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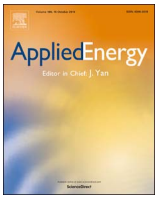


Internal resistance and polarization dynamics of lithium-ion batteries upon internal shorting

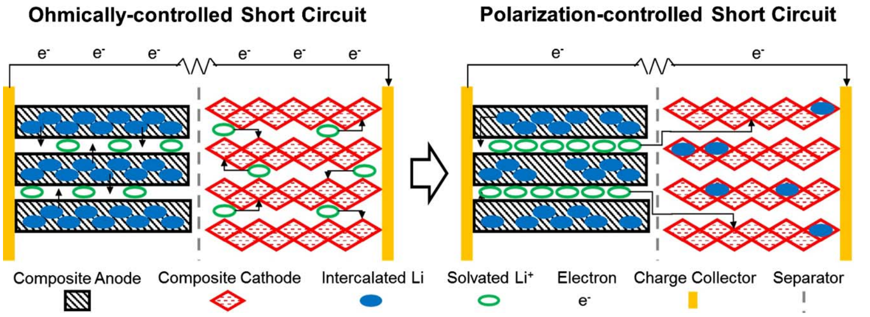
Daniel J. Noelle[a], Meng Wang[b], Anh V. Le[b], Yang Shi[a], Yu Qiao[a,b,*]

[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

- Understanding resistive dynamics informs thermal runaway mitigation strategies.
- Internal resistance at high discharge rates is dynamic and nonlinear.
- Electrical resistances dictate short circuit current in crucial first seconds.
- Rapid polarization depletes lithium-ion presence in electrolyte of cathode region.
- Ionic resistances throttle short circuit heating rates upon cell polarization.

GRAPHICAL ABSTRACT



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ABSTRACT

Internal resistance and temperature measurements are made for LIR2450 format $LiCoO_2$/graphite 120 mA h coin cells upon abusive discharge conditions. The dynamic contributions of electrical and ionic resistances to joule heat generation are investigated in the earliest stages of battery failure. It is shown that while ohmic, primarily electrical resistances initially dictate the joule heating rates, polarization, primarily ionic resistances become dominant as time progresses. Ionic conductivity and resistance of $LiPF_6$ salt in ethylene carbonate/ethyl methyl carbonate solvent are examined through concurrent concentration, viscosity, and temperature measurements to elucidate the intricacies of electrolyte polarization. Comparative analysis suggests that upon polarization at high discharge rates, resistance is concentrated in the electrolyte within the cathode region due to rapid depletion of lithium-ions available to facilitate charge transfer. Expected consequences are corroborated in external shorting and nail penetration experiments. The findings are used to predict how a cell would respond if electrical or ionic resistances are exacerbated upon shorting, so as to identify effective thermal runaway mitigation strategies.

1. Introduction

Lithium-ion batteries (LIB) carry safety risks inherent to their energy-dense chemistries and flammable components, which are of notable concern due to complications associated with thermal runaway [1,2]. LIB safety is particularly important for cells and modules in electric vehicles, which are prone to physical abuse in collision events [3,4]. When short circuit joule heating causes temperature to accrue to a critical point between 110 °C and 150 °C in high capacity cells [5], cascading exothermic electrochemical reactions and chemical decompositions compound to accelerate temperature increase, which can reach more than 500 °C in a matter of seconds [6]. These conditions lead to electrolyte ignition and possibly unit explosion [7]. Reported battery failures have gained the attention of both academic and

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

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Nomenclature

A	ionic conductivity relation proportionality constant (S·Pa·s·m^{2}·mol^{-1}·K^{-1})
c_p	effective system heat capacity (J·g^{-1}·K^{-1})
C	lithium-ion concentration of electrolyte (mol·m^{-3})
C_0	lithium-ion concentration of unpolarized electrolyte (mol·m^{-3})
$\overline{C}_i$	average lithium-ion concentration of electrolyte in select region (mol·m^{-3})
E_A	activation energy of electrolyte viscosity (J·mol^{-1})
$E_{A,1}$	first parameter defining activation energy of electrolyte viscosity (J·mol^{-1})
$E_{A,2}$	second parameter defining activation energy of electrolyte viscosity (m^{3}·mol^{-1})
h^*_{dis}	heat dissipation frequency coefficient (Hz)
I_x	current rate for select discharge type (A)
m	cell system mass (g)
$\dot{q}_{dis}$	rate of heat dissipation (W)
$\dot{q}_{gen}$	rate of heat generation (W)
$\dot{q}_{net}$	net rate of heating/cooling (W)
Q	charged current capacity (A·h)
$r_{p,i}$	specific resistance of polarized electrolyte in select region (Ω)
R	ideal gas constant (J·mol^{-1}·K^{-1})
R_{elec}	resistance of electrolyte (Ω)
R_{ext}	external shorting resistance (Ω)
R_{int}	internal resistance (Ω)
R_o	ohmic resistance (Ω)
R_p	polarization resistance (Ω)
$R_{p,i}$	polarization resistance contribution of electrolyte in select region (Ω)
t	time (s)
t_{ini}	initial time of heat dissipation frequency coefficient measurement interval (s)
T	temperature (K)
T_0	ambient temperature (K)
V_{emf}	electromotive force (V)
V_t	terminal voltage (V)

