

Unravelling degradation mechanisms and overpotential sources in aged and non-aged batteries

A non-invasive diagnosis

Appiah, Williams Agyei; Rieger, Laura Hannemose; Flores, Eibar; Vegge, Tejs; Bhowmik, Arghya

Published in: Journal of Energy Storage

Link to article, DOI: 10.1016/j.est.2024.111000

Publication date: 2024

Document Version Publisher's PDF, also known as Version of record

Link back to DTU Orbit

Citation (APA): Appiah, W. A., Rieger, L. H., Flores, E., Vegge, T., & Bhowmik, A. (2024). Unravelling degradation mechanisms and overpotential sources in aged and non-aged batteries: A non-invasive diagnosis. *Journal of Energy Storage*, *84*, Article 111000. https://doi.org/10.1016/j.est.2024.111000

General rights

Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.

- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.



Contents lists available at ScienceDirect

Journal of Energy Storage



journal homepage: www.elsevier.com/locate/est

Research papers

Unravelling degradation mechanisms and overpotential sources in aged and non-aged batteries: A non-invasive diagnosis



Williams Agyei Appiah^{a, c, *}, Laura Hannemose Rieger^a, Eibar Flores^b, Tejs Vegge^a, Arghya Bhowmik^a

^a Department of Energy Conversion and Storage, Technical University of Denmark, Kgs. Lyngby 2800, Denmark

^b New Energy Solutions, SINTEF Industry, Sem Sælands Vei 12, Trondheim 7034, Norway

^c Faculty of Engineering and Science, University of Agder, 4879 Grimstad, Norway

ARTICLE INFO

Keywords: Lithium-ion batteries Overpotentials Pseudo-two-dimensional model In-situ diagnosis Degradation mechanisms

ABSTRACT

In-depth analysis of overpotentials in complex electrochemical systems such as lithium-ion batteries is necessary for enhancing their energy and power density. However, dynamic operating conditions and complicated ageing mechanisms create challenges in determining the major sources of these overpotentials. We estimate the overpotentials of cells in a dataset consisting of aged and non-aged commercial lithium iron phosphate/graphite cells cycled under fast charging conditions. Using the pseudo-two-dimensional (P2D) model and the discharge profiles of the first 630 cycles, we conducted an in-situ monitoring of the sources of the overpotentials of cells that exhibited the longest, median, and shortest end of life. A derived analytical expression is used to decompose the total overpotential into lithium concentration overpotential, electrolyte concentration overpotential, ohmic overpotential and kinetic overpotential. The major source of overpotential is from the loss of lithium inventory and loss of active materials during cycling. This work highlights the importance of combining big data approach and physics-based models to learn from the overpotentials of complex electrochemical systems.

1. Introduction

Lithium-ion batteries (LIBs) are by far the most utilized energy storage device in a wide range of applications owing to their high energy and power densities, low and fast receding costs and enhanced cycle life [1–3]. Automotive applications such as hybrid electric vehicles (HEV) and electric vehicles (EV) require high power density for dynamic power changes under real-life driving conditions. However, there is an overpotential generated by the internal battery resistance, which reduces the battery voltage during operation. Consequently, the overpotential reduces the expected high power density (product of discharge voltage and discharge current) [4-6] and induce an intensive heat generation [7] in LIBs, limiting their applications in EVs and HEVs. The value of the generated overpotential varies depending on the type of battery, i.e., it is much higher in Li-metal batteries than LIBs. An extensive insight into the sources of overpotentials as a function of different ageing mechanisms via a non-invasive diagnostic tool, enabled by a large experimental data set, would accelerate battery optimization. For instance, battery manufacturers can economically tune the performance of the cell, identify new manufacturing processes and develop new cells based on their expected power density [8–11]. It is therefore crucial to focus on LIB overpotentials and their sources. This is challenging because they evolve from a variety of nonlinear degradation mechanisms which are influenced by the operating conditions of the battery [12–14].

