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Tracking degradation in lithium iron phosphate batteries using differential thermal voltammetry

Toshio Shibagaki, Yu Merla, Gregory J. Offer*

Department of Mechanical Engineering, Imperial College London, United Kingdom

HIGHLIGHTS

- Differential Thermal Voltammetry (DTV) carried out on LFP battery.
- Low cost installation only requiring surface temperature and voltage measurement.
- Correctly identifies aged cell amongst fresh cells during constant current loading.
- DTV peak shift is relating to internal resistance increment.
- Use of DTV to estimate capacity fade from an incomplete cycle.

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ABSTRACT

Diagnosing the state-of-health of lithium ion batteries in-operando is becoming increasingly important for multiple applications. We report the application of differential thermal voltammetry (DTV) to lithium iron phosphate (LFP) cells for the first time, and demonstrate that the technique is capable of diagnosing degradation in a similar way to incremental capacity analysis (ICA). DTV has the advantage of not requiring current and works for multiple cells in parallel, and is less sensitive to temperature introducing errors. Cells were aged by holding at 100% SOC or cycling at 1C charge, 6D discharge, both at an elevated temperature of 45 °C under forced air convection. Cells were periodically characterised, measuring capacity fade, resistance increase (power fade), and DTV fingerprints. The DTV results for both cells correlated well with both capacity and power, suggesting they could be used to diagnose SOH in-operando for both charge and discharge. The DTV peak-to-peak capacity correlated well with total capacity fade for the cycled cell, suggesting that it should be possible to estimate SOC and SOH from DTV for incomplete cycles within the voltage hysteresis region of an LFP cell.

1. Introduction

Lithium ion batteries are a key enabling technology for electric vehicles due to their high energy and power densities [1,2]. However, long-term operation and extreme temperature environments can cause increasing internal resistance and capacity fade [3]. Two of the principle causes of degradation are the growth of the solid electrolyte interphase (SEI) layer [4] and lithium plating [5,6] at the negative electrode. Degradation can influence the performance of a whole system or device, hence in-operando diagnostic methods that can correctly diagnose the state of health (SOH) are required.

Conventional non-destructive diagnostic techniques that can be conducted at the cell level such as slow rate cyclic voltammetry (SRCV) and electrochemical impedance spectroscopy (EIS) are not suitable for in-operando diagnostics. SRCV requires unique operating modes that are not commonly found during use, i.e. constant rate of change of voltage. EIS requires additional hardware that adds complexity and expense that can currently only be justified in high end applications [7], and the measurement is so sensitive to temperature that its use for SOH diagnosis is questionable [8]. In contrast incremental capacity analysis (ICA) has been attracting a lot of interest [9–12], as constant power charging (which is almost constant current) is very common for many applications, and it is conceivable that a constant current (dis)charge could be conducted periodically. By comparing the rate of change of voltage to the rate of change of current, it is possible to infer a great deal of information about the SOH of the cell. However, ICA works best at very low C rates, which are unlikely, and although it works at 1–2C charging, the peaks are offset by the overpotential caused by the impedance of the cell, which is a stronger function of temperature than degradation (except the most severe cases of catastrophic degradation).

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* Corresponding author.
E-mail address: gregory.offer@imperial.ac.uk (G.J. Offer).

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Therefore, temperature can introduce significant errors for any realistic application of ICA. In addition, if two or more cells are in parallel, it is not cost effective to measure the current independently and then ICA can only be used on the string of cells and cannot diagnose individual cells.

In previous work, a new technique called differential thermal voltammetry (DTV) [13–15] was proposed that makes use of the changing temperature which is the principle disadvantage of the other techniques. This method only requires cell temperature and voltage measurements during a constant current charge (or discharge) which are often already measured in electric vehicles (EVs) to monitor the state-of-charge (SOC) and for safety. This means cells in parallel can be individually diagnosed without measuring current, as long as each cell has a temperature measurement. The measurement requires data with a resolution (1–2 mV) and frequency (1 Hz) typical of that found in most commercial BMS, suggesting that there is no need to add extra instruments making the method application ready. The method needs the temperature (or heat flux) to change in order to conduct the analysis, and provides additional information from the entropic heat of the cell which the previous methods are not sensitive to. The DTV fingerprints, i.e. the peaks and troughs, can be analysed in the same way, using similar tools, theory and interpretations, as ICA, making the technique sensitive to the consequences of specific degradation mechanisms such as loss of lithium inventory (LLI), loss of active material (LAM), stoichiometric drift and capacity loss, etc.

Different degradation mechanisms will affect the rates of enthalpic and entropic heat generation differently, which has led to the development of direct measurements of entropy to diagnose degradation, as pioneered by Yazami and co-workers [16,17]. However, such measurements take a considerable amount of time and require careful control of temperature [18], and hence are not always suitable for in-operando application. ICA has been demonstrated for multiple chemistries, so consequently it should be possible to use the DTV method for multiple cell chemistries too. Previously, DTV experiments have been carried out on nickel manganese cobalt oxide (NMC) cathode batteries and have not been tested on other battery chemistries. Lithium iron phosphate (LFP) is a commercially successful battery chemistry because of its high energy, power densities and stability in high temperature environments [1].

