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AN EXPLORATION OF LI-ION CELL RELAXATION USING EIS

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KEYWORDS

EIS, impedance, Li-ion battery, relaxation, testing

ABSTRACT

This paper describes a systematic study of the effect of cell relaxation after a charge or discharge event. The EIS technique was used to investigate how the properties of the cells changed with time after charge or discharge up to a maximum of 15 hours. It was found that different chemistries show different relaxation rates and frequency dependence of R_o and R_d. The cells still showed a relaxation at 15 hours after a charge/discharge event. A suggested compromise of measurement accuracy and test length is to measure the properties of cells 4 hours after a charge/discharge event.

I. INTRODUCTION

Lithium-ion batteries have been common in portable consumer electronics since the early 1990. They have high energy density, high power density, long cycle life, low self-discharge and are also environmentally friendly compared to other type of batteries [1-3]. In recent years, lithium-ion batteries have become the main interest for high power and high energy storage systems like battery electric vehicles (BEV) [1, 4-8], power distribution grids [8-12], wind & solar battery systems [8, 9, 13]. Power and energy density plays a significant role in selecting a battery system for these types of applications.

The maximum power and energy that a battery can deliver are directly related to the impedance of the battery. The impedance of a battery cell defines how quickly the cell voltage will reduce during discharge and how fast it will increase during charge. To maximize the lifetime of a cell it needs to operate within a defined voltage window. Operating beyond this voltage window also poses safety risks.

The impedance of a battery cell is highly dependent on the chemistry, temperature, state of charge (SoC), age and amplitude of charge/discharge current. Extensive of work has been done to study cell impedance; the relationship between impedance and SoC has been developed by researchers [14-18]. Another group of researchers have presented temperature dependency of impedance [17-24]. In contrast to the SoC and temperature effect, age and charge-discharge current amplitude have received less attention. Ratankumar *et al.* and Buller *et al.* gave an indication of the effect of the current amplitude on cell impedance [25, 26]. Vetter *et al.* explained the root cause of the impedance rise of a cell with ageing [27]. It is also reflected by the results presented by other researchers [17, 28-31].

Despite several studies investigating the use of EIS to estimate SoC and SoH in electric vehicles and electrode properties, limited attention has been given towards understanding the effect of relaxation time prior to performing an EIS measurement. To ensure its repeatability and reproducibility in a vehicle or laboratory environment, it is crucial to develop suitable experimental protocols which minimise uncertainties. In this study, the authors investigated, what is believed to be the first study of the effect of relaxation time on EIS measurement of several cell chemistries and several cell formats.

II. EXPERIMENTAL METHOD

A. Cell details

EIS tests were carried out on commercially available lithium-ion cells of different chemistries and different cell-format. Seven cells were selected for this study with capacity ranging from 2.2Ah to 40Ah. All cell details are listed in Table 1.

Table 1 Cell details

Cell Manufacturer	Chemistry	Capacity (Ah)	Nominal Voltage (V)	Format
1	NMC	40	3.70	Pouch
2	Li-Titanate	13	2.26	Pouch
3	Mixed Oxide	17.5	3.60	Pouch
4	NMC/LCO	2.2	3.70	Cylindrical
5	LMO	3.4	3.60	Cylindrical

B. Test matrix and EIS test details

EIS tests were performed in galvanostatic mode at a frequency range of 100 mHz to 10 kHz and ten frequency points per decade. The amplitude of the current applied was adjusted for individual cell type within the range of C/25 to C/13 Root Mean Square (RMS) value. The spectra were obtained without any superimposed DC current.EIS tests were

EIS test were performed on each cell every 10 min for 15 h after adjusting to 50 % state of charge (SoC) using 1C charge/discharge current, at 25 $^{\circ}$C unless otherwise specified. The SoC, charge/discharge rate and temperature are selected to represent normal operating condition of the cell. The entire experiment was performed within a temperature controlled chamber using a battery cell cycler to adjust SoC. The EIS test was performed using a potentiostat outfitted with a 2A booster card.

III. RESULTS AND DISCUSSION

The Nyquist plots obtained from cells 1 to 5 at 25 $^{\circ}$C with SoC of 50 %, adjusted with a discharge rate of 1C are shown in Fig. 1. Based on the observations in Fig. 1, it is noticeable that relaxation process changes the total impedance of the cell. It is also evident that the pure resistance of the cell R_o does not change nor has a minor change with diffusion process except cell 3. This can be explained from the origin of pure ohomic resistance of the cell. Pure ohmic resistance mainly originate from resistance of electrolyte, electrode-electrolyte interface and current collectors of the cell [17, 18, 22, 41, 42].

