

Tracking degradation in lithium iron phosphate batteries using differential thermal voltammetry

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Keywords

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- Degradation
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- Differential thermal voltammetry
- Lithium iron phosphate
- Diagnosis

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). 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 (1-2mV) and frequency (1Hz) 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.

2.1 Characterisation test

The experiments were performed using commercial 20Ah lithium-ion pouch cells (A123 SYSTEMS, model AMP20M1HD-A) where the cell consists of a carbon graphite negative electrode and a lithium iron phosphate (LiFePO_4) 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 degradation appeared homogenous, the exact position of the thermocouple on the surface of the cell was not important. The third paper focussed on reproducing conditions that were expected to be more representative of realistic operating conditions [15]. Therefore, cells were tested in a thermal chamber under forced convection with a relatively constant air temperature. This demonstrated that even when the cell temperature was significantly higher than the air temperature, as long as the heat generation

dominated over the heat transfer, the technique still worked. Cells were also tested in parallel and heat flux sensors were introduced as a complimentary technique for when heat transfer dominated over heat generation.

2.2 Controlled accelerated aging

In order to validate the DTV method under various aging process, two accelerated aging load profiles were carried out on the LFP cells as shown in Table 1. The same incubator (Binder KB-23) was used to maintain the cells at 45 °C under forced air convection.

Cell 1 was held at 3.65V at 45°C equivalent to a trickle charge at maximum SOC. Cell 2 was cycled at 1C charge with a cut-off voltage of 3.65 V and 6C discharge with cut-off voltage 2.00 V with no constant voltage or relaxation phase at either end. In the figures the convention of 1C for charging, and 6D for discharging is used.

Table 1. Accelerated aging specifications.

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

2.3 Data processing

In order to obtain useful information, the temperature measurements had to be smoothed appropriately as the data is often noisy. Smoothing was carried out carefully by using repeated moving average. The smoothed data was compared back to the original temperature data to make sure it did not deviate significantly from the original curve shape and characteristic.

2.4 Pulse loading with OCV extrapolation method

As mentioned, pulse loading was carried out to determine the total overpotential and the OCV during charge and discharge. Conventionally this is done by loading the cell with a short pulse to increment its SOC and then rested for few hours to reach thermodynamic equilibrium. While this provides useful information, the method can take hours if not days to complete.

Merla et al. developed a novel method called the OCV extrapolation method which uses a specific algorithm to accurately extrapolate the OCV of the cell using only the first few seconds of rest data. The method has been tested for both charge and discharge for both NMC and LFP cells. This significantly cuts down the time required for the test only adding a couple of seconds for each data point to a constant current loading. Hence this method allows for the determination of OCV and internal resistance profile across the cell SOC in a normal charging/discharging time. This paper will not go into the details of the algorithm which is currently under writing in another work, however it is not too dissimilar from the original GITT method [24].

In this work, the pulse loadings were carried out using 10 A constant current (0.5 C) discharge pulse for 60 seconds followed by 6 seconds of rest from 3.65 V to 2.0 V at approximately 20 °C. The same procedure was repeated for charge to observe the difference in performance.

3. Results & Discussion

3.1 Capacity fade

The capacity fade of the cells, shown in Fig. 1, is taken from the loss of Ah compared to the Ah measured when the cell was fresh. The capacity is determined through a 0.5C discharge between 3.65 V and 2.0 V with a constant voltage hold until the current was 0.1 A. The tests are carried out on both cells every 4 days. The cycled cell was cycled approximately 90 times every 4 days. In order to stabilize the cell condition after accelerated degradation, 3 charge/discharge pre-cycles are conducted before each characterization. Kassem et al, employed a similar process [20].