The overpotentials in LIBs are known to originate mainly from the transport of Li-ions in the cathode, anode and electrolyte via both diffusion and migration processes [15–17], electrode/electrolyte interfacial charge transfer reactions [18–20] and electronic conduction in electrodes and current collectors [21,22]. In addition, external factors that influence the overpotential include the applied current density [23,24], operating temperature [25,26], state of health (SOH) [27,28] and the state of charge (SOC) [29,30]. Most of these factors are directly related to the degradation of the microstructure of LIB materials which can be visualized and quantified by new analytical techniques such as nuclear magnetic resonance (NMR) [31–33], transmission electron microscopy (TEM) [34], X-ray photoelectron spectroscopy (XPS) [35–37], attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) [38–40] and cryogenic electron microscopy (cyro-EM) [41].

https://doi.org/10.1016/j.est.2024.111000

Received 12 October 2023; Received in revised form 16 January 2024; Accepted 15 February 2024 Available online 22 February 2024 2352-152X/© 2024 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

^{*} Corresponding author at: Faculty of Engineering and Science, University of Agder, 4879 Grimstad, Norway. *E-mail addresses:* williams.a.appiah@uia.no (W.A. Appiah), arbh@dtu.dk (A. Bhowmik).

However, the aforementioned experimental techniques require complex setups and analysis that render them unsuitable for real-time monitoring of dynamic systems such as LIBs. Alternatively, electrochemical impedance spectroscopy (EIS) can be used to analyze the performance of LIBs and extract overpotential-dependent parameters such as the ohmic resistance, charge transfer resistance and diffusion of Li-ion by fitting EIS data to equivalent circuit models (ECM) [42,43]. However, EIS measurements are highly influenced by their sensitivity to SOC, temperature, and impedance wire connections [44,45], limiting their application as an in-situ diagnosis tool for batteries due to dynamic internal chemical reactions and variable external operating conditions [46–48].

Approaches adopting the use of electrochemical models (EMs) to conduct a detailed analysis of the relationship between overpotentials, and battery degradation factors are essential. EMs use a large set of parameters with specific physical meanings, making them appropriate for internal state characterization of degradation mechanisms. The single particle model (SPM) with 17 parameters is the simplest EM used for in-situ characterization of battery degradation mechanisms [49-51]. Although very effective for online SOH estimation, SPM does not consider variations in Li concentration and overpotentials in the electrolyte within the separator. This limits the application of SPM at high current densities [52] where overpotentials are significant. An alternative is the use of the pseudo-two-dimensional (P2D) model developed by Doyle et al. [53], which accounts for both solid and solution phase potentials and currents, using governing equations derived from first principles and over 30 parameters. A growing body of literature applies the P2D model to monitor overpotentials, by validating the model predictions with limited number of experimental data obtained from commercial cells or laboratory assembled cells [23,54-57]. The main limiting factor of these approaches is the different description of the various overpotentials which leads to apparently contrasting results. An example is the description of the electrolyte overpotential which is referred to as the potential difference of the electrolyte across an entire battery stack [56,58] and as the electrolyte potential drop across the separator [23,59]. In addition, the Li diffusion, ohmic and kinetic overpotential usually have different descriptions [56,58,59]. To harmonize the generally accepted definitions with respect to analysis of overpotentials in LIBs, Chen et al. [6], derived mathematical expressions based on the P2D model to study the overpotentials in a graphite-based porous electrode and Li metal counter electrode battery. However, achieving a complete picture of the overpotential status in LIBs requires modelling a full cell with porous cathode and anode, a state-of-the-art electrolyte, and parametrizing it with a large set of experimental data obtained at different operating conditions.

