Method of evaluating relative safety of porous electrode/ electrolyte combinations to spot heating

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Abstract

Thermal abuse situations involving batteries can conveniently be classified into two broad categories, one involving relatively uniform heating of the battery contents and the other involving highly localized heating inside a battery. Reliable prediction of battery behaviour during abuse is difficult to do by modelling and often quite expensive to do empirically. The relative safety of systems exposed to uniform heating can be quantified using hot box or accelerating rate calorimeter techniques. Here, a simple, inexpensive method of quantifying the relative safety of systems exposed to local heating is discussed. Laboratory size batteries of coin-cell format are reproducibly exposed to localized heating at a container/porous electrode interface using conventional spot welding equipment. Some electrode/electrolyte combinations used in lithium-ion-type batteries were evaluated in this manner. In particular, the effects of state of lithiation on and differences between $LiCoO_2$ and $LiNiO_2$ electrodes were studied.

Keywords: Safety; Spot heating; Lithium batteries; Electrode/electrolyte interface; Porous electrodes

1. Introduction

The safety characteristics of commercial batteries are generally expressed in terms of behaviour under abusive conditions designed to simulate possible real world scenarios. Many of these conditions effectively involve thermal abuse of the battery in one way or another. Generally speaking, thermal abuse situations involving batteries can conveniently be classified into two broad categories, one involving relatively uniform heating of the battery and the other involving highly localized heating inside a battery. Examples of the former category include abuse via external short circuit, oven exposure, overcharging (if generation of heat is the prime concern), etc. Examples of the latter include abuse via internal short circuit, nail penetration, crushing, dendrite formation (as with some rechargeable batteries that involve the plating of species), etc.

Reliable prediction of battery behaviour during abuse is difficult to do by modelling. The actual behaviour in an abuse situation often depends on engineering factors (eg., battery size, electrode thickness or porosity, etc.) as well as the properties of the electrochemical system employed. Thus, often during the early developmental stages of a battery product, empirical abuse data must be obtained from test batteries of a similar

size and design to that of the intended product. This type of evaluation, especially if it involves significant numbers of tests for statistical purposes and/or design iterations, can be quite expensive and prohibitive. It is therefore desirable to be able to quantify safety characteristics in some meaningful way at a laboratory scale, in a similar way to how fundamental performance characteristics can be determined in small laboratory batteries.

With regards to thermal abuse involving uniform heating, the relative safety of the battery system, in particular of lithium battery systems, can be quantified using hot box [1] or accelerating rate calorimeter [2] techniques. The latter technique is particularly useful in that meaningful information can be obtained using small amounts of battery material without the need for preparing prototype battery products. Previously it was noted that lithium-ion-type coin cells employing $LiNiO_2$ electrodes could be made to vent or explode when external tabs were spot welded on to the cell container [3]. Relative safety of such batteries to this type of spot heating abuse as a function of $LiNiO_2$ surface area could be determined to some extent.

The principle of performing spot welding abuse on coin cell size batteries was adopted and modified such that more reproducible results could be obtained and

such that the relative safety of similar battery systems exposed to local heating could be determined. Some testing of lithium-ion systems employing Li_xNiO_2 or Li_xCoO_2 cathodes and dimethoxyethane (DME) or diethyl carbonate (DEC) based electrolytes as a function of x was performed.

2. Experimental

The coin cell batteries employed as test vehicles for this work are depicted in the exploded view of Fig. 1. Electrode tablets were prepared using active electrode materials in powdered form (typically about 20 μm particles), KS series graphite (product of Lonza) or Super S carbon black (product of Ensagri) as conductive dilutants and poly(vinylidene fluoride) (PVDF) as a binder. The active cathode materials used were either $LiNiO_2$ prepared as described in Ref. [4] or $LiCoO_2$ (from FMC). The active anode material used was MCMB#10 (mesocarbon microbead carbon product of Osaka Gas, Ltd.).

