylar containers for incorporation in LIB cells has been demonstrated without influencing cycling stability [14], incurring mass increase of 5% in large-format pouch cells [13]. When strategically placed in vacancies arranged in optimized locations throughout the electrode stack, release of the shutdown agents occurs upon impact to allow for quick interlayer access via diffusion throughout the entire LIB geometric area, acting to halt joule heating immediately upon damage. The main drawback of this approach is that low-density poisons, relative to the high-density electrode stack, can occupy appreciable volumes. As such, identification of these diamines for their merits as reaction agent poisons presents an opportunity to improve upon breakable-container safety feature designs, or aid in developing new poison delivery devices,

Table 1
Dielectric constants (ε) of electrolyte solvent components, diols, and diamines at 25 °C.

	EC:EMC (1:1 w:w)	EC	EMC	1,2-ethanediol	1,3-propanediol	1,5-pentanediol	1,2-ethanediamine	1,3-propanediamine
ε (25 °C)	33.6 [19]	95.2 [19]	3.5 [19]	40.3 [20]	34.4 [20]	25.6 [20]	12.9 [18]	10.9 [18]

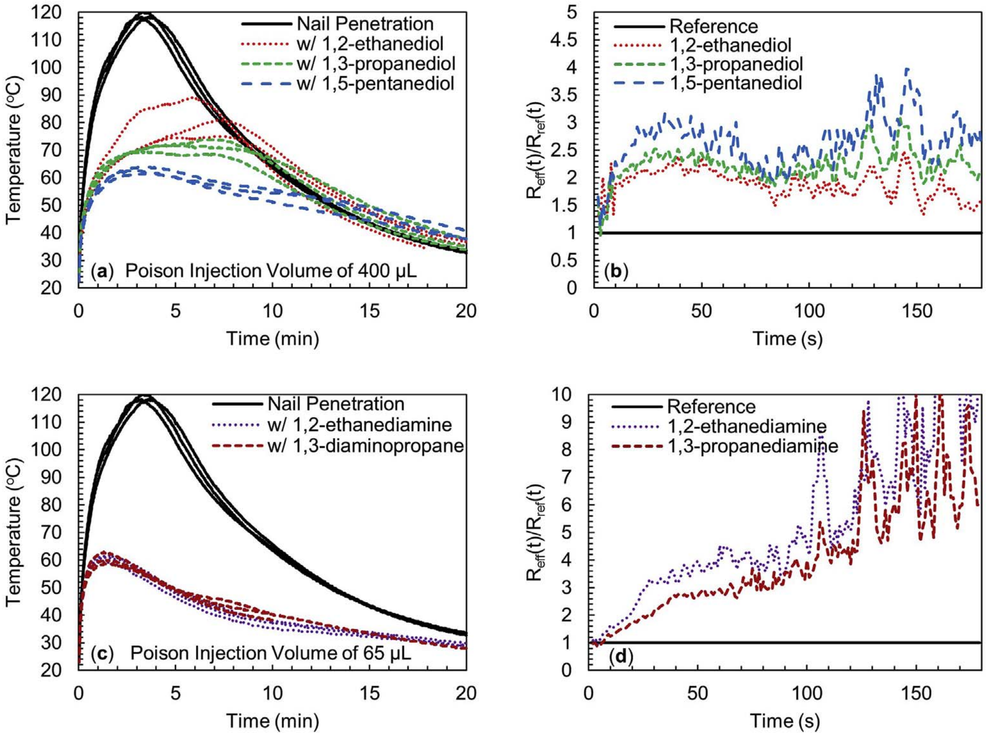

Fig. 3. Simultaneous nail penetration and poison injection temperature response with corresponding effective resistance increase to short circuit joule heating of LIR2450 cells with (**a**), (**b**) 400 µL of diols and (**c**), (**d**) 65 µL of diamines.

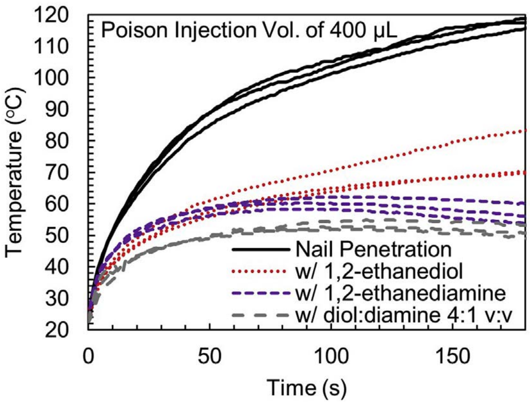

Fig. 4. Simultaneous nail penetration and poison injection temperature response of LIR2450 cells with 400 µL of 1,2-ethanediol, 1,2-ethanediamine, and 1,2-ethanediol:1,2-ethanediamine 4:1 v:v mixed solution.

providing more aggressive joule heating suppression capability and greater potency to minimize sacrifice in volumetric energy density for the sake of safety.