In this work, we adopted the P2D model to conduct an in-situ analysis on the sources of overpotentials in an aged and non-aged commercial LiFePO₄/graphite cells based on the first 630 cycles using the notations for overpotential given by Chen et al. [6]. We used an openly available data set of a variety of cells with various fast charging conditions and a cycle life ranging from 150 and 2300 cycles [60]. For a quantitative analysis of the overpotentials, we categorized the cells into those that exhibited longest, median, and shortest cycle life. We derived a mathematical expression using the governing equations in the P2D model to classify the total overpotential into lithium concentration overpotential, electrolyte concentration overpotential, ohmic overpotential and kinetic overpotential. Based on the analysis conducted on the cells at the 630th cycle, we demonstrate the correlation between the overpotentials and the degradation mechanisms such as the loss of lithium-ion inventory (LLI) and loss of active materials in the cathode (LAM_{dePE}) during cycling in LiFePO₄/graphite LIBs. These results show the relevance of combining data generation and physics-based models to unravel the sources of overpotentials in dynamic complex systems such as LIBs in a non-invasive manner.

2. Data and methods

The data used in this work is an open-source dataset created by [60]. The dataset consists of commercial 124 LiFePO₄/graphite Li-ion batteries (A123 Systems, APR18650M1A) with a nominal capacity of 1.1 Ah cycled in a temperature-controlled chamber at 30 °C. All batteries are charged with one- or two-step fast-charging schemes ranging from 3.0C to 8.0C to 80 % SOC, followed by a uniform 1C CC-CV charging step. All the cells were discharged at 4C to a lower cut-off voltage of 2.0 V. The cells exhibited a wide range of total lifetimes from 150 to 2300 cycles. The dataset is divided into three batches of cells that were cycled at different times. The last batch was cycled a year later than the first two batches after being stored at room temperature, resulting in a difference in calendar ageing between batches. The original dataset contains 41 and 40 cells for the non-aged and aged batch respectively. Due to intrachemistry differences between batteries, even batteries with the same charging regime have a different EOL, making the aggregation of e.g. the overpotential trajectory as a simple average intractable. To be able to compare cells with similar charge/discharge regimens we therefore focus on exemplary batteries.

The aged batteries include 2018-04-12- b3c10 (labelled as Battery-AS), 2018-04-12- b3c16 (labelled as Battery-AM) and 2018-04-12b3c7 (labelled as Battery-AL), with a cycle life of 1078, 1638 and 1836 respectively. The non-aged batteries include 2017-05-12-b1c20 (labelled as Battery-NS), 2017-05-12-b1c17 (labelled as Battery-NM) and 2017-05-12-b1c4 (labelled as Battery-NL), with a cycle life of 636, 719 and 870 respectively. All batteries are charged with a charging speed of 4.8C until 80 % SOC (except for Battery-NM, being charged with an average charging speed of 4.8C composed of 5.4C until 60 % SOC and subsequently 3C until 80 % SOC due to no additional battery being charged with a uniform 4.8C). Considering that the analysis for Battery-NM is consistent with the remaining batteries charged at identical speed this does not seem to impact the results.

The analysis of the data was carried out in Python. All code is openly available, and results can be reproduced with the code made available in [61]. To obtain the charge and discharge overpotential, we estimated the average cell voltage during charging and discharging at each cycle and subtracted it from the average open circuit voltage (OCV) described in Fig. 2b. To study the degradation mechanisms from the discharge profile of each cell at the 1st and 630th cycle, we used a sparse non-linear optimizer (SNOPT) to fit the experimental discharge profiles to those of the model predictions and extracted the capacity fading parameters. This task was conducted in COMSOL Multiphysics. A schematic diagram of the methodology employed to ascertain the correlation between the degradation mechanisms and overpotentials of aged and non-aged cells with different cycle life is presented in Fig. 1.