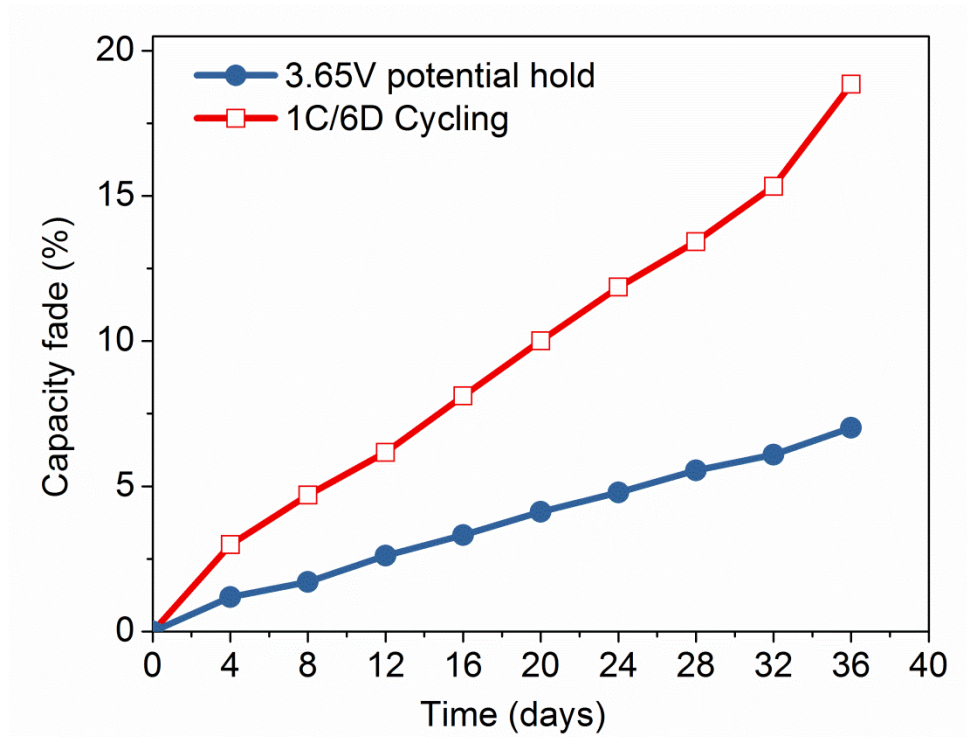


Figure 1. Capacity loss measurement of the 2 cells after accelerated degradation (0.5C discharge and constant voltage hold at 2V until current has decayed to 1%). The cycled cell had approximately 90 cycles per 4 days.

As seen from the capacity loss in figure 1, the cycled cell shows more than two times as much capacity loss as the cell held at high potential. This could be since during the cycling process, SEI cracking can occur leading to a faster rate of SEI growth on the newly exposed electrode surfaces. Due to this process, more lithium is consumed by forming the new SEI [14,25,26].

In addition, the surface temperature of the cycled cell almost reaches 60 °C during the cycling process inside the incubator, whilst the high potential cell remains close to 45 °C. According to Kassem et al, capacity loss is faster for cells stored at 60 °C compared to 40 °C [20,26]. Moreover, according to [4], high cycling rate enhance capacity fade rather than high SOC which matches our results. The results presented here are therefore a consequence of multiple degradation mechanisms occurring and interacting with each other. The purpose of this work, was not therefore,

to categorically prove that degradation specific consequences could be diagnosed, which would require a large statistically relevant sample size, but to demonstrate that DTV is a promising technique for lithium ion batteries with lithium iron phosphate cathodes.

3.2 Internal Resistance

The internal resistances of the cells are measured using pulse charge and discharge with the OCV extrapolation method.