Greek

δ_i	thickness of select region (m)
ε	permittivity of electrolyte solvent
ε_1	first parameter defining permittivity of electrolyte solvent
ε_2	second parameter defining permittivity of electrolyte solvent (K^{-1})
μ	viscosity of electrolyte (Pa·s)
μ^*	reference viscosity of electrolyte (Pa·s)
μ^*_1	first parameter defining reference viscosity of electrolyte (Pa·s)
μ^*_2	second parameter defining reference viscosity of electrolyte (m^{3}·mol^{-1})
σ	ionic conductivity of electrolyte (S·m^{-1})

Subscribe

i	select region, =a, c, or s
x	select discharge type, =app or sc
a	anode
c	cathode
s	separator
app	applied
sc	short circuit

industrial researchers to identify the causes, and to understand the progression of events that beset thermal runaway. These objectives serve to minimize risk by informing responsible day-to-day operation and aiding in development of effective failsafe technologies [8,9].

Risks associated with joule heating and electrochemical degradation during normal operation are well controlled in electric vehicles. Intelligent battery management system (BMS) algorithms [10,11] coupled with efficient battery thermal management system (BTMS) designs [12–14] ensure that the temperature throughout the battery pack is maintained in a suitable temperature range below 40 °C at all times. Additionally, the state of health is constantly monitored by the onboard computer system [15,16], which identifies any hazardous conditions to be addressed [17]. As a result, thermal runaway is of minor concern under normal operating conditions. However, vehicles may still catch fire in accidents if the battery pack is physically damaged. Collisions can cause the formation of short circuit discharge pathways which the BMS cannot control, nor the BTMS can manage. The battery pack is afforded extensive protection to minimize the possibility and extent of damage, but it is acknowledged that unmitigated damage may still take place in certain circumstances [4,9].

The exothermic decomposition events encompassing thermal runaway have been extensively studied [5,6]. By understanding the nature of how heat generation accelerates as temperature rises, thermal runaway mitigation technologies can be incorporated within the cells and modules to halt temperature increase, and specialized battery materials can be employed to tolerate excessive temperature [9]. Most failsafe features are thermally triggered, taking effect at a specific temperature above the normal LIB operating range ($>$ 80 °C), but below the critical acceleration point ($<$ 150 °C) [8,18–27]. They typically involve phase change materials or positive temperature coefficient materials that slow down temperature increase upon activation. Such technologies are capable of handling short circuits of moderate power, but may fail to manage severe short circuits in large-format LIB cells. In the event of a vehicle crash, it is preferable that LIBs have inherent failsafe features that take effect in the joule heating regime, irrespective of temperature and immediately upon shorting, but work in this area is uncommon [28–31].

In severe short circuit scenarios, joule heating dynamics are dictated by the internal resistance of the LIB cell [32–34]. The sum of the resistive contributions from a multitude of internal components limit the discharge current and consequent temperature increase [35,36], which in turn alters the resistance of those components in various ways. The resistive influence of fast kinetic processes manifest rapidly. Those processes include charge transfer between the electrode and electrolyte, as well as electron movement through the composite electrode and across current collector interfaces [37]. Resistive effects of slower processes, like charge-carrying ion diffusion in electrolyte and solid-state ion diffusion within active electrode particles, become apparent on longer timescales [38]. Initially, the resistive kinetic contributions are more significant, such that the short circuit is ohmically-controlled, but as time progresses and resistive diffusion phenomena become dominant, the aggressive discharge transitions to be polarization-controlled. Surveying those resistive phenomena in the diverse network of sensitive materials organized in unwieldy and inaccessible arrangements within an LIB cell is difficult, particularly when engaged in fast, dynamic electrochemical and chemical processes [34,39].

Many experimental studies concerning severe short circuit failure have been performed on large-format LIB cells [34–36,40–44]. These tests produce fast temperature increases that often result in fire or explosion. Such study is critical to understanding the dangerous heat transfer propagation characteristics within cells and through modules. However, they do not offer systematic information concerning the