3. Pseudo-two-dimensional model development

To conduct an in-situ analysis of the cells via parameter identification, we adopted the P2D model developed by Doyle et al. [53]. The layout of a P2D model for the porous graphite anode and LiFePO₄ cathode with a porous separator filled with a liquid electrolyte is presented in Fig. 2a. L_n denotes the thickness of the anode, $L_{s}-L_n$ is the thickness of the separator and $L_p-L_s-L_n$ is the thickness of the cathode. The model equations used in this work are well described in previous work by [62]. In summary, they are related to the material balance in the electrolyte [Eqs. (A3), (A8) and (A12)], potential in the solution phase [Eqs. (A4), (A9) and (A13)] and solid phase [Eqs. (A2) and (A11)], the Butler-Volmer equation for the kinetic reaction [Eqs. (A5) and (A14)] and the transport of ions in the spherical particles in the anode [Eq. (A1)] and cathode [Eq. (10)]. Table 1 shows a summary of the governing equations, boundary, and initial conditions. The parameters used in the model are presented in Table 2.

The output voltage of the battery (V_{batt}) is described by Eq. (A19). By substituting Eqs. (A7) and (A16) for the anode and cathode



Fig. 1. A schematic diagram of the methodology employed to ascertain the correlation between the degradation mechanisms and overpotentials of aged and nonaged cells with different cycle life.



Fig. 2. (a) Schematic diagram of P2D model for graphite anode and LiFePO₄ cathode Li-ion battery. (b) Estimated open circuit voltage (OCV) of LiFePO₄/ Graphite cell.

Table 1

P2D model governing equations for LiFePO₄/Graphite battery.