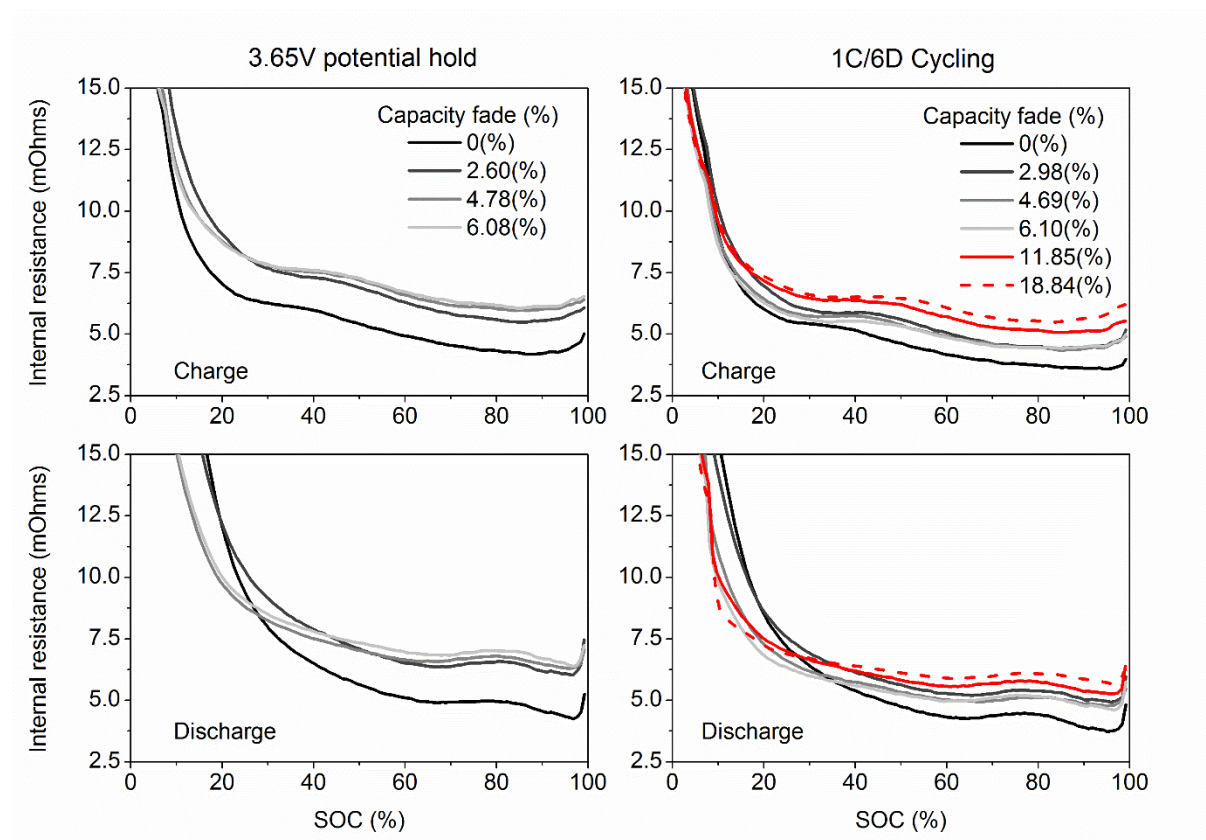


Fig.2 Internal resistance calculated from OCV Extrapolation for the 2 cells at characterisation cycles with roughly equivalent capacity fade after accelerated degradation for both charge and discharge

Fig.2 shows the internal resistance of these two cells at various stages of accelerated aging process.

It indicates the progression of total internal resistances. It can be observed that the internal resistance rapidly increases below 20 % SOC when charging and below 20-50% when discharging. It can be interpreted that this change corresponds to the increasing charge transfer and diffusion

resistances at lower SOC. A steady increase in all resistance parameters can be seen in both cells.

The main cause of this resistance rise has previously been attributed to an decrease in the charge-transfer kinetics and other interfacial contributions [20]. The power fade of the high potential cell is slightly higher than the cycle cell. This could be due to several degradation mechanisms. The trickle charging at 100% SOC may have induced lithium plating which would spontaneously react with the electrolyte to form SEI. However, even this level of analysis based upon the resistance and capacity measurements alone is straying into conjecture. Essentially these two techniques on their own are not sufficient to properly diagnose the state of a cell, and to confirm these hypotheses or not, any further analysis requires the use of ICA or DTV.

3.3 Differential Thermal Voltammetry

Fig.3 shows the results from DTV for the two cells. The peaks represent regions on the discharge curve where the voltage is not changing rapidly, but significant heat is generated. A transition between peaks is typically a result of the voltage changing rapidly, and is indicative of one of the electrodes undergoing a phase transition, similarly to ICA. A significant difference between ICA and DTV is that negative peaks are possible, as the temperature can also decrease if the entropic heat absorption from an endothermic reaction in an electrode is significantly larger than the enthalpic heat generation at that current. Negative peaks will disappear and become positive as the current increases, as the rate of entropic heat generation scales linearly with current whilst enthalpic heat generation scales by the square of current. The total amount of entropic heat generation should therefore be close to constant. It should also be mentioned that a negative peak which arises from dominating entropic heat absorption flips positive when the direction of the current is changed as the endothermic reaction will become exothermic in a reverse reaction.

Unlike other intercalation cathodes, where the lithium ion concentration in the cathode changes monotonically and relatively uniformly throughout, for LFP cells individual cathode particles undergo a phase transition from the lithiated form of LFP to the de-lithiated form via a domino-cascade mechanism [27]. This leads to the characteristic voltage plateau caused by the almost constant

potential of the cathode. This means that the DTV technique is not very sensitive to the LFP and the peaks therefore represent different stages in the graphitic anode, with peak transitions representing the transition between the different stages/phases of the graphite as it is lithiated/de-lithiated.

