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Thermo-electrochemical instrumentation of cylindrical Li-ion cells

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HIGHLIGHTS

- A novel in-situ thermo-electrochemical cell instrumentation method is developed.
- A range of reference electrode options is evaluated.
- Fibre optics are used to monitor temperature inside cylindrical cell's core.
- Instrumentation developed is used to measure performance of a commercial Li-ion cell.
- Cell instrumentation proposed is applicable to a wide range of cell formats.

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ABSTRACT

The performance evaluation and optimisation of commercially available lithium-ion cells is typically based upon their full cell potential and surface temperature measurements, despite these parameters not being fully representative of the electrochemical processes taking place in the core of the cell or at each electrode. Several methods were devised to obtain the cell core temperature and electrode-specific potential profiles of cylindrical Li-ion cells. Optical fibres with Bragg Gratings were found to produce reliable core temperature data, while their small mechanical profile allowed for low-impact instrumentation method. A pure metallic lithium reference electrode insertion method was identified, avoiding interference with other elements of the cell while ensuring good contact, enabling *in-situ* observations of the per-electrode electrochemical responses. Our thermo-electrochemical instrumentation technique has enabled us to collect unprecedented cell data, and has subsequently been used in advanced studies exploring the real-world performance limits of commercial cells.

1. Introduction

Lithium-ion cells have established themselves as the dominant family of cell chemistries for portable electronics [1], electric vehicles [2] and battery grid storage [3]. However, despite substantial improvements in energy density over the past quarter of a century, Li-ion cells remain the performance-limiting factor in the aforementioned applications. High-energy Li-ion cells suffer from high internal resistance [4], which can result in excessive temperature increases under high load or charging currents, with the possibility of the cell undergoing thermal runaway [5] and explosion. The high internal resistance also increases the overpotential of the cell, which can drive the anode and cathode potentials outside of their respective safe operating windows, resulting in capacity loss due to lithium plating and electrolyte decomposition. While these factors are well known, application of this knowledge to real-world cell design can be challenging. This is because commercial cells are hermetically sealed two-electrode systems with no internal temperature sensors and therefore no way of monitoring the core temperature or electrode-specific potentials. As such, this usually results in the use of conservative safety limits based on full cell potential and surface temperature, which do not allow the cell's actual limits to be fully exploited. Therefore, a number of cell instrumentation techniques were trialled on commercial 18650 cylindrical cells in an attempt to obtain individual anode and cathode potentials and *in-situ* core temperature profiles, with minimal impact on the electrochemical characteristics of the cell.

Previous studies have investigated the incorporation of a reference electrode into cylindrical cells [6–12]. While many of these have involved the fabrication of cells from scratch in the laboratory [8–10], some have involved adding reference electrodes to commercial cells [6,7,11,12]. However, the invasive nature of the insertion techniques risks either damaging the cell or changing its performance characteristics. Drilling into the core of the cell [11] can cause a short circuit by leaving metal burrs from the cell can in the core, or directly damaging the electrode jellyroll if the drill bit is imperfectly aligned. Adding more electrolyte to the cell [12] lowers its internal resistance [13], and thus

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alters its electrochemical performance limits and behaviour. If the electrolyte in question does not match the original contents of the cell, this can result in the formation of a different Solid Electrolyte Interphase (SEI) *vs.* that formed in an unmodified cell [13], which can further alter the electrochemical characteristics of the cell. Another study submerged an opened cylindrical cell into a vessel of electrolyte next to a reference electrode [7], which not only exacerbates the previous issue, but also affects the accuracy of the measured potential profiles due to the increased distance between the reference electrode and the jellyroll. Therefore, building on from previous success with the instrumentation of commercial pouch cells [14], we attempted to apply this minimally invasive electrochemical instrumentation technique to the more challenging cylindrical cell format, and developed further modification techniques that were tailored to this specific application.

Core temperature sensing in cylindrical cells has previously involved the use of thermocouples [15–20], which measure only a single temperature point and are incapable of multiplexing onto a single wire; are subject to electrical interference; are a spark risk due to current carrying wires; can adversely impact the cell performance unless properly insulated; and require a cold junction element and extra calibration since they measure relative changes in temperature. This study pioneers the use of optical fibres utilising Fibre Bragg Grating (FBG) for cell temperature measurements which, by virtue of having no current carrying components, bypass the issues mentioned above. The use of optical fibres paves the way for multipoint temperature measurements using a single sensing element, as a number of FBGs can be placed on a single thread, providing multiple temperature measurement points using a single low-profile non-electrical sensor. Here, we will focus on obtaining accurate temperature profiles of a cell core using a single FBG on the optical fibre to prove that FBGs can be employed successfully in this application.

In this work we describe the approach and methodology leading to a fully thermo-electrochemically instrumented Li-ion cell. The instrumentation devised here offers an unprecedented view of the internal cell thermodynamics, enabling assessment of real thermal and electrochemical performance limitations. An array of modification techniques is illustrated in detail, offering a solution to the lack of understanding of the *in-situ* operating parameters of Li-ion cells. This is of importance to researchers and engineers working on current and new cell generations, enabling significant performance improvements without jeopardising safety.

