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Hierarchical degradation processes in lithium-ion batteries during ageing

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ABSTRACT

The ageing of lithium-ion battery (LIB) is critical from the application perspective. In this paper, an electrochemical based electrical (ECBE) model is developed to link the model parameters to specific ageing mechanisms. Based on the model parameterization, we report on time resolved degradation processes of LIB during the cycle ageing. The sequence of internal components degradation mechanisms in graphite/lithium cobalt oxide (LCO) coin cells subjected to up to 1000 galvanostatic charge-discharge cycles are revealed. It is found the LIB degradation proceeds according to a series of inter-connected processes, including: i) Solid electrolyte interphase (SEI) formation on the graphite electrode surfaces; ii) LCO phase transformation from active hexagonal to less active spinel phases; iii) Joule heating due to the increased cell resistance resulting in cracking and re-formation of SEI together with surface spallation at the LCO electrode, as well as degradation of the separator; iv) Active Li losses owing to metal plating on the electrodes during overcharge and overdischarge; v) Exfoliation of the graphite anode and the degradation of LCO cathode; and vi) Intergranular contact disconnection within electrodes. These processes contribute to the overall decay in the storage capacity and the LIB terminal voltage differently as shown experimentally.

1. Introduction

With the growing awareness of climate change (e.g. global warming) and energy crisis, battery-powered hybrid/electric vehicles (HEV/EV) are developed to reduce the cumulative greenhouse-gas (GHS) emission and dependence on fossil energy (e.g. gasoline and diesel) [1,2]. Lithium-ion battery (LIB) has been widely accepted as a promising candidate to be used in these HEV/EV since early 2000 s mainly due the high power and energy density, long cycle life, memoryless property and reasonably low cost [3–5]. The long cycle life of LIB is one of the most important advantages for its use in HEV/EV as it can help save cost and reduce environmentally hazard impact caused by the wastes from the batteries [6].

In an effort to extend the battery cycle life, comprehensive understanding of the underlying ageing mechanisms that cause degradation in its energy storage performance such as capacity loss and cell impedance raise is necessary. As an LIB ages it may be operated beyond its temperature and voltage stability windows, which accelerates the degradation of battery performance and may even results in catastrophic failures [7–9]. A better understanding of the root causes of degradation processes offers a possible strategy to act on them, therefore, extends battery's lifetime and safety [10–14]. However, the complexity of LIB system makes it challenging for the study of ageing. Capacity fade and cell impedance increase do not originate from one single cause but from several underlying processes which could be related to each other [15]. This requires the investigation of various degradation processes in LIB during charge/discharge cycles in order to determine the predominant degradation mechanisms at different time scales.

Extensive studies have been conducted on the degradation of cell components in LIB after prolonged cycling with experimental and

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Nomenclature

LIB	lithium-ion battery
ECBE	electrochemical based electrical
LCO	lithium cobalt oxide (LCO)
SEI	solid electrolyte interphase
AFM	atomic force microscopy
SEM	scanning electron microscopy
TEM	transmission electron microscopy
XRD	X-ray diffraction
NDT	non-destructive techniques
ECM	equivalent circuit model
emf	electromotive force
SoC	state of charge
OCV	open-circuit voltage
SA	simulated annealing
COV	cut-off voltage
CCCV	constant current/constant voltage
SoH	state of health
R_e	electrodes' ohmic resistances, ohm
R_{CT}	charge transfer resistance, ohm
C_{dl}	double layer capacitance, F
Z_{BV}	Butler-Volmer impedance, ohm
Z_W	Warburg element impedance, ohm
Q_m	maximum charge storage capacity of battery, Ah
Q_{max}	maximum capacity of electrode, Ah
m_1	effectiveness of the LCO cathode in storing Li-ions
m_2	effectiveness of graphite anode in providing its stored Li-ions
V_{emf}	emf of battery, V
U	dimensionless interaction energy coefficient
i	current, A
t	time, s
k	polarization coefficient, ohm
Q_d	discharge capacity of batterya, Ah
V_t	terminal voltage, V
V_{oc}	open circuit voltage, V
η	over-potential, V