DTV is carried out at 10 A (0.5 C) and 40 A (2 C) constant current charge/discharge between 3.65 V and 2.0 V at approximately 20 °C. 0.5 C and 2 C are chosen in this work to represent slow and fast charging applications. Ideally the current should not be lower than 0.5C to have measurable heat generation and no higher than 3C to avoid enthalpic heat masking the entropic heat generation.

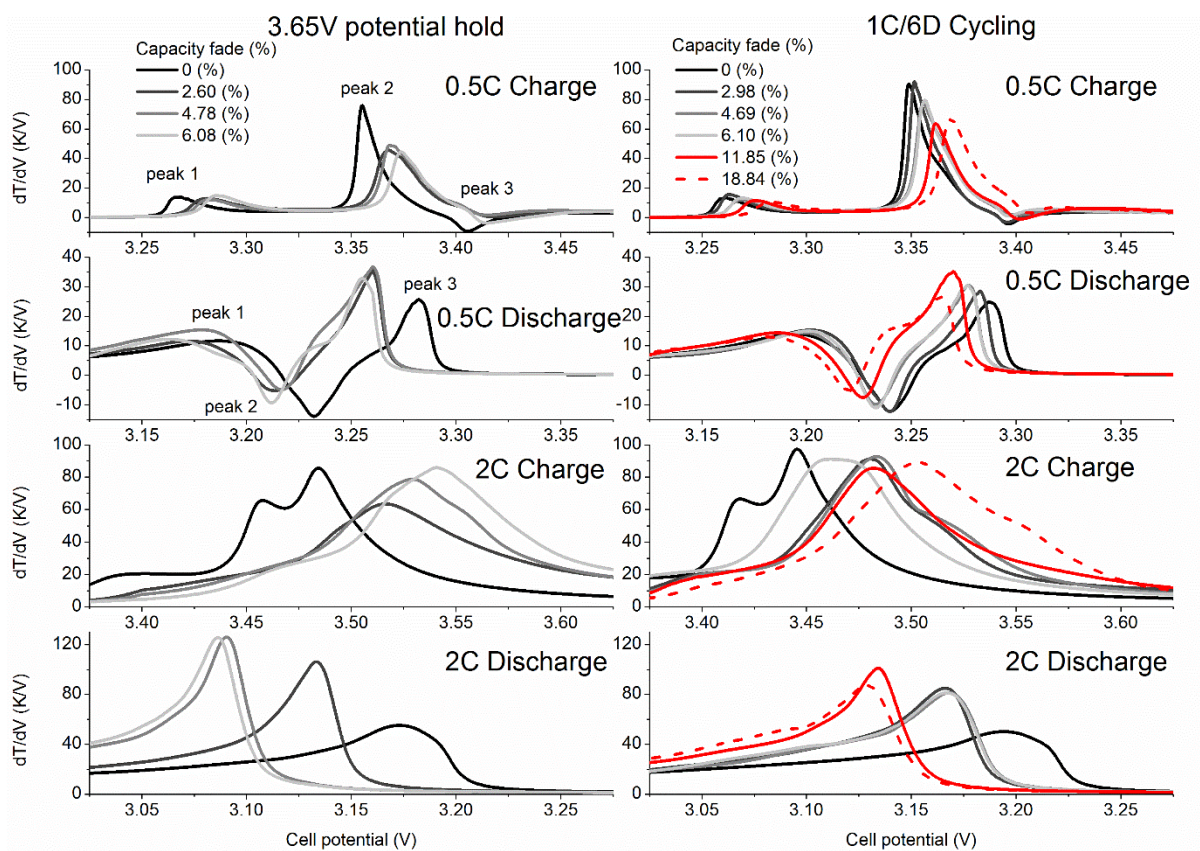


Fig.3 DTV results for the two cells at different C rates and various stages of the ageing process.

It can be seen that DTV at 0.5C generates curves with several peaks including a negative peak which comes from the endothermic entropic heat. On the other hand, DTV at 2C generates curves with just one maxima except for the fresh cell charge. In this case, the several peaks which can be seen at 0.5 C merge at 2 C rate as concentration and thermal gradients combined with current inhomogeneities

can result in different regions of the cell undergoing transitions at different times, broadening the peaks leading to overlaps [28].

It can be noted that the peak position shifts towards higher potential at charge and lower potential at discharge as the cell ages. This is due to the greater overpotential as a result of the increasing internal resistance caused by degradation. These results match the internal resistance results calculated by the OCV extrapolation method. The term overpotential is used in this paper to describe the difference in the observed voltage from the thermodynamic potential of the cell.

