



## Minimally Invasive Insertion of Reference Electrodes into Commercial Lithium-Ion Pouch Cells

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Two procedures to introduce a lithium metal reference electrode into commercially manufactured lithium-ion pouch cells (Kokam SLPB 533459H4) are described and compared. By introducing a stable reference potential, the individual behavior of the positive and negative electrodes can be studied in operando under normal cycling. Unmodified cells and half-cells made from harvested electrode material were cycled under identical conditions to the modified cells to compare capacity degradation during cycling and thus validate each modification procedure for degradation testing. A configuration that did not affect the performance of the cell over 20 cycles was successfully developed.

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Understanding the behavior of the individual electrodes in commercial lithium-ion cells gives insight into the degradation mechanisms that result in capacity and power fade and enables design of better battery management systems (BMSs), for example by allowing more accurate predictions of future cell behavior.<sup>1</sup> However, commercial lithium-ion cells are two-electrode systems i.e. only the potential difference between the working electrode (WE) and counter electrode (CE) may be measured. Therefore, the performance of the electrodes cannot be monitored in isolation and it is impossible to determine the electrode which is ultimately determining cycle life. The introduction of a stable fixed reference electrode (RE) potential allows the WE and CE behavior to be investigated separately.

Previous studies have introduced a RE into commercial cylindrical 18650 cells.<sup>2-5</sup> However, the modifications may not always have resulted in the ideal conditions, for example by (a) exposing the cell to a different electrolyte from that originally used in the cell,<sup>2</sup> (b) positioning the RE some distance from the WE and CE,<sup>3</sup> or (c) risking damaging the cell through invasive and complex drilling procedures to insert the RE into the centre of the cell.<sup>2,4,5</sup> Previous studies of pouch cells have typically involved the construction of bespoke 3-electrode cells in the lab<sup>6,7</sup> rather than the modification of existing commercial cells, thus not allowing a direct, in-situ comparison with unmodified commercial cells.

Here we discuss the development of two different modification procedures to insert a RE into commercial lithium-ion pouch cells with minimal intrusion on the original structure and chemistry of the cell: (1) the “patch” method, and (2) the “wire” method. This allows separate cycling and degradation data for the WE and CE to be obtained. The accuracy of the results obtained from the cell modifications and impact on capacity degradation over 20 cycles are compared with the original 2-electrode configuration and also the cathode and anode materials (extracted from the full cell) cycled in 2-electrode half-cells vs. a Li metal CE.

### Experimental

**Full cells.**— The cells used in this study are Kokam 740 mAh pouch cells with cathodes comprised of LiMO<sub>2</sub>, where M is a combination of nickel, manganese and cobalt, and graphite anodes. Prior to all disassembly or modifications performed on the full cells, they were fully discharged under CCCV (constant current, then constant voltage) as per the manufacturer’s data sheet.<sup>8</sup>

**Half-cell fabrication.**— 15 mm diameter discs were punched from a sheet of electrode material recovered from a disassembled pouch cell.

This was rinsed in dimethyl carbonate (DMC, Sigma-Aldrich). When electrode substrates were double-sided, one side of active material was removed by washing with N-Methyl-2-pyrrolidone (NMP, Sigma-Aldrich). The electrode discs were vacuum dried before inserting into a coin cell with a Whatman glass microfiber separator, LP30 electrolyte (1 M LiPF<sub>6</sub> in 1:1 w:w ethylene carbonate (EC) and DMC, BASF) and a Li foil CE of 15 mm diameter.

**“Patch” modification method.**— An unmodified cell was transferred to a glove box with argon atmosphere, where a 5 mm incision was made in the pouch at the opposite end to the existing terminals. The pouch material was peeled back to reveal the electrode stacks encased in polymer separator. The exposed aluminum edges of the pouch cell material were covered with insulating, adhesive-free polymer tape to prevent short-circuits. A 2 cm<sup>2</sup> U-shaped piece of lithium metal foil was used as a RE by placing it over the hole, covering it completely. A copper current collector was placed on top of the RE (Figure 1a). The assembly was then tightly bandaged in place using a large piece of inert polymer film and several windings of adhesive tape. The modified cell was vacuum sealed into a large outer pouch using an Audionvac vacuum sealer, with the electrodes connected to the outer terminals using sealed feedthroughs.

