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The impact of high-frequency-high-current perturbations on film formation at the negative electrode-electrolyte interface

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ABSTRACT

Long term ageing experimental results show that degradation resulting from coupled DC and AC current waveforms lead to additional degradation of lithium-ion batteries above that experienced through pure DC cycling. More profoundly, such experiments show a dependency of battery degradation on the frequency of AC perturbation. This paper addresses the underlying causality of this frequency dependent degradation. Cell autopsy techniques, namely X-ray photoelectron spectroscopy (XPS) of the negative electrode surface film, show growth of surface film components with the superimposition of an AC waveform. XPS results show that high frequency AC perturbations lead to the increased formation of a passivating film. In order to determine the cause of this increased film formation, a heterogeneous electrochemical model for the $LiNiCoAlO_2/C_6$ lithium ion battery coupled with governing equations for the electrical double-layer and solid electrolyte interface film growth is developed. Simulation results suggest that the increased growth of surface film is attributed to frequency dependent heat generation. This is due to ion kinetics in the double layer which are governed by the Poisson-Boltzmann equation. Additional thermal and reference cell relaxation experiments are undertaken that further corroborates the conclusion that heat generation within the battery is a function of the AC excitation frequency through resistive dissipation and the entropy of the cell reaction.

1. Introduction

Lithium-ion (li-ion) cells are recognised as a central technology in the process of achieving a clean and sustainable energy future through the electrification of road transport and the use of grid-connected energy storage to underpin the increased use of renewable energy sources [1,2]. Within each application, a key enabling technology is the design and integration of the power electronic subsystems that are required to manage the flow of energy [3]; such subsystems are known to generate undesired electrical noise [4–6]. For example, Fig. 1 shows the current waveform from charging a Nissan Leaf vehicle using a commercially available 3 kW Eltek Valere bi-directional vehicle charger. Fig. 1 highlights the measured harmonic content present on the electrical input to the battery.

High frequency current oscillations, or ripple, if unhindered will add a further perturbative load onto the vehicle's battery system. In recent work, Uddin et. al. [7] measured the electrical noise on the DC link of a high voltage bus on a pre-production series hybrid electric vehicle during a regenerative breaking event [7]. This data was used to define the current waveforms that batteries are exposed to during typical electric operation. Long term battery degradation resulting from cycling batteries under such waveforms was studied in [7]. The authors show that exposing the battery to coupled direct current (DC) and alternating currents (AC) lead to additional battery degradation that is related to the frequency of the perturbative ripple current. Through the experimental data presented, the authors were able to quantify the impact of AC excitation at the cell-level. However, the authors were not able to provide any reasoning for the battery degradation. Furthermore, given the novelty of the result presented [7], it was not possible to explain the causality of degradation due to AC ripple excitation directly from literature.

This paper extends the research presented in [7] by seeking to explain the underlying causality of degradation resulting from high frequency ripple current. This is achieved through a combination of further experimental analysis and novel mathematical modelling.

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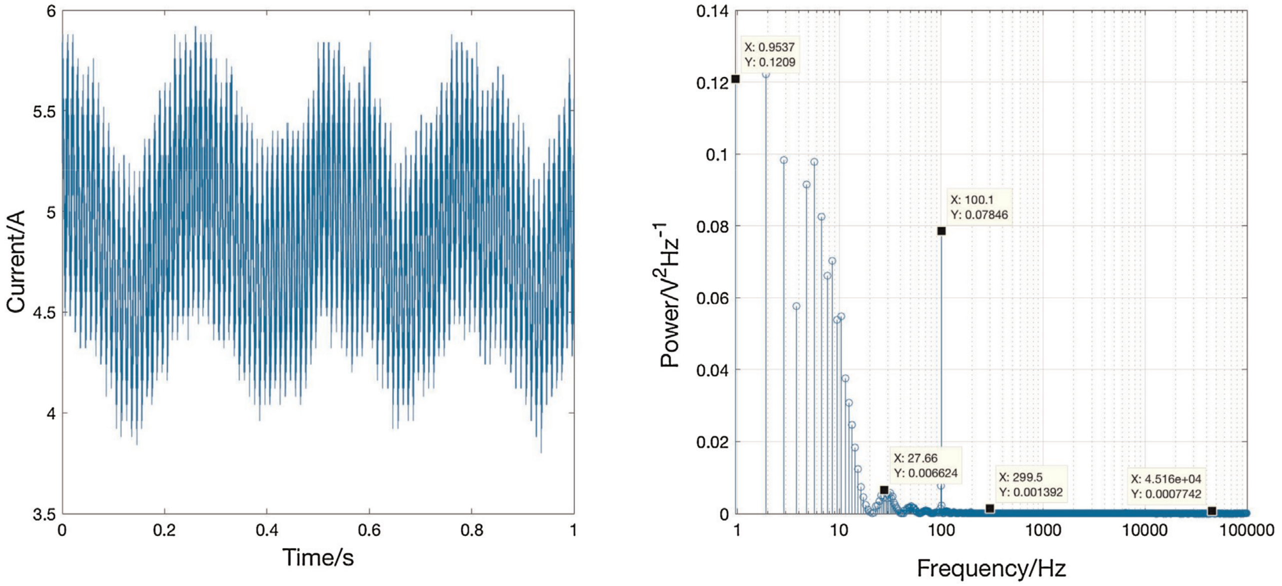

Fig. 1. The left hand panel shows the measurement of a coupled DC-AC current. The scope settings were: 100ms per division, with 10^6 samples taken per second. The right hand panel is the power spectrum of the measured current.