Region		Governing equations	Eq. No	Boundary or initial condition
Anode	Diffusion in solid particles	$\partial c_1 = 1 \partial (\partial c_1)$	A1	$c(\mathbf{r}, 0) = c^0$
mode	Dinusion in solid particles	$\frac{\partial c_{1,n}}{\partial t} = D_{1,n} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{1,n}}{\partial r} \right)$		$\frac{c_{1,n}(r, \sigma)}{-D_{1,n}\frac{\partial c_{1,n}}{\partial r}}\Big _{r=0} = 0, -D_{1,n}\frac{\partial c_{1,n}}{\partial r}\Big _{r=R_{n,n}} = j_n$
	Potential in solid phase	$\sigma_{1,n}^{eff}rac{\partial^2 \Phi_{1,n}}{\partial x^2}=a_{1,n}Fj_n$	A2	$\sigma_{1,n}\Big _{x=L_n} = 0 \qquad -\sigma_{1,n} rac{\partial \Phi_{1,n}}{\partial x}\Big _{x=0} = 0$
	Material balance in solution phase	$\varepsilon_{2n}\frac{\partial c_{2n}}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon_1^{1.5} D_{2n} \frac{\partial c_{2n}}{\partial x} \right) + (1 - t_+^0) a_{1n} j_n$	A3	$egin{array}{ll} c_1 _{t=0} &= c_1^0 \ - D_{2,n} rac{\partial c_{2,n}}{\partial x} \Big _{x=0} &= rac{I_{app}(1-t_+)}{F}, \end{array}$
				$D_{2,n} \frac{\partial c_{2,n}}{\partial x}\Big _{x=L_n} = D_{2,sep} \frac{\partial c_{2,n}}{\partial x}\Big _{x=L_n}$
	Potential in solution phase	$-\frac{\partial}{\partial x}\left(\varepsilon_{2,n}^{1.5}\kappa\frac{\partial\phi_{2,n}}{\partial x}\right)+\frac{2RT(1-t_{+}^{0})}{F}\frac{\partial}{\partial x}\left(\varepsilon_{2,n}^{1.5}\kappa\frac{\partial lnc_{2}}{\partial x}\right)=$	A4	$\kappa_n \frac{\partial \Phi_{2,n}}{\partial x}\Big _{x=L_n} = 0, \kappa_n \frac{\partial \Phi_{2,n}}{\partial x}\Big _{x=L_n} = \kappa_{sep} \frac{\partial \Phi_{2,sep}}{\partial x}\Big _{x=L_n}$
	Butler-Volmer kinetics	$j_n = \frac{i_n^0}{r_n^0} \left[exp\left(\frac{0.5F}{RT} \eta_n^{ct}\right) - exp\left(-\frac{0.5F}{RT} \eta_n^{ct}\right) \right]$	A5	-
		$i_n^0 = Fk_n(c_{1,n,max} - c_{1,n,surf})^{0.5} c^{0.5} {}_{1,n,surf} c_{2,n}^{0.5}$	A6	-
		$\eta_n^{ct} = \Phi_{1,n} - \Phi_{2,n} - U_n^0$	A7	-
Separator	Material balance in solution	$\varepsilon_{sep} \frac{\partial c_2}{\partial t} = \frac{\partial}{\partial x} \left(\varepsilon_{sep}^{1.5} D_{2,sep} \frac{\partial c_2}{\partial x} \right)$	A8	$c_2 _{t=0} = c_2^0$
	phase			$D_{2,n}\frac{\partial c_2}{\partial x}\Big _{x=L_n} = D_{2,sep}\frac{\partial c_2}{\partial x}\Big _{x=L_n} D_{2,sep}\frac{\partial c_2}{\partial x}\Big _{x=L_s} = D_{2,p}\frac{\partial c_2}{\partial x}\Big _{x=L_s}$
	Potential in solution phase	$-\varepsilon_{sep}^{1.5}\kappa\frac{\partial\phi_{2,sep}}{\partial x}+\frac{2RT(1-t_{+}^{0})}{F}\varepsilon_{sep}^{1.5}\kappa\frac{\partial lnc_{2}}{\partial x}=0$	A9	$\kappa_{sep} rac{\partial \Phi_{2,sep}}{\partial x}\Big _{x=L_p} = \kappa_p rac{\partial \Phi_{2,p}}{\partial x}\Big _{x=L_p} -$
				$\kappa rac{\partial \Phi_{2,n}}{\partial x}\Big _{x=L_n} = -\kappa rac{\partial \Phi_{2,sep}}{\partial x}\Big _{x=L_s}$
Cathode	Diffusion in solid particles	$\frac{\partial c_{1,p}}{\partial t} = D_{1,p} \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial c_{1,p}}{\partial r} \right)$	A10	$c_{1,p}(r,0) \Big _{t=0} = c_{1,p}^0$
				$- \left. D_{1,p} rac{\partial \mathcal{C}_{1,p}}{\partial r} ight _{r=0} = 0 \qquad - \left. D_{1,p} rac{\partial \mathcal{C}_{1,p}}{\partial r} ight _{r=R_{p,p}} = j_p$
	Potential in solid phase	$arepsilon_{1p}^{1.5}\sigma_{1p}rac{\partial^2 \Phi_{1p}}{\partial x^2}=a_{1p}Fj_p$	A11	$-\sigma_{1,p}rac{\partial \Phi_{1,p}}{\partial x}\Big _{x=L_2}=0$ $-\sigma_{1,p}rac{\partial \Phi_{1,p}}{\partial x}\Big _{x=L_p}=I_{app}$
	Material balance in solution phase	$arepsilon_{2p}rac{\partial c_{2,p}}{\partial t}=rac{\partial}{\partial x}igg(arepsilon_1^{15}D_2rac{\partial c_{2,p}}{\partial x}igg)+ig(1-t_+^0ig)a_{1,p}j_p$	A12	$-D_{2p}\frac{\partial c_{2p}}{\partial x}\Big _{x=L_{n}}=0, D_{2,sep}\frac{\partial c_{2p}}{\partial x}\Big _{x=L_{s}}=D_{2p}\frac{\partial c_{2p}}{\partial x}\Big _{x=L_{s}}$
	Potential in solution phase	$-rac{\partial}{\partial x}\left(\kappa_{eff,p}rac{\partial \varPhi_{2,p}}{\partial x} ight)+rac{2RT(1-t^0_+)}{F}rac{\partial}{\partial x}\left(\kappa_{eff,p}rac{\partial lnc}{\partial x} ight)=$	A13	$-\kappa_p \frac{\partial \Phi_{2,p}}{\partial x}\Big _{x=L_p} = 0 \kappa_p \frac{\partial \Phi_{2,p}}{\partial x}\Big _{x=L_p} = \kappa_{sep} \frac{\partial \Phi_{2,sep}}{\partial x}\Big _{x=L_s}$
	Butler-Volmer kinetics	$ \begin{aligned} & a_{1Jp} F_p \\ & j_p = \frac{i_p^0}{F} \left[exp\left(\frac{0.5F}{PT} \eta_p\right) - exp\left(-\frac{0.5F}{PT} \eta_p\right) \right] \end{aligned} $	A14	-
		$i_n^0 = Fk_p (c_{1,p,max} - c_{1,p,surf})^{0.5} c_{1,p,surf}^{0.5} c_{2,p}^{0.5}$	A15	-
		$\eta_{p}^{ct} = \Phi_{1,p} - \Phi_{2,p} - U_{p}^{0}$	A16	-
	Diffusion coefficient	$D_{1} = \frac{D_{1p}^{0}}{D_{1p}^{0}}$	A17	
		$\mathcal{D}_{1,p} = (1 + SOC)^{1.6}$		
_	Reaction rate constant	$k_p = k_p^0 exp(-3 \times SOC)$	A18	
Battery	Output voltage	$V_{\mathrm{batt}} = \Phi_1 ig _{x=L_p} - \Phi_1 ig _{x=0} - R_f I_{app}$	A19	-