The degradation in LFP cells has already been extensively studied previously [11,19]. In particular, Dubarry et al. showed using ICA that LLI was the main consequence of SEI layer growth consuming lithium and that this was the most important degradation mechanism [3]. Kassem et al. also showed that LFP battery stored at high temperature (45 °C or 60 °C) exhibited capacity fade which was mainly caused by cyclable lithium loss (i.e. LLI) [20]. Ouyang et al. suggested that each peak in the ICA curve corresponded to different phases of the transition process [21].

An important feature of LFP cells is their hysteresis, the asymmetric behaviour between charge and discharge caused by the phase change of the LFP material [22]. Despite this Berecibar et al. [23] showed that the peaks in ICA can be used as markers for SOC and hence SOH diagnosis can be carried out without requiring a complete charge/discharge which otherwise is necessary to return the cell to a point where the voltage can be directly correlated to SOC (i.e. close to 100% or 0% SOC).

In this work, LFP batteries were placed under accelerated aging experiments and diagnosed using the DTV method in order to validate its application for this particular chemistry. Whether DTV can be used to diagnose SOH and if the peaks in DTV can be used as SOC markers, in the same way as ICA, is also considered. In addition, the influence of the charging and discharging rate on the DTV method is also considered.

2. Experimental

In this paper we are adopting the convention of D rate for discharge and the C rate is only used for charge. We feel this is a much more intuitive way of presenting and discussing data when testing batteries, and would encourage the community as a whole to adopt this terminology.

Table 1
Accelerated aging specifications.

Cell	Load	Temperature
1	Held at constant 3.65 V (100% SOC)	45 °C
2	Cycling at 1C (20A) charge, 6C (120A) discharge	45 °C

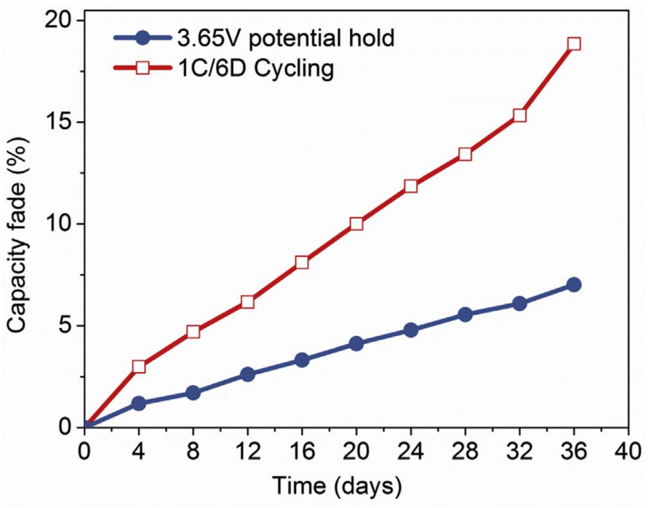

Fig. 1. Capacity loss measurement of the 2 cells after accelerated degradation (0.5C discharge and constant voltage hold at 2 V until current has decayed to 1%). The cycled cell had approximately 90 cycles per 4 days.

2.1. Characterisation test

The experiments were performed using commercial 20 Ah lithium-ion pouch cells (A123 SYSTEMS, model AMP20M1HD-A) where the cell consists of a carbon graphite negative electrode and a lithium iron phosphate ($LiFePO4$) positive electrode.

The characterisation tests were conducted at 20 °C inside an incubator (Binder KB-23) every 4 days using two diagnosis methods. A variant of the GITT method [24], pulse loading with open circuit voltage (OCV) extrapolation, was carried out to obtain the OCV curve and total resistance. Constant current charging and discharging was carried out to obtain the ICA and DTV analysis simultaneously. It should be noted that it is particularly important both procedures were carried out for both charge and discharge as LFP cells demonstrate resistance as well as voltage hysteresis.

K-type thermocouples were placed on the cell surface between the cell tabs for temperature measurement using a Picologger (model USB TC-08) to log the thermocouple readings. Maccor battery cycler (model Series 4000) was used for loading and measurement.

Temperature measurement is critical for the DTV technique, and this was discussed extensively in the three previous works on the development of the technique [13–15]. In the first paper DTV was introduced and demonstrated under conditions of natural convection, when heat generation within the cell was expected to dominate significantly over heat transfer from the cell [13]. The second paper demonstrated that the technique could be used to diagnose between two pathway specific forms of degradation, and compared using temperature measurements taken using a thermal imaging camera against the single surface thermocouple [14]. The use of the thermal imaging camera suggested that, at least for these experiments where the