Prediction of battery storage ageing and solid electrolyte interphase property estimation using an electrochemical model

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HIGHLIGHTS

- Electrochemical model to predict storage ageing under constant temperature.
- Model uses ageing data from cells at three different SoC for validation.
- Modified correlation to account for variation in side reaction current density.
- Prediction of SEI properties such as molecular mass, density and conductivity.
- This study allows development of a combined storage-cycling framework.

ARTICLE INFO

ABSTRACT

Ageing prediction is often complicated due to the interdependency of ageing mechanisms. Research has highlighted that storage ageing is not linear with time. Capacity loss due to storing the battery at constant temperature can shed more light on parametrising the properties of the Solid Electrolyte Interphase (SEI); the identification of which, using an electrochemical model, is systematically addressed in this work. A new methodology is proposed where any one of the available storage ageing datasets can be used to find the property of the SEI layer. A sensitivity study is performed with different molecular mass and densities which are key parameters in modelling the thickness of the SEI deposit. The conductivity is adjusted to fine tune the rate of capacity fade to match experimental results. A correlation is fitted for the side reaction variation to capture the storage ageing in the 0%–100% SoC range. The methodology presented in this paper can be used to predict the unknown properties of the SEI layer which is difficult to measure experimentally. The simulation and experimental results show that the storage ageing model shows good accuracy for the cases at 50% and 90% and an acceptable agreement at 20% SoC.

1. Introduction

With increased demand for portable electronic devices, penetration of vehicles with electrified powertrains and appeal of electricity storage in grid applications, research into lithium-ion batteries (LIB) has intensified. Within the class of LIB technologies, the Nickel-Cobalt-Aluminium (NCA) cell chemistry is favoured over other chemistries such as Nickel-Manganese-Cobalt (NMC) and Nickel-Manganese-Oxide (LMO) due to longer cycle life and relatively better power delivery capabilities, which is a requirement for many modern devices. However, very few studies have suitably documented the ageing performance of this particular cell chemistry under storage, a thermodynamic equilibrium state where LIBs spend most of their time. Thus, it

is important to understand the underlying nature of chemical reactions during battery storage to find the conditions that accelerate battery degradation and hence to suggest mitigation methods to enhance the life of a lithium-ion battery.

It is well established that elevated Temperature, high State of Charge (SoC), large Depth of Discharge (DoD) and large C-Rates accelerate the degradation reactions under cycling [1]. Existing ageing models such as those discussed within [2–6], are dominated by data-driven based approaches which directly relate the capacity of a battery to the stress factors or operating conditions. In the automotive industry, an electric vehicle (EV) spends 90% of the time in parked storage conditions [7,8], therefore the storage condition has a strong influence on the overall ageing of the battery. The parameters of a storage ageing

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Table 1
Newman model equations.

	Governing equations	Boundary conditions
Conservation of charge		
Electrolyte phase	$\nabla \cdot (\kappa^{eff} \nabla \phi_e) + \nabla \cdot \kappa_D^{eff}$ $\nabla In(c_e) + J_1 + J_s = 0$	$\left.\frac{\partial \phi_e}{\partial x}\right\|_{x=0} = \left.\frac{\partial \phi_e}{\partial x}\right\|_{x=L} = 0$
		$\left.\frac{\partial \phi_s}{\partial x}\right\|_{x=\delta^+} = \left.\frac{\partial \phi_s}{\partial x}\right\|_{x=\delta^+} = 0$
Solid Phase	$\nabla \cdot (\sigma_{eff} \nabla \phi_s) = (J_1 + J_s)$	$-\sigma_{s,n}^{eff} \left.\frac{\partial \phi_s}{\partial x}\right\|_{x=0} = \frac{-I_{app}}{A_n}$
		$= \sigma_{s,p}^{eff} \left.\frac{\partial \phi_s}{\partial x}\right\|_{x=L} = \frac{I_{app}}{A_p}$
Conservation of lithium		
Electrolyte phase	$\frac{\partial}{\partial t}(\varepsilon_e c_e) = \nabla \cdot (D_{e,eff} \nabla c_e) + \frac{1-t_0^+}{F}(J_s + J_1)$	$\left.\frac{\partial \phi_e}{\partial x}\right\|_{x=0} = 0, \left.\frac{\partial \phi_e}{\partial x}\right\|_{x=L} = 0$
Solid Phase	$\frac{\partial}{\partial t}c_s = \frac{D_s}{r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}c_s\right)$	$\left.\frac{\partial c_s}{\partial r}\right\|_{r=0} = 0, \left.\frac{\partial c_s}{\partial r}\right\|_{r=R_S} = \frac{-J_1}{a_s F}$
Kinetics		
Electrochemical reaction rate	$J_1 = a_{n,p} i_0 \left\{ \exp\left(\frac{\alpha_{n,p} F\eta}{RT}\right) - \exp\left(-\frac{\alpha_{n,p} F\eta}{RT}\right) \right\}$	
Exchange current density	$i_0 = F k_e (c_e)^{\alpha_a} (c_s^{max} - c_{s,e})^{\alpha_a} (c_{s,e})^{\alpha_c}$	
Overpotential for the positive electrode	$\eta_p = \phi_s - \phi_e - U$	
Overpotential for the negative electrode	$\eta_n = \phi_s - \phi_e - U_n - (J_1 + J_s)\frac{G_{SEI}}{a_n}$	
Overpotential for the storage ageing reaction	$\eta_s = \phi_s - \phi_e - U_{ref} - (J_1 + J_s)\frac{G_{SEI}}{a_n}$	

