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Extending battery life: A low-cost practical diagnostic technique for lithium-ion batteries

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HIGHLIGHTS

- Differential Thermal Voltammetry (DTV) carried out on battery packs under cooling.
- Technique can cope with unknown, unequal and changing current between cells.
- DTV diagnosed the state of health of individual cells under charge/discharge.
- Easy installation to existing systems due to simple hardware/software requirements.
- Differential heat flux voltammetry introduced as a complimentary method.

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ABSTRACT

Modern applications of lithium-ion batteries such as smartphones, hybrid & electric vehicles and grid scale electricity storage demand long lifetime and high performance which typically makes them the limiting factor in a system. Understanding the state-of-health during operation is important in order to optimise for long term durability and performance. However, this requires accurate in-operando diagnostic techniques that are cost effective and practical. We present a novel diagnosis method based upon differential thermal voltammetry demonstrated on a battery pack made from commercial lithium-ion cells where one cell was deliberately aged prior to experiment. The cells were in parallel whilst being thermally managed with forced air convection. We show for the first time, a diagnosis method capable of quantitatively determining the state-of-health of four cells simultaneously by only using temperature and voltage readings for both charge and discharge. Measurements are achieved using low-cost thermocouples and a single voltage measurement at a frequency of 1 Hz, demonstrating the feasibility of implementing this approach on real world battery management systems. The technique could be particularly useful under charge when constant current or constant power is common, this therefore should be of significant interest to all lithium-ion battery users.

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1. Introduction

In order for hybrid & electric vehicles to compete with internal combustion engine vehicles, they must meet the high power and energy requirements demanded from modern applications at an acceptable cost [1]. A major factor slowing down the transition to electric vehicles is the cost of the battery pack [2] which for example in Tesla vehicles account for approximately one quarter of the total production cost [3].

Understanding battery lifetime is essential in order to maximise the economics of batteries; if a battery reaches its end-of-life (EOL) before the EOL of the product then it must be replaced, incurring significant cost for either the consumer or the OEM under warranty, and this can also affect the residual value for second life applications. Battery lifetime is a function of degradation, which involves multiple coupled & path dependent degradation mechanisms, yet,

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industry standard measures of degradation or state-of-health (SOH) are based upon simple capacity and power fade. Capacity fade is defined as the percentage decrease of capacity compared to beginning of life (BOL) typically carried out under 1C discharge at 25 °C. Power fade can be defined as the percentage increase in the real impedance measured at 1 kHz but often at an unspecified state-of-charge (SOC).

Batteries degrade through various mechanisms over time [4,5] and individual cells in a pack may age differently [6]. Unfortunately, it is possible for 2 cells that have been used differently to have the same degree of capacity fade, and even power fade, yet for one of them to be safe to use for many more cycles and the other not. Hence these crude measures of degradation are wholly unsuitable for most applications. This is even possible within a single battery pack, due to thermal inhomogeneities within a pack and/or unequal current paths between cells in parallel or within large cells [6]. This unequal degradation can lead to reduced overall pack performance and lifetime which means particular cells may need to be controlled or replaced accordingly. Hence a good and low-cost diagnosis method capable of accurately identifying such cells with detailed state-of-health information is required.

Considerable research has been carried out to develop new techniques to monitor battery SOH however many are not suitable for in-operando use as they require expensive equipment such as electrochemical impedance spectroscopy (EIS) [7,8], in-situ nuclear magnetic resonance [9] or X-ray computational tomography [10,11]. Data mining techniques such as extended Kalman filters [12], neural network and linear prediction error methods [13] have also been researched for SOH estimation in a BMS. Many in-operando techniques based on the temperature measurements are mostly derived from the original work by Maher and Yazami [14] who made entropy and enthalpy measurements at specific cell potentials giving information on the state of both electrodes. The techniques using current are usually called incremental capacity analysis, and are exemplified by the latest work of DuBarry et al. [15] who have developed models which compare the dQ/dV peaks with its fresh cell equivalent to quantify cell SOH in terms of degradation modes such as loss of lithium inventory, loss of active materials and ohmic resistance increase. In their work, each dQ/dV spectra represents a combination of processes at both positive and negative electrodes. However, little work has been done on how to implement these techniques at a pack level although Offer et al. has demonstrated a relatively simple method to identify a faulty cell and/or connection in a battery pack [6] by measuring the potential drop of each cell during a current interrupt tests.