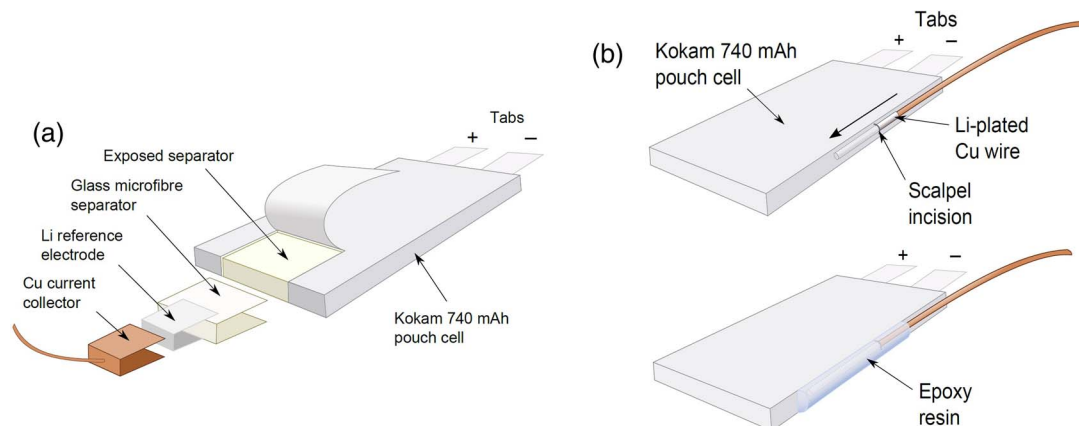
**“Wire” modification method.**— Initially a lithium-plated copper wire was prepared to be used as the reference electrode. This was done using a 2-electrode electrochemical cell in an argon glove box using a 0.8 mm diameter copper wire WE, lithium foil CE and commercial LP30 electrolyte. Lithium metal was then plated galvanostatically with a current density of 10 mA cm<sup>-2</sup> for 30 minutes. The coated wire was then rinsed in DMC and vacuum dried. A ceramic scalpel was then used to create a 5 mm incision in the side of the pouch cell inside the glove box. The RE was inserted into the incision, which was then sealed using fast-setting epoxy resin (Araldite) and left to dry overnight (Figure 1b).

**Electrochemical testing.**— The 3-electrode pouch cells were CCCV precharged between the WE and CE to the specified maximum potential ( $V_{\max}$ ) for the cell<sup>8</sup> and then CC cycled at C/10 between  $V_{\max}$  and  $V_{\min}$  for 20 cycles at 40°C in a Stuart S160 incubator, using a Biologic VMP3 potentiostat. The half-cells were similarly precharged and cycled, with  $V_{\max}$  and  $V_{\min}$  determined by the initial results of the 3-electrode pouch cell cycling and the C/10 current determined by preliminary runs with test cells. Unmodified Kokam 2-electrode cells were simultaneously cycled under the same parameters to act as a control. The charge/discharge rates in the experiments were kept relatively low (C/10) since this was the first time that the modified cells had been tested and, as such, we wanted to avoid damage. As we

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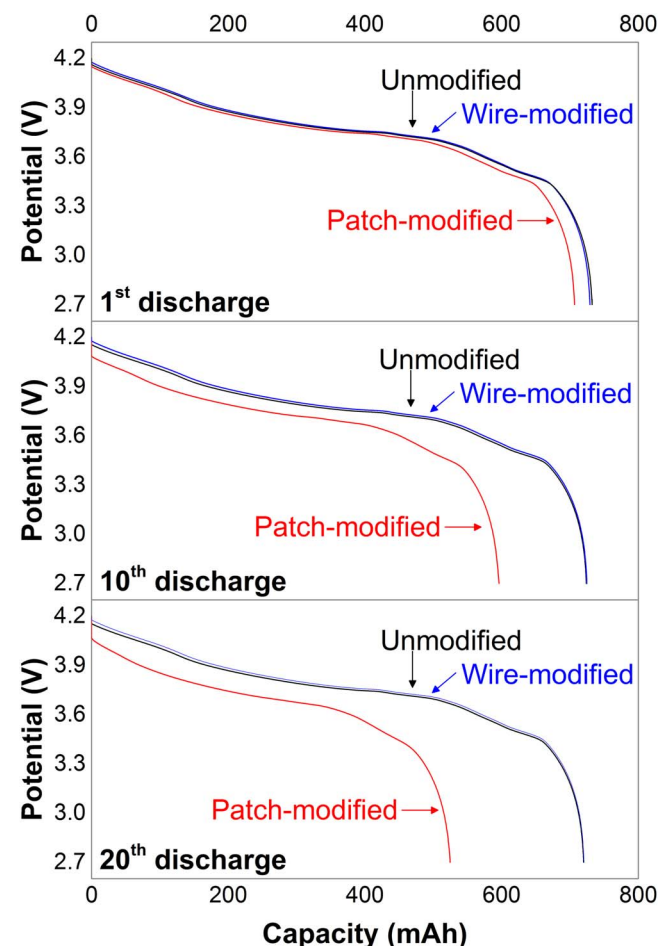


