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Lithium sulfur battery nail penetration test under load

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ABSTRACT

Lithium batteries suffer from a number of safety concerns which limits their use in some applications. Nail penetration tests are used by the battery industry to compare the safety of different batteries during an incursion by a metallic object through a battery that physically violates the containment and locally damages the internal structure. For most lithium chemistries, such as mixed metal oxide or lithium iron phosphate cathodes, these tests result in rapid and dangerous failure. Lithium sulfur is an important next generation ultra-high energy density battery chemistry which is also inherently safer. Results are reported for nail penetration tests on 16 Ah lithium sulfur batteries showing how they heat up by less than 10 °C during a 10 min penetration and then cool down rapidly after removal of the nail. Results of a nail penetration test under load are also reported for the first time, showing how the battery was capable of continuing to provide 1.6 A (*C*/10) of current to an external load, with only a 1% drop in voltage. The results should be of interest for applications requiring ultra-high energy densities, improved safety, and continuous provision of power for a short period after damage, particularly military, aviation, portable electronics and automotive industries.

1. Introduction

Lithium sulfur (Li–S) is an important next generation battery chemistry due to the potential for ultra-high gravimetric energy densities (2600 Wh/kg theoretical) and the low-cost and abundance of sulfur. Li–S is the most mature of the ultra-high energy density battery chemistries, and is the closest to market. However, in order to improve them even further, research is focused on understanding and improving rate capacity, coulombic efficiency, self-discharge and capacity fade [1,2].

A major advantage of Li–S batteries is their inherent safety mechanisms. For low enough charging currents, Li–S cells are protected from overcharging via the polysulfide shuttle reaction, where polysulphides are transported between the two electrodes, and alternating reduction and oxidation reactions take place [3].

Nail penetration tests are used by the battery industry and battery users to compare the safety of different batteries during extreme events [4]. They attempt to simulate an incursion by a metallic conductive object through a battery, which physically violates the containment shell and locally damages the internal structure. The tests have been standardized around penetrating a battery with a steel nail at a certain rate and for a certain length of time. For chemistries currently favored in applications, such as mixed metal oxide or lithium iron phosphate, these tests normally result in rapid and dangerous failure, with temperatures exceeding 300 °C [5–7]. The steel nail causes short circuits between the battery layers which typically result in a rapid discharge through the nail, which causes extreme localized heat generation, which then leads to thermal runaway [8]. In addition, the deformation caused by the nail insertion can create a direct short-circuit between different layers in the cell, leading to continued discharge even after the nail has been removed. It has also been shown that slow, shallow nail penetrations are more likely to lead to very high temperatures and thermal runaway than fast, deep penetrations [6].

This short communication reports nail penetration tests for lithium sulfur batteries. It also presents a nail penetration test under load for the first time, and shows how a lithium sulfur battery is both safe during a nail penetration test, and also capable of continuing to operate and provide current to an external load.

2. Experimental

16 Ah pouch cells were provided by OXIS Energy Ltd. (Abingdon, UK), and had dimensions of 180 × 75 × 8 mm. These cells were produced for Lincad Ltd. (Ash Vale, UK) and the Defence Science

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and Technology Laboratory (Dstl) as part of a research program to produce safe, lightweight batteries for military use.

The cells were fabricated in a dry room maintaining a dew point of −50 °C. The electrolyte used was 1.0 mol dm^{-3} Li(OTf)$_3$ in sulfolane containing less than 30 ppm of water. The cathode consisted of a sulfur-based vacuum dried slurry (70:20:10 sulfur (Acros):PEO (Mw = 4000000, Sigma Aldrich):carbon black (Ketjenblack, PTS UK Ltd.)) coated onto both sides of an aluminium foil current collector (Coveris Advanced Coating) of surface capacity 2.07 mAh cm^{-2}. 100 μm lithium foil (Rockwood Lithium) served as anode and current collector and a 20 μm polypropylene separator (Celguard) was used to prevent electrical contact between electrodes.

A thermal imaging camera (FLIR A655sc) was used to monitor the surface temperature of the cell around the nail penetration site, and the cell was painted black using Krylon paint. Multiple T-type thermocouples were also positioned on the opposite side of the cell in order to validate the thermal imaging data, as shown in Fig. 4. The data from the thermocouples was logged using a Grant Squirrel Data logger (model 2F16).

A containment and extraction system were put in place around the entire set-up as a precaution but were not necessary.