The method of Differential thermal voltammetry (DTV) [16,17] was previously reported by the authors as a complimentary tool to incremental capacity analysis (ICA), showing how simple temperature measurements could be used to infer similar information. DTV only requires temperature and voltage measurements and is carried out by measuring the change in cell surface temperature during constant current discharge and does not require temperature to be carefully controlled. The DTV parameter, dT/dV is calculated by taking the time differential of the temperature, dT/dt divided by the time differential of the potential, dV/dt. Plotted against cell potential, the result gives similar information as ICA and slow rate cyclic voltammetry but with additional data about the entropic state of the electrodes.

DTV was presented as a suitable diagnosis method for use in real-world applications, however the previous validation experiments were all carried out on individual cells under natural convection thermal boundary conditions. In high power applications such as in electric vehicles, the cells would be connected in a pack with a thermal management system to maintain the cells at safe operating temperature. In addition, the experiment was only validated for constant current discharge which meant that the diagnosis required a dedicated discharge cycle, which is uncommon in many applications.

In this paper, DTV experiments have been carried out on a battery pack made from four commercial lithium polymer cells in parallel placed under forced air surface cooling to emulate an electric vehicle application. One cell was deliberately aged prior to the experiments to demonstrate how the technique could diagnose unequal degradation. The test was performed at both constant current charge and discharge to demonstrate its use under charging conditions. Differential heat flux voltammetry (DHFV), dHF/dV is also introduced as a complementary method when dT/dt is too small to measure accurately under strong cooling conditions.

2. Methods

2.1. Battery testing

The experiment was performed using a battery pack made from four commercial 5 A h lithium-polymer pouch cells connected in parallel (Dow Kokam, model SLPB11543140H5) where each cell consists of a carbon graphite negative electrode and a nickel-manganese-cobalt ($Ni_xMn_yCo_z$) positive electrode. Heat flux sensors with K-type thermocouples (OMEGA HFS-4) were placed on the surface at the centre of the cell. Shunt resistors (RS 810-3273) were placed in series with each cell to measure the current across every individual cell. It should be noted, that current measurements were undertaken in order to compare the DTV technique to ICA and to understand how the current changes for cells in parallel, but the current measurement is not required for, and was not used for the DTV calculation. One deliberately aged cell and three fresh cells were placed together in the pack to determine whether the diagnosis methods could correctly determine the SOH of the individual cells. The aged cell was previously stored at 55 °C at 4.2 V for approximately 15 days. The pack was prepared in a way to minimise differences in external resistance such as equal cable lengths, fastening torque (8 kNm) and cleaned contact surfaces.

During the experiments, the pack was placed inside an incubator (Binder KB-23) with forced air convection flowing over the pack surface (as illustrated in Fig. 1) while keeping the incubator door open to emulate a surface cooling system to recreate real conditions such as those in electric vehicles. A Maccor Battery Tester series 4000 was used for measurements and loading during pack experiments whereas a Bio-Logic BCS-815 was used for individual cell experiments. Pico TC-08 was used for heat flux sensor

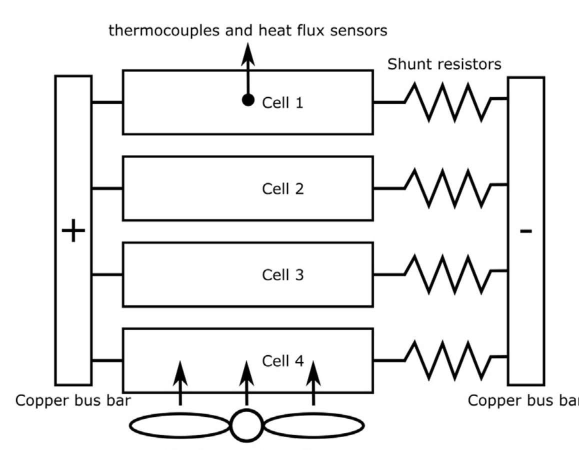

Fig. 1. Experimental set-up for pack analysis.

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