For a real in-operando diagnostic technique a full spectra analysis is unlikely to be possible or necessary. Instead is desirable to fit and analyse peak parameters, and then compare how simple measures such as peak height, position or width correlate with degradation. Fig. 4 and 5 show the evolution of the peak parameter for the largest positive peak for the two cells at different C rates under both charge/discharge.

The largest positive peak is chosen as it has the clearest and most consistent shift. It can be said that DTV peak parameters could be tracked and fitted to models and theory in the same way as ICA, as reported by Berecibar et al. [23].

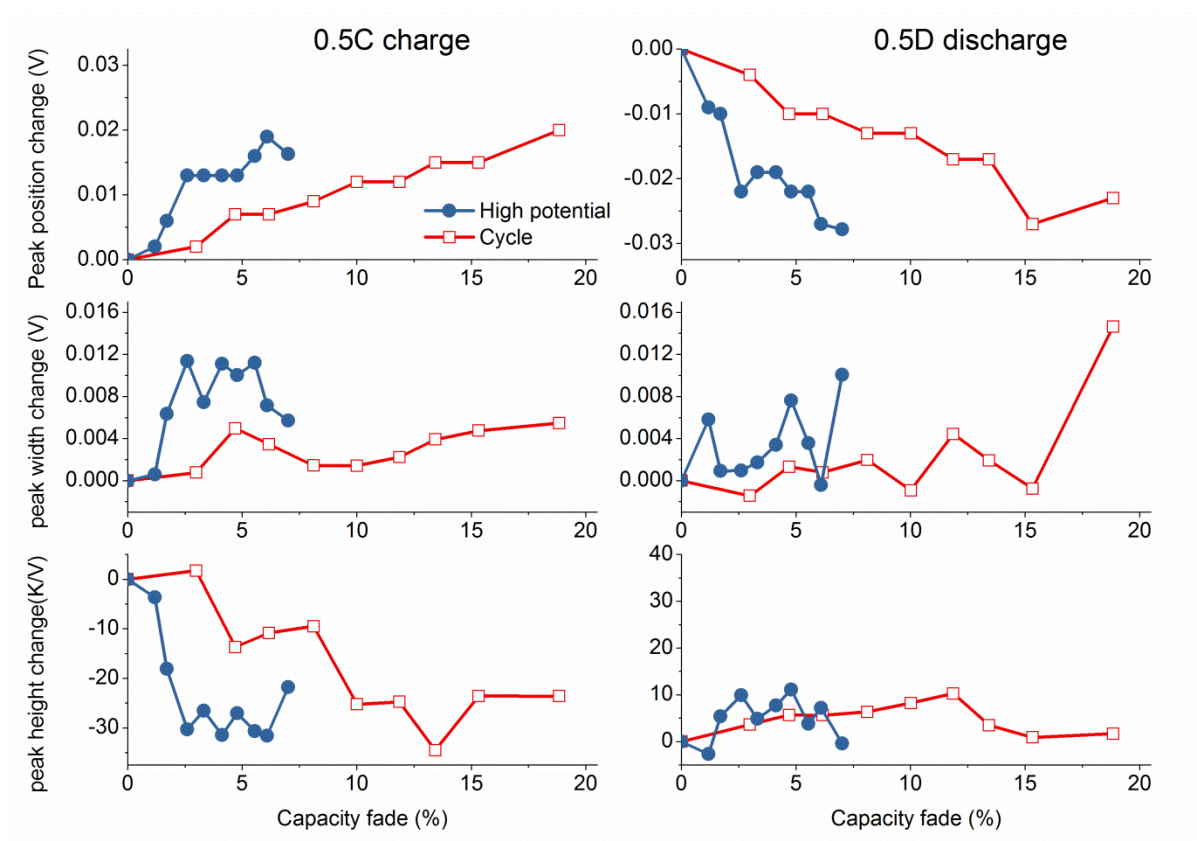


Fig.4 Peak parameters measured at 0.5C and 0.5D at approximately 20 °C at various stages of the ageing process.