X-ray photoelectron spectroscopy (XPS) is employed to study the degraded cells used in our previous work [7]. A heterogeneous electrochemical model based on continuum theory has been developed and used to investigate the dependency of cell degradation on the frequency of an AC perturbation. The model relates battery degradation to the frequency dependant heat generation in the electrical double layer resulting from superimposed AC loads which is known to promote more pronounced growth of solid electrolyte interface (SEI) film [8]. Thermal and reference electrode relaxation experiments are presented that demonstrate the processes involved, to further understand and explain battery degradation when the cell is exposed to AC current excitation.

This paper is structured as follows: in the next section, experimental methodologies pertaining to results presented in this paper are agglomerated and presented. In Section 3, a heterogeneous electrochemical model that accounts for ion dynamics in the electrical double-layer through the Poisson-Boltzmann equation is presented. The model suggests that the cause of cell degradation under coupled AC and DC waveforms is the increased heat generation. The model results are substantiated by experimental results presented in Sections 4. Long term cell ageing test results, where cells were cycled 1200 times under an AC and DC coupled waveform, are presented; XPS autopsy results for these cells show a frequency dependant growth of surface film. Finally, in Section 5 we conclude and state further work.

2. Experimental

2.1. Long Term Ageing Test

It is beyond the scope of this paper to explain, in detail, the original experimental ageing study. This work is presented in [7]. A full description of the aims and objectives, the methods and equipment employed are presented. However, for completeness a brief summary is provided in this subsection, highlighting key aspects of the work.

Fifteen commercially available 3.0 *Ah* 18650-type cells were cycled [7]. Each cell had a LiC_6 negative electrode, $Li(Ni_{0.822}Co_{0.148}Al_{0.030})O_2$ (NCA) positive electrode, separated by a polyethylene separator, sandwiched between two current collectors and immersed in an electrolyte solution comprising of ethylene carbonate (EC), ethyl methyl carbonate (EMC), vinylene carbonate (VC) and $LiPF_6$ salt.

Each cell was cycled using a DC current signal (I_{DC}) superpositioned with an AC perturbation $I_{AC}\sin(\omega t)$ such that the overall current (I) waveform was:

$$I = I_{DC} + I_{AC}\sin(\omega t) \tag{1}$$

with a resulting cell potential:

$$V = V_{DC} + V_{AC}\sin(\omega t - \theta) \tag{2}$$

where θ is a phase shift between the cell potential and current waveform. The test signals were generated using a bespoke amplifier to generate the AC waveform and a Bitrode cell cycler to generate the DC load profile. In addition, a Tektronix non-contact current probe and oscilloscope was used for data acquisition and test monitoring. A LAUDA heating and cooling system was used to ensure that the ambient temperature was maintained at 25°C.

The DC portion of the cycle started with a $0.8C_{cycle}$ discharge (where C_{cycle} is the de-rated battery C-rate, i.e., the value of retained discharge capacity after an ageing characterisation test) from 95% SOC_{cycle} to 65% SOC_{cycle} (where SOC_{cycle} is the state of charge defined by C_{cycle}). Following a rest period of 10 minutes, each cell was then charged using a standard Constant Current–Constant Voltage (CC-CV) protocol, in which the cell was charged (CC) to the upper cell potential limit of 4.1 *V*(corresponding to 95% SOC_{cycle}) at which point charging continued using a CV method until the value of current reduced to 0.15 A. Superimposed onto the DC cycle was one of four AC current excitations, of frequency: 10 *Hz*, 55 *Hz*, 254 *Hz* and 14.8 *kHz*–with a peak-to-peak current of $1.2C_{cycle}$. To improve the robustness of the test method and the efficacy of the results, three cells of the same type were exercised using each current waveform defined above.

Ageing characterisation was carried out after 300, 600, 900 and 1200 complete charge–discharge cycles. The characterisation tests involved a 1 C capacity retention tests; pulse power tests using 10 second pulses at 20%, 40%, 60%, 80% and 100% of the manufacturers recommended maximum continuous charge and discharge current at 90%, 50% and 20% state of charge (SoC); electrochemical impedance spectroscopy tests were also carried out at 90%, 50% and 20% SoC using a Solartron ModuLab EIS System.