A 2.5 mm diameter steel nail was used to fully penetrate the cell. Six tests were conducted, three at open circuit on fresh cells, two at open circuit on cells that had been cycled until they had been degraded to 80% of their initial capacity, and one fresh cell that was being discharged at 1.6 A (*C*/10). For the open circuit tests, the voltage was measured using the squirrel data logger. The test under load was carried out using a Metrohm Autolab Potentiostat/Galvanostat (Autolab PGSTAT30) with a 10 A Booster (Autolab BSTR10A) connected. The potentiostat was controlled using the software Nova.

Prior to each test, the cells were charged to between 2.42 V and 2.47 V, which relates to over 95% SOC. For each test the nail was removed after between 9 and 11 min, and data was continually logged before, during and after penetration.

3. Results and discussion

Fig. 1 shows the voltage traces of the tests. During penetration the open circuit tests show a voltage drop of between 0.020 V and 0.026 V, and the test under load shows a drop of 0.015 V. With the nail inserted the voltage of all of the cells drops at a steady rate and all cells see a rise in voltage when the nail is removed, indicating that the cells are discharging through the nail. After removal, the voltage of the cells at open circuit rise and then level off, indicating that the severity of short-circuit is reduced with the removal of the nail. The voltage of the cell under load rises a little and then continues to fall due to the ongoing discharge.

During and after nail penetration, no smoke, flames or charring were observed, and there was very little electrolyte evacuation from the penetration hole. The painted surface of the cells can be seen in Fig. 2.

During all tests there was a modest rise in temperature. Fig. 3 shows the maximum temperature of the different tests, measured at location 2 as shown in Fig. 4. The maximum temperature rise for the different cells was between 4 °C and 10 °C. This compares to rises of 80 °C and 140 °C for intercalation lithium chemistries seen in previous tests under similar conditions [5,6].

Fig. 4 shows the thermocouple data from the test under load, and this matches well with the data from the thermal imaging camera, which can be seen in Fig. 5. The drop in temperature seen by thermocouple 2 is thought to be due to the thermocouple becoming dislodged upon the removal of the nail.

Fig. 5 shows snapshots from the thermal imaging camera, along with temperature data along the line drawn in the images. One minute after insertion of the nail, an increase in temperature at the site of penetration up to a maximum of 33.5 °C can be seen. This heat then spreads throughout the cell as the test progresses. After removal, the surface of the nail shows up brightly on the thermal imaging camera. Although the emissivity of the nail is not known and therefore this cannot be used as an accurate measurement of temperature, it is likely that the nail, and therefore the surrounding area of the cell, is hotter than the pouch material.

Once the nail was removed, the cell began to cool down. At this point, a current of 1.6 A was still flowing from the cell, and continued to flow for approximately 3 min until the load was switched off.

In comparison with nail penetration tests on intercalation lithium cells, lithium sulfur cells show very small temperature rises, no catastrophic failure and the cells are able to continue to provide current during penetration and for a short period after the

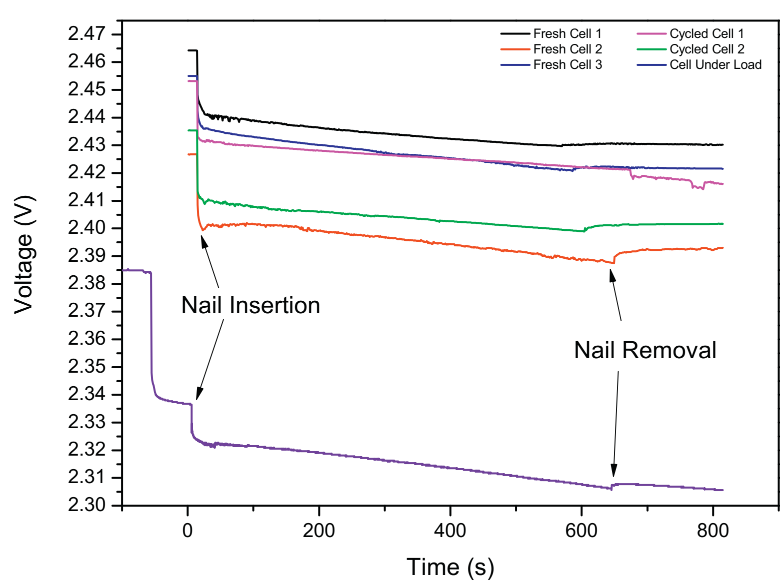

Fig. 1. Graph of voltage vs time for the nail penetration tests.