To produce dry electrode blends, first the PVDF binder was dissolved in n-methylpyrollidinone (NMP) solvent. Then the appropriate active material and Super S solids were added, followed by a thorough mixing. This resulting slurry was then spread on a heated plate in a fumehood to dry. Manual mixing with a spatula was performed during the drying stage to prevent significant segregation of the binder. The dried blend was then collected and loosely sieved to break up agglomerates. Puck shaped tablets were then created by pressing a weighed amount of dry blend in a conventional cylindrical die of inner diameter 17.4 mm.

The electrode formulations used were as follows:

- cathode: 1 part $LiNiO_2$ or $LiCoO_2$ plus 0.05 parts KS6 graphite plus 0.06 parts PVDF by weight

- anode: 1 part MCMB#10 plus 0.02 parts Super S plus 0.10 parts PVDF by weight

The tablets used had the following physical characteristics:

- cathode: weight 496 ± 4 mg, thickness 593 ± 20 μm
- anode: weight 364 ± 4 mg, thickness 997 ± 20 μm

(Upon release from the die after pressing, both types of tablet expand slightly in diameter). The mole ratio of cathode to anode in these cells was therefore about 1:1 (moles $LiNiO_2$ or $LiCoO_2$ to moles carbon expressed as C_6).

Two different electrolyte formulations were used in these experiments. These were solutions prepared by adding 1 M $LiPF_6$ salt to either 1 l of a propylene carbonate/dimethoxyethane (1/1 by volume) solvent mixture, henceforth denoted as electrolyte 'DME based' or to 1 l of a propylene carbonate/diethyl carbonate (1/1 by volume) solvent mixture, henceforth denoted as electrolyte 'DEC based'.

2325 size (23 mm diameter, 2.5 mm thick) coin cells were constructed in a conventional way using Celgard® 2502 microporous film as the separator, a 304SS cap at anode potential, and a Shomac 30-2 (special oxidation resistant grade) stainless-steel case at cathode potential. Cells were then charged slowly (over a period of approximately 100 h) at 21 °C such that a specific value of x in the cathode material Li_xCoO_2 or Li_xNiO_2 was obtained.