**Figure 1.** “Patch” (a) and “Wire” (b) 3-electrode modification procedures performed on Kokam 740 mAh pouch cells.

grow more confident in the modified cell behavior and stability, we will increase the rates in future experiments.

### Results and Discussion

The galvanostatic full cell potentials measured during the 1<sup>st</sup>, 10<sup>th</sup> and 20<sup>th</sup> discharges of the patch and wire modified cells are compared with that of the unmodified cell in Figure 2. What is readily apparent



**Figure 2.** Comparison of full cell discharge profiles for unmodified and modified cells over the first 20 cycles.

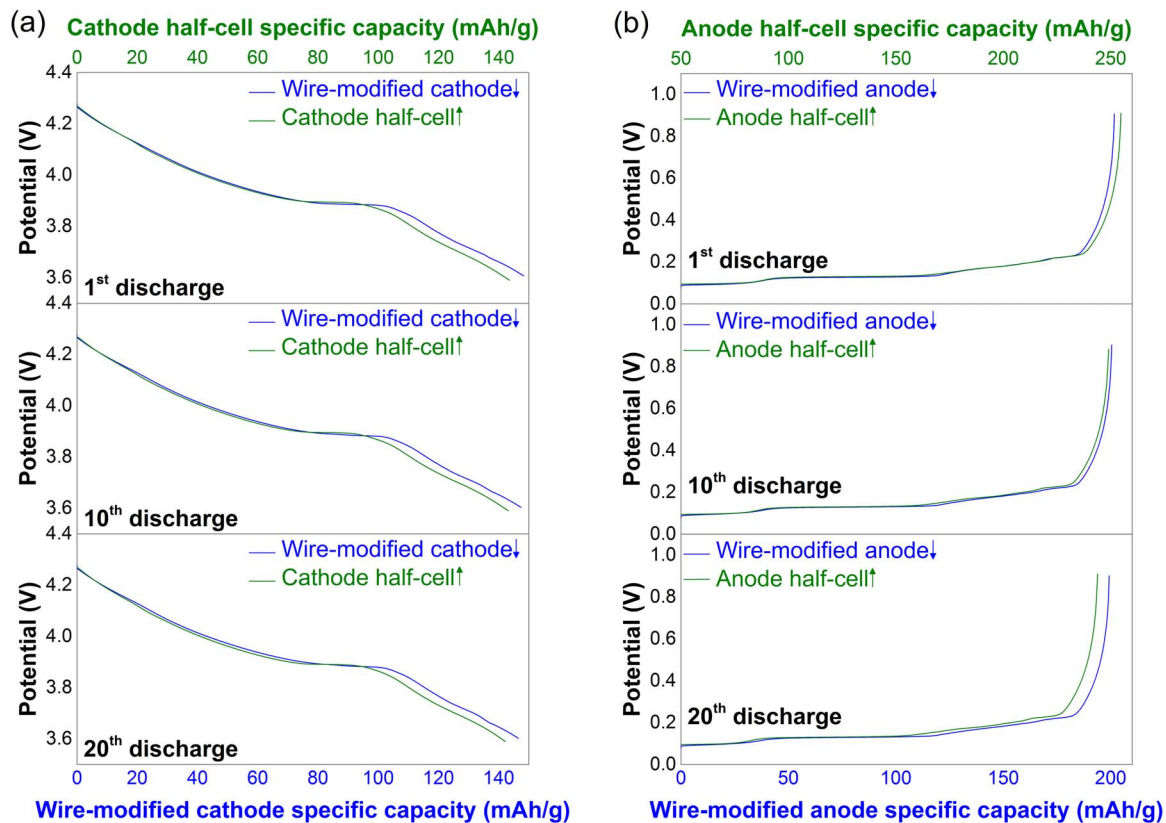
is that the patch method shows significantly different behavior to that of the unmodified or wire methodologies. In all three discharges shown the patch cell shows increased overpotentials and significantly restricted discharge capacity. By applying external pressure to the cell the performance could be enhanced; however, performance close to that of the unmodified cell could never be achieved. It is believed that this method simply disrupts the physical structure of the electrode stack too much and therefore the performance of the cell suffers significantly.

