



Short communication

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

Daniel J. Noelle^a, Yang Shi^a, Meng Wang^b, Anh V. Le^b, Yu Qiao^{a,b,*}^a Program of Materials Science and Engineering, University of California – San Diego, La Jolla, CA, 92093, USA^b Department of Structural Engineering, University of California – San Diego, La Jolla, CA, 92093, USA

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 LiCoO₂/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-

* Corresponding author. 9500 Gilman Drive, MC 0085, University of California - San Diego, La Jolla, CA, 92093-0085, USA
E-mail address: yqiao@ucsd.edu (Y. Qiao).

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 LiPF₆ 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 LiCoO₂/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 ($\dot{q}_{\text{gen},x}$ where $x = \text{eff or ref}$). 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} ,

$$R_x \propto \dot{q}_{\text{gen},x}^{-1} \quad (1)$$

3. Results and discussion

Modern-day, commercialized LIB electrolyte consists of a

conductive inorganic lithium salt, most commonly LiPF₆, 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 -poly-methylenediols HO-(CH₂)_n-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 LiPF₆ 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

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