The total resistance of the cell R_d which incorporates pure ohomic resistance and electrochemical impedances of the cell defines the energy and power behaviour of an application. R_d is plotted against relaxation period in

Fig. 2. Depending on the cell, R_d was found at different frequencies; which is listed in Table 2. This variation can originate from cell chemistry, capacity, size, shape and temperature. Trend lines had been added to the graphs showing in Fig. 2. The trend has a generalized equation as shown in equation 1:

$$\boldsymbol{y = \alpha ln(x) + b} \qquad \text{Equation 1}$$

Values of α and b of this equation for different cells are presented in Table 2. The R^2 value of trend lines varies from 0.9581 to 0.9948, indicating good fit with data.

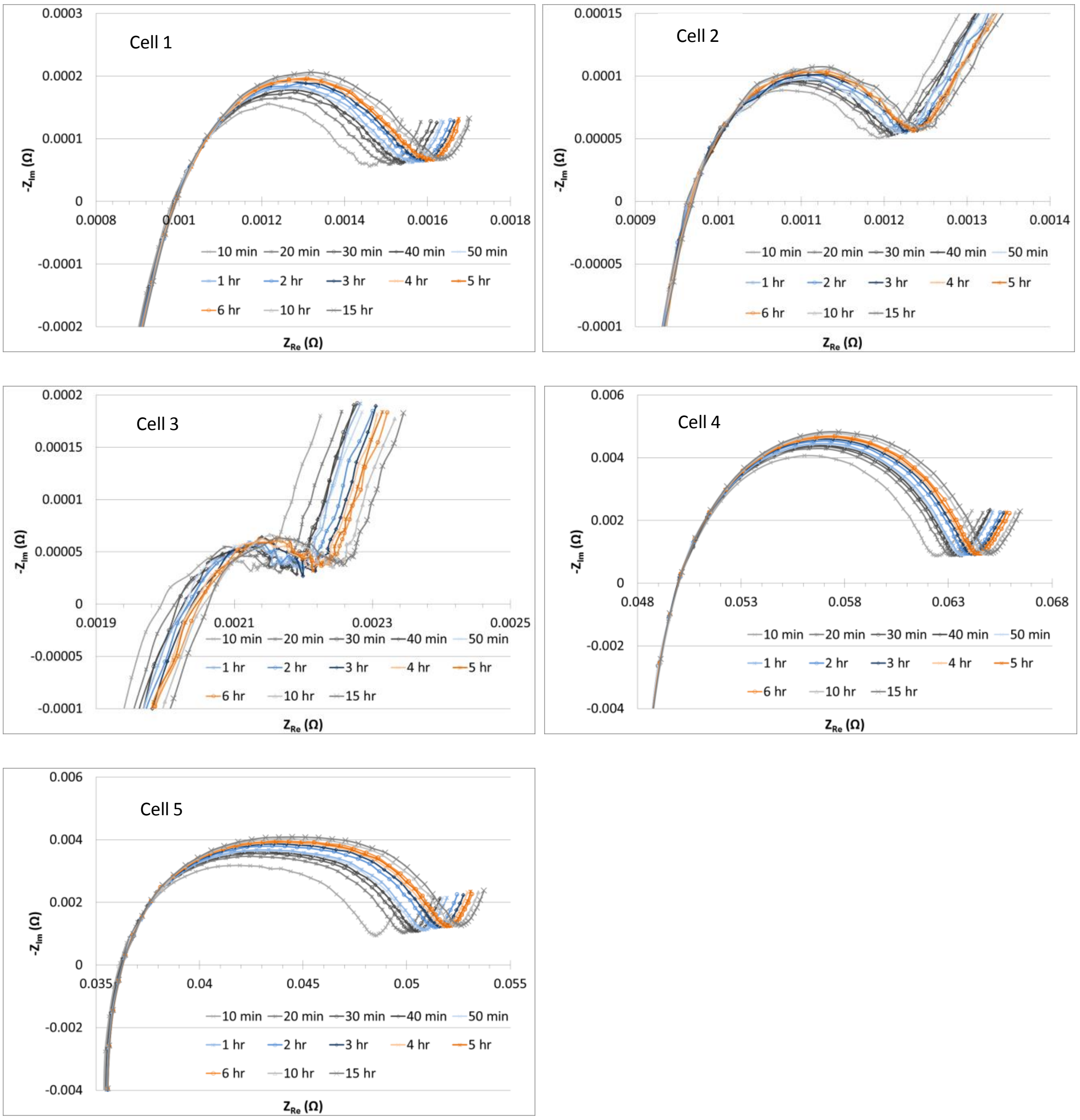

Fig. 1 Nyquist plots obtained after adjusting SoC to 50%, at 25°C using 1C discharge current (note: scale varies from graph to graph but the ratio between 'X' and 'Y' axis value remains same to show the change of shape).