Diol poisons require high loadings to arrest joule heat generation and are not as effective at exacerbating resistance, so they are not feasible candidates for encapsulation within an LIB cell. However, diols have useful heat transfer properties and are inherent to many thermal management systems in large volumes, including those controlling LIB pack temperature in electric vehicles. Thermal management systems have previously been considered for functionalization as emergency thermal runaway mitigation devices to absorb heat, through incorporation of endothermic phase change materials [21], or LIB module flooding with high specific heat and fire retardant fluids [22]. Recognizing thermal management systems are innate vessels of diol fluid, as well as the merits of diols as electrolyte poisons, thermal management systems could also be considered for functionalization as active shutdown poisoning systems, without adding poisoning fluid mass to the vehicle system.

The most common diol used in thermal management fluids is 1,2-ethanediol. Thermal management fluids also incorporate corrosion inhibitors to protect the conduits through which they travel. Primary diamines are commodity chemicals with a wide range of uses, and have been considered for corrosion inhibitor applications for many decades [23]. Specifically, 1,2-ethanediamine has shown to be an effective corrosion inhibitor in modern thermal management fluid formulations, for automotive heat exchangers comprising 1,2-ethanediol [24].

While 1,2-ethanediol is the least effective of the reaction agent poisons discussed in this narrative, its resistive contributions are immediately apparent upon mixing with electrolyte. In contrast, 1,2-ethanediamine is very effective in exacerbating electrolyte resistance, but its resistive influence is delayed as it takes time for the poisoning reaction to proceed, such that increasing injection volume above 65 µL does not have an appreciable consequence in further temperature suppression. In simultaneous nail penetration and injection testing of LIR2450 cells with a 400 µL injection volume of 1,2-ethanediol and 1,2-ethanediamine mixed in a 4:1 v:v ratio, it is demonstrated that a mixed solution of the two fluids is more effective at suppressing joule heating than either of them individually (see Fig. 4). Peak temperature accrued is reduced by 70% of the unmitigated reference value, and time to reach peak temperature is delayed by about 25% with respect to pure diamine injection.

Given that both diol and diamine fluids demonstrate efficacy as reaction agent poisons for LIB shutdown, and exhibit both usefulness as well as abundance in fluid formulations characteristic of thermal management systems, they could be considered for advanced safety feature device designs. For example, battery management and thermal management systems are closely coupled with LIB cells in electric vehicle modules, with electrical and thermal sensing capable of control over pressurized thermal management fluid motion through the LIB pack [25]. One might envision that with greater integration of the thermal management system's fluid conduits with the LIB cells, a thermally or mechanically triggered device could guide the fluid into the LIB cells to actively shut them down, upon overtemperature, short circuit, or mechanical damage. Maintained outside of the LIB cells' electrochemical environments prior to the triggering event, the shutdown fluid is available in an emergency, without risking disruption of everyday performance. Novel safety features could be incorporated to protect vehicle occupants in emergency situations through multifunctional design, given knowledge of the electrolyte poisoning characteristics of diols and diamines.

This investigation demonstrates encouraging results in controlled testing of LIR2450 cells, serving to identify and vet the merits of poisoning candidates for further engineering development and validation in large-format cells, where joule heating dynamics and diffusion characteristics are more challenging, and abuse conditions are less predictable. The poisons discussed in this narrative are only useful if they are delivered effectively, and it is critical any containers or delivery devices hold the liquids in manner such that they do not prematurely disrupt electrochemical performance. Modifications to the LIB cell, such as electrode stack reorientation or vacancy formation, might also increase the efficacy of poisoning strategies. Device optimization is essential to maximize the safety margin, and knowledge of these chemical species presents opportunities to increase that margin in addressing joule heating during the earliest stages of short circuit failure, bridging the gap between traditional primary protection structures and thermally-activated failsafe features.

4. Conclusion

Diols and diamines are shown to be aggressive electrolyte reaction agent poisons capable of shutting down lithium-ion batteries in an emergency. By manipulating the permittivity and viscosity of electrolyte, ionic resistance is forcibly exacerbated to slow short circuit discharge and corresponding joule heating kinetics, to curb temperature accruement in a short circuit event. Diamines demonstrate particularly aggressive behavior and potency associated with an ethylene carbonate passivation reaction, elucidating their suitability for encapsulation within the battery cell, to be rigged for release in mechanical-abuse-activated scenarios. Diol and diamine mixed solutions show synergistic effects in simultaneous nail penetration and poison injection experiments of battery cells. Recognizing their merits as thermal management fluids and corrosion inhibitors, multifunctional applications may be feasible with modification of the battery management systems inherent to electric vehicles as advanced safety features.

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