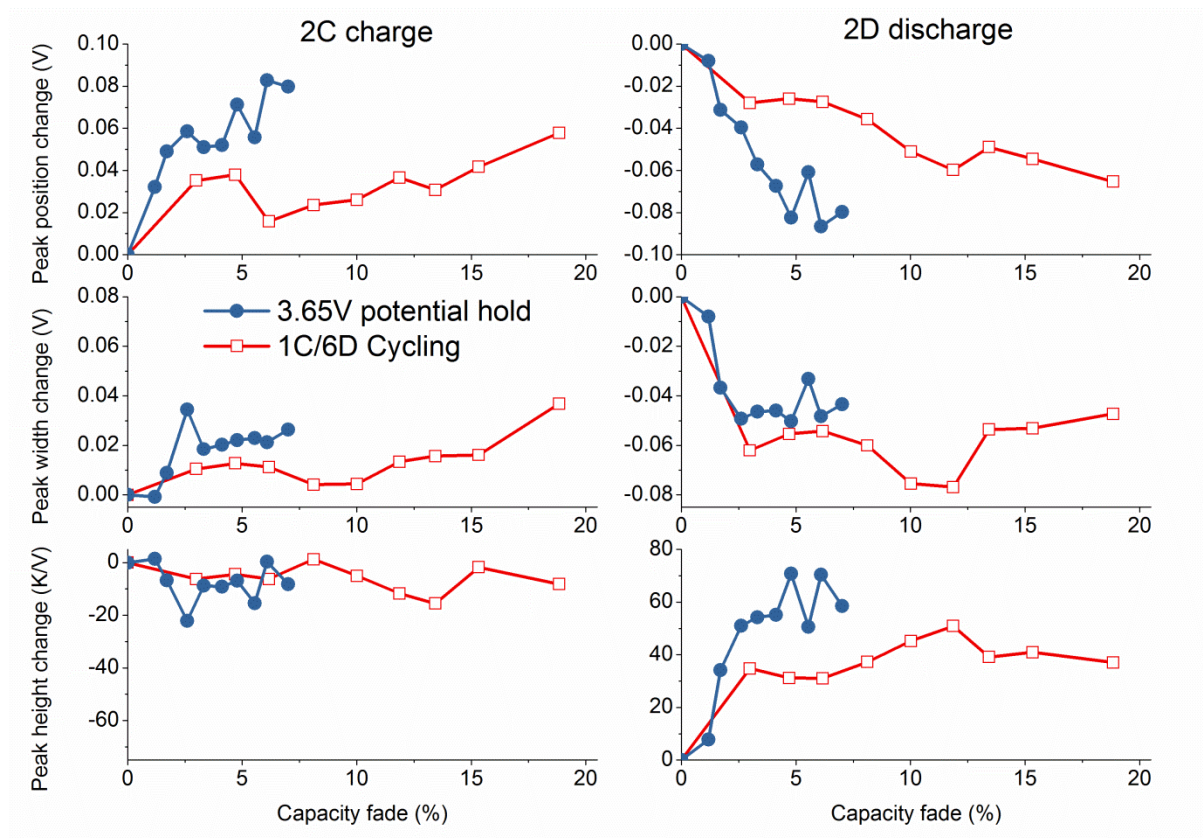


Fig.5 Peak parameter evolutions measured at 2C and 2D at approximately 20 °C at various stages of the ageing process.

The extracted peak positions show a steady shift to higher/lower potentials which is greater at 2C than 0.5C, which can be explained by the greater overpotential of the cells during charge/discharge due to the increasing cell impedance which is consistent with the internal resistance results shown in Fig. 2.

As mentioned previously, the peaks broaden and can overlap as a result of concentration and thermal gradients within the electrode. Degradation in diffusion resistances and reaction kinetics can enhance these gradients. Increase in peak width as seen during charging DTV, provides indication of this aging process in both cells. As the area underneath a peak correlates to the capacity within the combined electrode phases, the height of such cells are in turn seen to decrease. This therefore presents a challenge when using DTV in-operando, as reliable use of the technique will depend upon good battery pack design to prevent the occurrence of significant thermal

gradients. This is important for other reasons, as thermal gradients can themselves cause accelerated degradation [28].

For 2C charging the peak height remains relatively constant, whilst the peak width increases slightly. This must mean that the total heat generated increases slightly, which is consistent with the increase in resistance. In contrast for 2C discharging, the peak height increases significantly, with a small decrease in peak width, suggesting a complex interplay between the total heat generated. Increasing peak heights can be considered to be due to the increase in resistance, generating more heat. As the peak width is measured at its half-height, such peaks narrow as the cell degrades. It can be inferred from this result that there may be a greater concentration gradient in the electrodes during a charge process and that the entropic heat is net positive during a discharge process. The different patterns in behaviour during charge and discharge demonstrate that different information can be inferred from each loading.