The apparatus used for performing external spot welding abuse on the preceding coin cells is shown schematically in Fig. 2. A conventional a.c. power supply, in this case a 2.5 KVA, 30 cycle unit from Ewald Instruments Corporation, supplied energy to an indirect, parallel gap, force-fired weld head, Model 127 from Unitek. For purposes of confirming the reproducibility of the energy applied to the test cells, a digital storage scope was used to monitor the weld current and voltage across the weld electrodes.
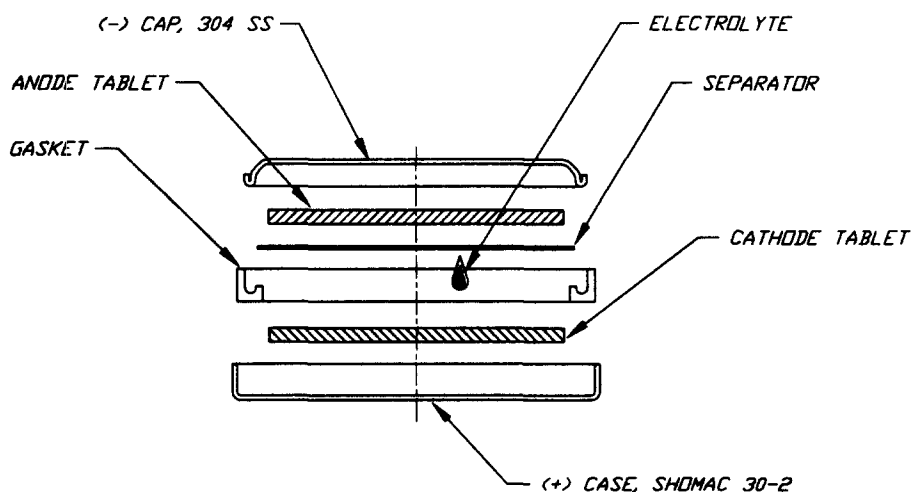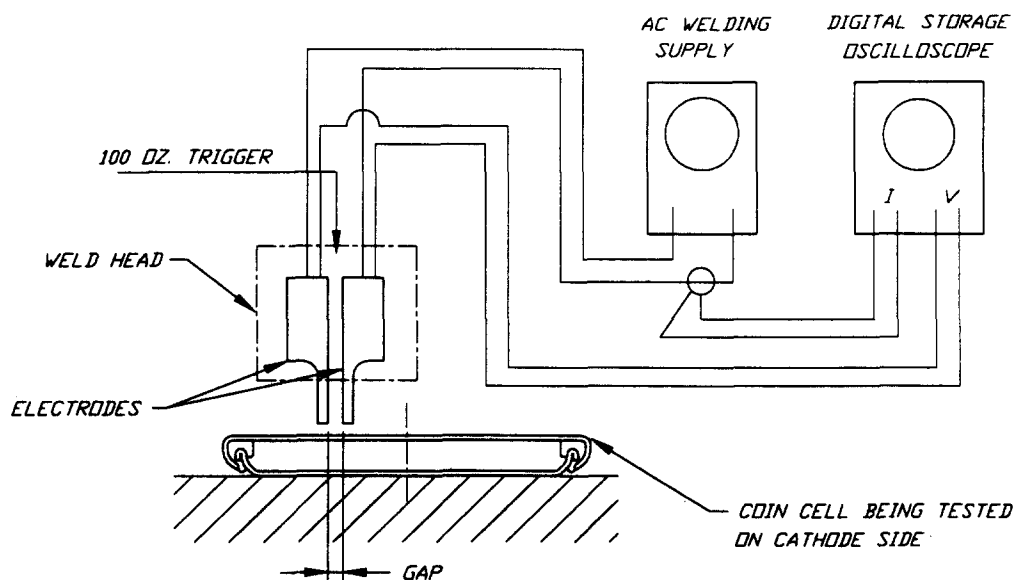

Fig. 1. 2325 Coin cell.

Fig. 2. Spot heating test apparatus.

Reproducible tests results could be obtained using this a.c. supply but not using a short pulse, capacitative discharge(CD)-type supply which was tried initially as the power source. The CD supply pulse width is of the order of milliseconds, and it was presumed that this very short time scale either led to non-uniform heat generation (possibly as a result of variable interface resistances) or was not long enough to reliably ignite a runaway reaction in the cell. The a.c. supply was set to run for 30 cycles at line frequency, i.e., 0.5 s, and thus was several orders of magnitude longer than the unsuccessful CD pulse and more in line with timescales similar to real world spot heating abuse. The magnitude of the a.c. pulse was varied to determine the relative sensitivity of the test cells to this type of spot heating abuse. A low safe starting value was chosen for an initial spot heating test. The setting was then increased in units of 2% of the full scale setting with corresponding additional spot tests usually until the cell vented or until the container was breached.

The electrode dimensions, gap, and applied force were all carefully controlled for purposes of reproducibility. Unitek electrodes were used that had a quadrant-shaped interface profile of radius 1.0 mm. This profile is maintained in principle with wear in the vertical direction as long as dressing of the electrodes is performed as necessary to maintain a flat contact surface. The gap was set at 0.32 mm and was reset after every cell venting or breaching of the cell container. This was necessary because, in the former instance, the violence of the venting usually moved the electrodes in their clamps, and, in the latter instance, in order to clean vented electrolyte off the electrodes. The weld head was set to fire at 100 oz applied force.