2. Experimental

The cells considered in this study are high-energy commercial 18650s based on nickel cobalt aluminium (NCA) chemistry. Prior to modification, all cells were discharged to their minimum operating voltage of 2.5 V as specified by the manufacturer, and transferred to an argon glove box with O_2 and H_2O concentrations below 0.1 ppm. Reference electrodes and optical fibre sensors were prepared in advance, and the cells were modified according to one of the following techniques as described below and shown in Figs. 1 and 2.

2.1. FBG core temperature sensor

The FBG sensors used in this study for temperature measurements are based on raw silica fibres connected to a Yokogawa AQ6370 spectrum analyser, a three-port optical circulator (Thor Labs) and an optical coupled laser source with a nominal broadband light spectrum of 1525–1590 nm as the data transmission method. When sensing temperature using an optical fibre, ultraviolet light is used to etch an FBG onto the fibre. The FBG consists of a periodic pattern of etching of a given distance apart, i.e. a grating. Once etching is complete and the optical fibre has been inserted into the cell, light from the broadband light source is injected down the fibre via the three-port optical coupler. The FBG is transparent to most of the broadband light, but reflects a small portion of light back up the fibre; this frequency band is then detected by the spectrum analyser. The reflected light combines to produce the strongest signal at a wavelength that is equal to double the distance between the gratings, known as the Bragg wavelength and defined in Equation (1):

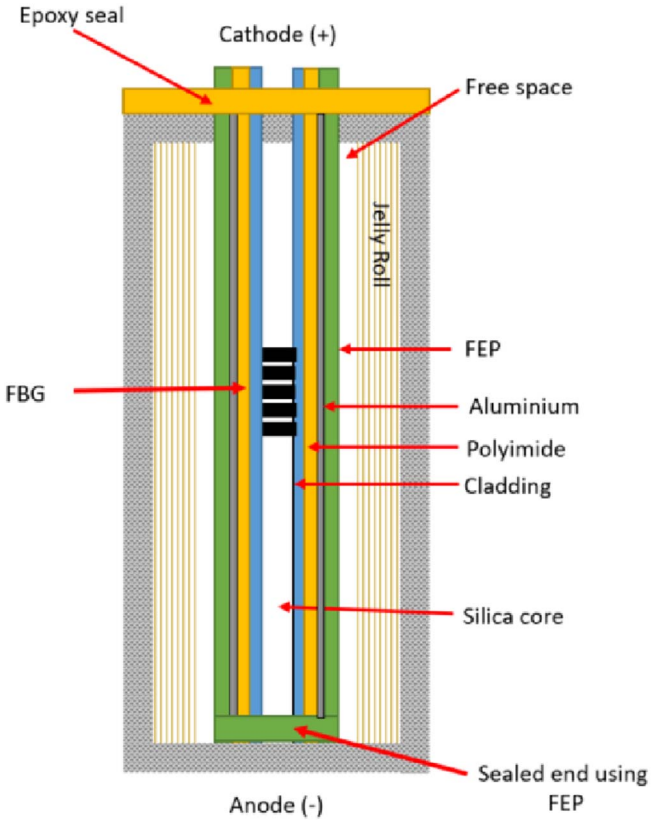

Fig. 1. Optical fibre assembly detail.

$$\lambda_{Bragg} = 2n\Lambda \quad [1]$$

where λ_{Bragg} is the Bragg wavelength, n is the refractive index and Λ is the space between the Bragg gratings. Changes in temperature or mechanical strain on the fibre cause the distance between the gratings to alter, resulting in a change in the FBG's refractive index, which in turn causes a change in the Bragg wavelength of light reflected back up the optical fibre. Since λ_{Bragg} is dependent on Λ, multiple FBGs with unique spacings between their gratings can be used on a single fibre. It can be seen from Equation (1) that there is a linear relationship between the Bragg wavelength of the FBG and its temperature or mechanical strain. However, differentiating between these two parameters can be challenging. This can be resolved in two ways. One approach is to exclude the unwanted strain or temperature effect by eliminating the response in the sensing element itself, e.g. by adding strain relief. An alternative solution is to incorporate a second FBG sensor in near proximity that is isolated from the disturbance in question, then subtract the difference in wave shift from the first FBG sensor [21]. The FBGs used in this study have a manufacturer-specified temperature conversion factor of 11 p.m./°C.

The FBG sensors evaluated in this work were Single Mode SMF-28 9/125 μm fibres sealed with cladding and a polyimide recoat during manufacture, which provided temperature stability in the range of -270 °C to 300 °C. However, optical fibres in their bare form would also be exposed to corrosive chemicals present in Li-ion cells, leading to fibre degradation. Therefore, the fibres were sealed in an outer skin of 1.6 mm diameter fluorinated ethylene propylene (FEP) sleeving to prevent the fibre from being affected by the electrolyte solution present