From these results it can also be inferred that above 2C the enthalpic heat would begin to dominate and the peak height should increase exponentially. For 2D discharging, the entropic heat from peak 2 is positive and hence the increase in enthalpic heat as the cell resistance increases is far more apparent, hence the peak height increases as the cell ages. These results correlate well with the increase in internal resistance. Thus at 2C/D the peak position and peak height are both strongly correlated to increasing resistance. This conclusion is consistent with the previous conclusions of Merla et al [14].

It can be seen in all the results that although the capacity fade measurements are monotonous the DTV results are not. This clearly presents a challenge when considering the use of DTV for in-operando diagnostics, particularly if those peak parameters are used to estimate important information for the user or that may affect how the cell is used in the future. Challenges that remain to be overcome involve errors in the temperature measurements, the effect of unequal heat

transfer as the cell heats up differently as it ages and challenges in processing the data to obtain the peak parameters using standardised procedures and not human assisted interpretation.

3.4 Comparing capacity fade to peak parameters

Berecibar et al. [23] reported that phase transitions could be used as markers for SOC during the charge discharge curves for LFP and that it was therefore possible to diagnose SOH for partial cycles. As seen in previous publications on SOH tracking using ICA curves, a selection process is required from a number of possible curve features such as peak-to-peak distance to determine which feature of interest is the most applicable for SOH tracking [29,30].

In order to test if this is possible for DTV the peak-to-peak capacity is compared against total capacity for the charge at 0.5C and discharge at 0.5D as shown in Fig. 6, and the relative decrease in peak-to-peak capacity compared to total capacity is shown in Fig.7. It can clearly be seen that there is a direct correlation between the peak-to-peak capacity and total capacity for the cycled cell, suggesting that the peak position parameter could be used for SOH diagnosis in an application.

There is a weaker correlation for the cell held at high potential during charge DTV, the result appears too noisy to infer significant information. It is observed that peak 1 to peak 3 distance taken during a discharge cycle is the most encouraging with similar linear slopes relating the peak-to-peak distance with total capacity fade.