For most of the testing reported here, the waveforms of the current and voltage pulses were checked each time. The reason for this was simply that, for causes unknown at the time, the energy output of this specific apparatus clearly varied once for a given set of energy settings. In preliminary trials, the cathode side of five cells with $Li_{0.5}CoO_2$ cathodes (electrode weights and thicknesses differed from others tested) was spot weld tested until the containers of all were breached. (Thus, no venting occurred.) All containers were reproducibly breached at a 54% setting (but none at a 52% setting) on this occasion. Later however as shown in the data to follow, identical cell containers were reproducibly breached at a 34% setting. It was clear from waveform observations that something must have happened between these tests. However, unless otherwise indicated in the data to follow, given energy settings always gave similar waveforms. (Note, the actual energy applied at the electrodes did not increase linearly with %-setting based on the waveforms.)

Laboratory coin cells like those described here often bulge somewhat in the centres as a result of gas generation in the cell during use. The container thus can lift away from the tablet electrodes inside. Thus, the heat generated by a weld applied to such a bulge may not actually contact the electrode/electrolyte combination in question. For this reason, electrode contacts were made at points at radii about half that of the cell itself. Since the more energetic weld settings usually created visible damage of the container, fresh sites were chosen for every weld applied.

A fumehood is mandatory due to the violence of the ventings of this type of coin cell. Often, the cells would rocket 0.5 m and impact on the fumehood wall. Contents would either catch fire or at least glow red as combustion

Table 1
Summary of spot heating results for coin cell series with various porous electrode/electrolyte combinations

Cell series	Electrode tested	Electrolyte	Range of open-circuit voltage (V)	No. cells tested	Range of settings % full scale until event[a]	Event	Comments
1(a)[b]	$Li_{0.4}NiO_2$	DME based	3.92–3.93	10	38–42	Violent vent, combustion, smoke	Energy settings in series 1(a) and (b) do not correspond with those used in other series
1(b)	$Li_{0.6}C_6$	DME based	3.92–3.93	5	48	Red glow visible during weld: deep impression on cap but did not breach container; no vent	Container breaching occurred at 54% setting based on testing prior to series 1(a) and (b)
2	$Li_{0.4}NiO_2$	DME based	3.87–3.88	5	20	Violent vent, combustion, smoke	One cell test was started at 20% setting; thus actual event setting may have been lower
3	$Li_{0.4}NiO_2$	DME based	3.89	3	20	Violent vent, combustion, smoke	Cells first charged to $Li_{0.3}NiO_2$ then discharged to $Li_{0.4}NiO_2$
4	$Li_{0.3}NiO_2$	DME based	4.09–4.10	5	20	Violent vent, combustion, smoke	Same batch of cells as series 3 but never discharged
5	$Li_{0.5}CoO_2$	DME based	3.87–3.88	5	34	Container breached: no vent, minor puff of vaporized electrolyte	
6	$Li_{0.4}CoO_2$	DME based	4.03–4.04	5	26–30	Violent vent, combustion, smoke	Event occurred at 26% on three cells, 28% on one cell. Last cell did not vent on initial weld at 30%. As this seemed unusual, weld was repeated at 30% whereupon the cell vented
7(a)	$Li_{0.4}NiO_2$	DEC based	3.87–3.88	4	20	Violent vent, combustion, smoke	
7(b)	$Li_{>0.4}NiO_2$	DEC based	3.19	1	24	Violent vent, combustion, smoke	Low voltage cell

a Settings increased in units of two until event, except as noted in comments.
b The same cells were used for series 1(a) and (b) tests. After five reproducible results testing the cathode side to destruction, the remaining cells were tested by first welding on the anode side in a non-destructive manner (<54%) followed by a cathode side test.

took place. Significant quantities of smoke were always produced.