electrochemical model are crucial to the development of a comprehensive ageing model for the condition seen by a battery in real world applications. The development of a storage electrochemical model is therefore an important step to understand real world ageing.

Under an electrochemical modelling framework, the ageing reactions related to static and non-static conditions reduces to a single factor-parasitic ageing side reaction intensity, therefore quantifying this side reaction is important for an electrochemical model. Unlike cycling, certain chemical reactions, like the reactions contributing to SEI formation under storage conditions, are always active and cannot be stopped. Ramadass et al. [9] presented an electrochemical-ageing model which quantifies the side reaction and exchange current density for a SONY 18650 battery under cycling. The model is very successful in predicting SEI layer growth and degradation characteristics. Hence the electrochemical model is a suitable framework with the required flexibility to facilitate a study of the chemical reactions under different storage stress factors [10].

Very few works have compared the experimentally observed degradation characteristics with the properties of the SEI layer or chemical characteristics of a battery. Specifically nobody has previously attempted to electrochemically model and experimentally validate storage ageing which, the authors believe, is a knowledge gap which needs to be filled in order to achieve a comprehensive electrochemical model for real world battery use. The modelling approach presented in this work is an attempt to correlate the parameters of the SEI layer with experimentally observed degradation characteristics which the data-driven models have failed to demonstrate so far. Therefore, theoretical or experimental SEI layer property estimations are essential for the modelling framework adopted in this work. It is important to note that a sizable amount of work has already been done to analyze SEI layer composition, for example Aurbach et al. [11], discussed different layers of various compositions, properties and conductivity.

This paper focuses on two main aspects of storage ageing predictions: SEI composition-property estimation, and introducing a new methodology to develop a single side reaction parameter to represent storage ageing. A method to parametrise an electrochemical model for any cell chemistry is presented in Ashwin et al. [12] and this is used as the basis for parametrising the electrochemical model for storage ageing at different SoCs confined to the side reaction equation proposed

by Ramadass et al. [9]. A static storage experimentation is conducted where the cells are stored at constant temperature at 25 °C at three different SoC values, 20%, 50% and 90%. A sensitivity study is conducted for the first time by varying molecular weight and density of the deposit-key factors in deciding the SEI thickness. Further fine tuning of the conductivity is also needed to adjust the rate of capacity degradation. The second part of the work focuses on finding a single correlation for degradation reaction exchange current density for all storage cases considered. Often, the exchange current density for the side reaction is taken to be a constant value independent of SoC [9]. In reality, the side reaction can vary with SoC since the cell exhibits different degradation characteristics at different SoC. The correlations presented in Ramadass et al. [9] show similar degradation characteristics at lower and higher SoCs which is counter intuitive to observations. Therefore, the fitted correlation approach presented in this paper for the exchange current density for the entire SoC range can compensate for the deviation in reaction rate. The combined model is revalidated with the measured datasets to check the accuracy. This methodology can bridge the gap between data-driven and electrochemical models and the experimental data can be effectively used for parametrising an electrochemical ageing model.

To-date no one has generated a correlation based electrochemical model to predict storage ageing. To do this, the standard form of the solvent reduction side reaction was modified since it was originally derived for side reactions from cycling. In this initial work temperature is assumed constant and therefore the only variable is SoC. In this way the ageing effects can be isolated to the dependence of a single parameter which is not possible for the case of cyclic ageing. The key contribution of this work is an electrochemical model validated for storage rather than cycling which is a prerequisite for combined cycling-storage electrochemical model.

2. Governing equations

Storage is an operating condition where the externally applied current (I_{app}) and the intercalation current density (J_1) reduces to zero. This is a limiting condition for the Butler-Volmer equation which happens only when the over-potential of the intercalation reaction (η) is zero. Governing equations are presented in Table 1.