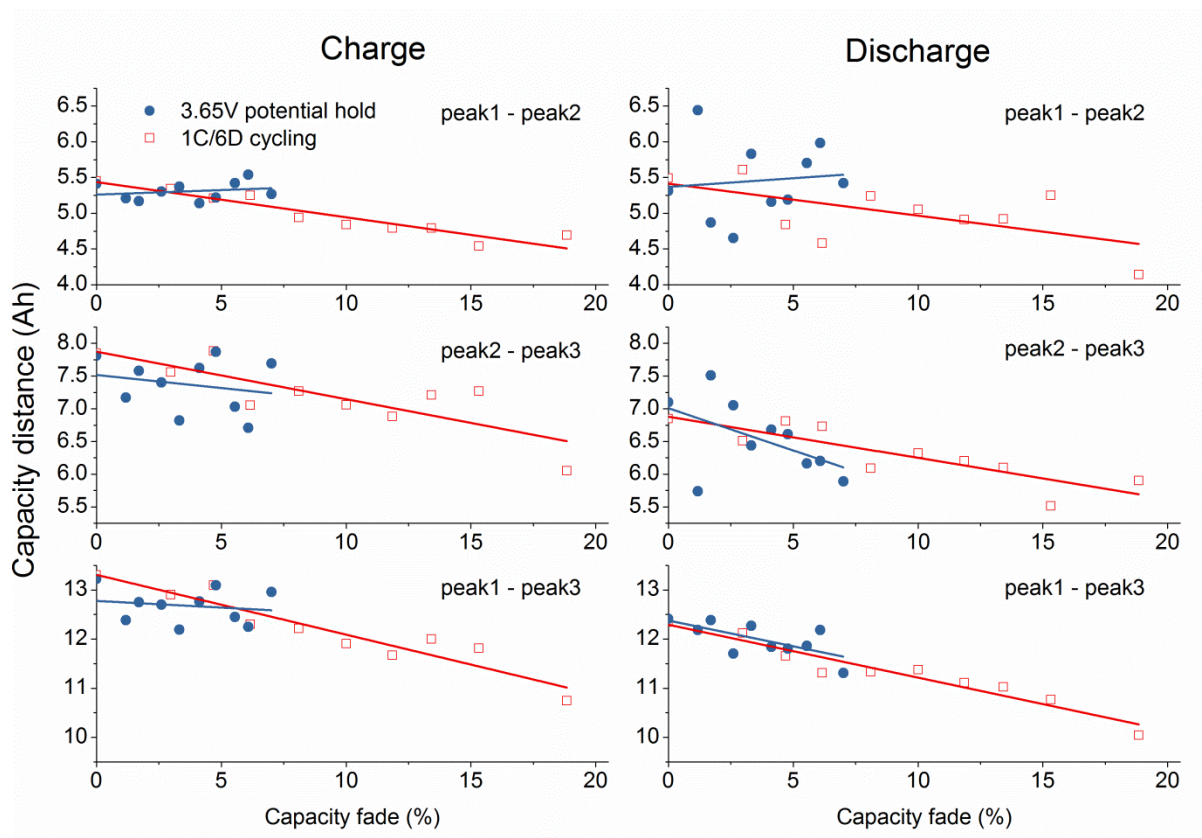


Fig.6 Peak-to-peak capacity compared to total capacity at 0.5C and 0.5D at approximately 20 °C at various stages of the ageing process.

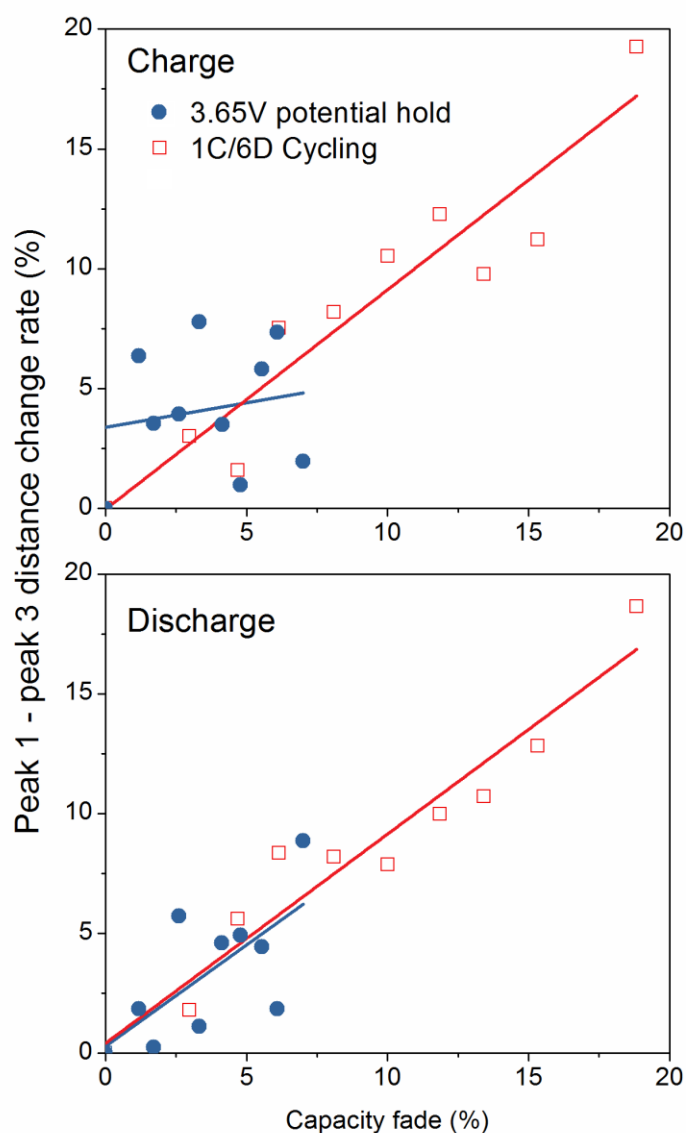


Fig.7 Relative change in peak-to-peak capacity compared to relative change in total capacity at 0.5C and 0.5D at approximately 20 °C at various stages of the ageing process.

4. Conclusion

Lithium iron phosphate batteries were aged in two ways, by holding at a high potential corresponding to 100% SOC and cycling at 1C/6D at elevated temperature. In both cases, differential thermal voltammetry (DTV) was capable of diagnosing degradation in a similar way to incremental

capacity analysis (ICA). It was possible to directly correlate peak parameters with capacity fade, resistance increase and inhomogeneous electrode performance suggesting that the technique could be used for SOH estimation in real applications. There was good correlation between the peak-to-peak capacity and total capacity fade for the cell cycled at elevated temperature, suggesting that complete charge or discharge (i.e. returning close to 100% or 0% outside the hysteresis region) would not be necessary to estimate SOC or SOH for cells used in this way.

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