3. Results

A series of seven small batches of differing experimental cells were constructed and spot weld tested as described earlier. A summary of the results of this testing is given in Table 1. The range of power supply settings that produced a given event (either violent vent, breaching of container, or other) are shown for all cells tested. In series 1, the same cells were used to get results for both the cathode/electrolyte combination and the anode/electrolyte combination. The term '$Li_{0.6}C_6$' merely refers to the stoichiometry of the anode under the assumption that all the lithium extracted from the cathode is inserted into the MCMB. In fact, some of this lithium is actually irreversibly lost during this process and some presumably is inserted into the Super S. Also, the energy levels corresponding to specific power supply settings differ in series 1 from those of series 2 to 7. In series 7, one cell in the prepared batch had a significantly lower open-circuit voltage than its peers, probably as a result of an internal short.

4. Discussion

In general, the results obtained were quite reproducible. The one notable exception was perhaps the cell in series 6 that required two hits at 30% setting to achieve a violent vent. If tested in the absence of knowledge of results from its peers, a minimum of 32% would have been recorded.

Definite differences in sensitivity to this type of spot heating test could also be seen between different electrode/electrolyte combinations. For example, the $Li_{0.4}NiO_2$/electrolyte combinations consistently seemed more sensitive to spot heating than the $Li_{0.4}CoO_2$/electrolyte combination (series 2, 3, 7(a) versus series 6). In the only comparison available where the electrolyte type was changed, i.e., $Li_{0.4}NiO_2$/DME based (series 2) versus $Li_{0.4}NiO_2$/DEC based (series 7(a)), there was no noticeable effect on sensitivity.

The state of lithiation had a pronounced effect on sensitivity in the Li_xCoO_2/DME based combination. Violent venting was obtained when $x = 0.4$ (series 6), but venting could not be initiated when $x = 0.5$ (series 5). In the latter case, the spot heating was sufficient to melt and breach the cell container, implying temperatures of order of 1400 °C were present at the interface of case with the electrode. In the Li_xNiO_2/

electrolyte cases, there is a suggestion that for $x > 0.4$, there may be some improvement in sensitivity based on series 7(b). However, in the limited testing where x varied between 0.4 and 0.3, there was no effect on sensitivity (series 2, 3 versus series 4).

Series 3 was prepared to confirm that the manner in which x was obtained (i.e., via insertion or removal) did not have an effect on the results. However, since series 4 (from which series 3 was derived) also gave similar results, such a confirmation was not really accomplished in a satisfactory way.

It did seem clear that the sensitivity results could be determined on one electrode independently from the other one. (Compare series 1(a) to (b).)

Thus, although the results reported here are somewhat limited, the method described herein offers potential advantages for the scientist developing safe commercial battery systems. For instance, a lithium-ion commercial battery product based on $LiCoO_2$/coke electrochemistry is available that is resistant to crush abuse [5]. Now, for example, when initially considering whether the cathode in this product might be replaced by $LiNiO_2$, it is unclear what the effect will be on product safety. Thermogravimetric analyses on both materials [6] indicated that both are unstable upon heating in cases where $x < 1$, with oxygen being evolved as decomposition proceeds. Thus, batteries with either electrode may be hazardous upon heating since an oxidant and fuel (e.g., electrolyte, separator) are available. The results shown herein would suggest however that a similar battery using a $LiNiO_2$-based system could be less safe to spot heating.

Suggestions for further work would therefore include a determination of the safety behaviour of commercial-type batteries using both $LiCoO_2$ and $LiNiO_2$ cathodes to evaluate the usefulness of this method. Additionally, it would be of interest to exactly simulate the electrodes from known commercial batteries in the laboratory coin cell test vehicle. A 'sensitivity' for electrode/electrolyte combinations with known commercial safety characteristics might then be quantified in a relative manner and used as a benchmark. Other new electrode/electrolyte combinations under consideration could then be compared to these benchmarks. Perhaps useful predictions about relative safety to spot heating in commercial versions using the new combination might be made. Finally, what does the inability to ignite a violent vent in this laboratory-type test mean about the fundamental system safety in any size battery?

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