Greek symbol

ζ	dimensional constant accounting for phase transition in equilibrium potential of two electrodes

Subscript

+	positive side
−	negative side
max	maximum

modelling approaches. For the experimental approach, characterization techniques such as atomic force microscopy (AFM) [16], scanning electron microscopy (SEM) [17], transmission electron microscopy (TEM) [18], Raman spectroscopy [19], X-ray diffraction (XRD) and neutron scattering techniques [19] are used. These techniques are mostly ex-situ and destructive because the investigations are conducted by cross-checking fresh and aged cells and compare their positive and negative electrodes in order to find out the morphological, electrical, and structural changes that occur during ageing. Experimental investigations require complex instruments and must be performed in controlled operating conditions that are both costly and not portable, which makes them unsuitable for the prognosis and diagnosis purposes. Nevertheless, these investigations provide valuable information on the degradation mechanism of LIB which will be referred to in this work.

The modelling approach is considered as in-situ non-destructive techniques (NDT) and very useful for prognosis and diagnosis. Modelling approaches with NDT can be divided into three groups, i.e. physical models, mathematical models, and electrical models [20]. Physical models explain the chemical and physical processes within the cells. Specific degradation mechanisms such as the electrode degradation and solid electrolyte interphase (SEI) are considered [21]. While physical models enhance our understanding of the degradation mechanisms, they are computationally intensive. Also, physical models mostly focus on one or two degradation mechanisms but ignore the others [22]. The microscopic approach of physical models also limits their practicality for industrial applications since different manufacturing technologies, cell design and raw materials used for fabrication will result in different models.

Mathematical models are based on either empirical or statistical methods. The empirical methods predict the capacity fade or resistance increase by fitting large amount of experimental data, and the accuracy depends on both the amount and accuracy of the measurement data which can be costly [23]. The statistical methods also require large data sets achieved by complex measurements in order to determine all the possible interactions on the degradation mechanisms. Although mathematical models allow for on-line estimation, the fitting and training processes are generally tedious [24]. Moreover, the mathematical models have no direct physical relationship between the model parameters and the battery characteristics, making them inappropriate for diagnosis purposes.

Electrical models are based on the equivalent circuit representation of key battery dynamics [25–29]. While the equivalent circuit model (ECM) is generally faster, depending on the algorithm used, not all the internal parameters of LIB are modelled as they are lumped together [30]. The maximum capacity of LIB, which is the most important parameter for the LIB ageing, cannot be modelled. This is because ECM does not model the degradation of the electromotive force (emf) and the degradation of various cell internal components, especially for the degradation of maximum storage capacity of the cell [23]. They thereby fall short to the prognosis and diagnosis.

An electrochemical based electrical (ECBE) model has been developed in our previous works [31–34]. The ECBE model is developed based on the first principle of electrochemistry, and then converts the corresponding partial differential equations into the circuit model. The ECBE model has been used to determine the maximum capacity of LIB at the beginning of each discharge cycle, and hence an accurate estimation of the State of Charge (SoC) [31]. It has also been used to examine and characterize the comprehensive effect of temperature on cycling aging rate in LIB when it is operating in the temperature range from 25 to 55 °C [32], and with this characterization, one can investigate the effect of abusive overcharge and high temperature on the degradation rate of all the internal components in a LIB, and identify the internal components in a cell that are most vulnerable to the specific abusive operation [33,34].

In this work, we further explore this ECBE model to study the degradation processes in LIB coin cells. The ECBE model is built to link the equivalent circuit parameters to the internal dynamics of LiB. In this way, the ageing process can be well interpreted by estimating the parameters of ECBE model from the charge/discharge curves. The proposed ECBE model-based estimation method is verified to determine the maximum charge storage capacity accurately with experimental data. Based on the ECBE model-based estimation, the degradation processes of graphite/lithium cobalt oxide (LCO) coin cells have been systematically studied. It is found the LIB degradation proceeds according to a series of inter-connected processes. The