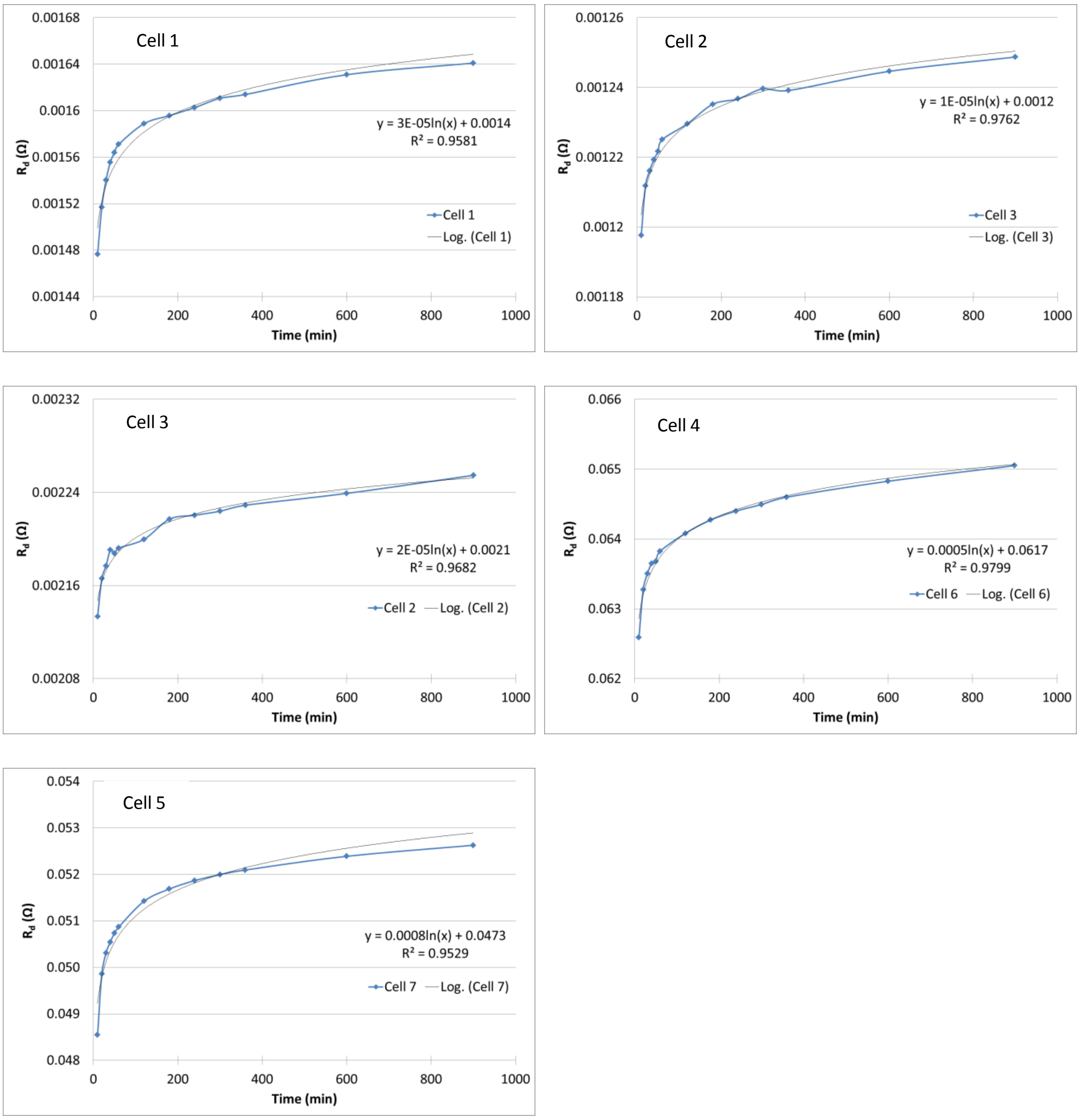

Fig. 2 Relaxation of R_d for different cell (a) for cell 1 R_d is at 0.63 Hz, (b) for cell 2 it is at 0.63Hz, (c) for cell 3 it is at 2 Hz, (d) for cell 4 it is at 1 Hz.

Table 2 Logarithmic parameters, value and associated frequency of R_d of the cells and value of R_o are listed.

Cell No.	Coefficient α	Constant b	R_d value at 15 h (mΩ)	Frequency of R_d (Hz)	R_o value at 15 h (mΩ)	Frequency of R_o (Hz)
1	3E-05	0.0014	1.64	0.63	1.00	251.2
2	1E-05	0.0012	1.25	2.00	0.95	158.5
3	2E-05	0.0021	2.26	2.51	2.07	79.43
4	5E-04	0.0617	65.05	1.00	50.15	794.33
5	8E-04	0.0473	52.63	0.63	36.41	1584.89

IV. CONCLUSION

Findings

- Different chemistries show different relaxation rates.
- 4 h is the suggested minimum waiting time before an EIS measurement should be taken.
- The relaxation process continues even after 15 h.
- The frequency of R_d and R_o depends on chemistry and capacity.

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