Conversely, the performance of the 3-electrode cells constructed using the wire method is in excellent agreement with that of unmodified cells. The potential profiles are almost completely overlaid and it is extremely difficult to distinguish any significant differences. In addition, it should be noted that even when two unmodified full cells are cycled that some minor variation in performance is observed. As seen in Table I, the wire-modified cells exhibited an average capacity degradation that is within the standard deviation of the respective groups of unmodified cells over the first 20 cycles.

To examine the quality of WE and CE potential profiles obtained from 3-electrode cells, these were compared with half-cells constructed with material extracted from a disassembled full cell, shown in Figure 3. The half-cells were constructed in 2-electrode configuration as coin cells (in a typical methodology for characterising lithium battery electrodes<sup>9,10</sup>). The potential profiles are in excellent agreement for both electrodes with both potential profiles almost exactly overlaying that obtained in the half-cell vs. Li. The anode half-cell exhibits a specific capacity 50 mAh/g greater than that of the wire-modified cell because the full cell is cathode capacity-limited and therefore never reaches the negative potential limit used in the half-cell cycling condition. This highlights the need for measurement of material performance in 3-electrode configuration of a full cell where the cycling conditions may be significantly different to those we may impose in a half-cell cycling experiment. The minor discrepancy in specific capacity between the wire-modified cell cathode and cathode half-cell is well within the expected experimental error within these measurements where the mass of the electrodes

**Table I.** Average capacity loss of modified and unmodified cells, per cycle, over 20 cycles. Three cells were tested for each set of parameters.

Cell modification technique	Average capacity loss per cycle over 20 cycles (%)
Unmodified (2-electrode)	$0.1698 \pm 0.0701$
Patch-modified (3-electrode)	$1.1227 \pm 0.497$
Wire-modified (3-electrode)	$0.1726 \pm 0.1398$



**Figure 3.** Comparison of cathode (a) and anode (b) potential profiles of wire-modified cell with respective half-cells. The horizontal axes for the full and half-cells in (b) differ to reflect the proportion of anode active material that is utilized within the full cell, since it is cathode-limited.

within the full cell could only be estimated from post mortem analysis of similar cells. Overall it can be concluded that the performance of the wire-modified pouch cell is in excellent agreement with the expected potential profiles suggesting that this methodology truly allows us to evaluate changes occurring independently in the cathode and anode electrochemistries in a commercially obtained pouch cell.

### Conclusions

A lithium reference electrode has been successfully introduced to a commercial Li-ion pouch cell in a minimally-intrusive manner that does not impact on the capacity or capacity retention of the cell over the first twenty cycles. This allows working and counter electrode potential profiles to be obtained from a commercial pouch cell for the first time. Having proven successful in shorter-term cycling studies, the suitability of this technique for longer-term cycling tests encompassing hundreds of cycles and higher C-rates will be assessed in a future paper. The data obtained from repeated electrochemical characterizations of WE and CE may also be used in an open circuit voltage model to investigate different electrode-specific aging mechanisms.<sup>11</sup> Moreover, the presented technique can be used to construct 3-electrode cells for the validation of lithium-ion cell models aimed at simulating electrode and cell potentials, using a simple and reproducible procedure without detrimental modifications.

### Acknowledgments

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