Table 2

P2D model parameters for LiFePO₄/Graphite battery.

Parameter	Value	Parameter	Value
L_p^{a}	$58\times10^{-6}~\text{m}$	Т	298 K
L_{sep}^{a}	$25 imes 10^{-6}$ m	t_{+}^{0}	0.248
L_n^{a}	$40 imes 10^{-6} \text{ m}$	I_{app}^{a}	4 A
R_p^a	$1.7 imes 10^{-6} \text{ m}$	x_0^{b}	0.10
R_n^a	$2.5\times 10^{-6}\ \text{m}$	y_0^{b}	0.99
$D_{J\!\!P}^{0 b}$	$3.02\times 10^{-18}\ m^2\ s^{-1}$	c_2^{0a}	$1200 \text{ mol } \text{m}^{-3}$
$D_{1,n}^{\mathbf{b}}$	$5.8\times 10^{-14}\ m^2\ s^{-1}$	$\sigma_{1,p}^{c}$	91 S m ⁻¹
D_2^{b}	$3.5\times10^{-10}\ m^2\ s^{-1}$	$\sigma_{1,n}^{c}$	$100 {\rm ~S} {\rm ~m}^{-1}$
$\varepsilon_{2,p}^{a}$	0.4	$c_{1,n,\max}^{d}$	30537 mol m^{-3}
$\varepsilon_{2,n}^{a}$	0.30	R	$8.314 \text{ J} \text{ mol}^{-1} \text{ K}^{-1}$
Esep	0.37	F	96487 C mol ⁻¹
$\varepsilon_{1,p}^{a}$	0.43	$k_{\rm p}^{\rm 0b}$	$2\times10^{-11}\ \text{m}\ \text{s}^{-1}$
$\varepsilon_{1,n}^{a}$	0.645	$k_n^{\rm b}$	$2\times 10^{-11}\ \text{m s}^{-1}$
$c_{1,p,max}^{d}$	22836 mol m ⁻³		

^a Parameter set in cell design of identical battery chemistry [62].

^b Fitted parameter.

^c Obtained from COMSOL library.

^d Parameters based on literature [59,62].

overpotential respectively, Eq. (18) can be expanded to

$$\begin{split} V_{batt} &= \left(\Phi_{2,p} \big|_{x=L_p} + \Phi_{2,n} \big|_{x=0} \right) + \left(U_p \Big(c_{1,p}^s \Big) \Big|_{x=L_p} - U_n \Big(c_{1,n}^s \Big) \Big|_{x=0} \right) \\ &+ \left(\eta_p^{ct} \big|_{x=L_p} - \eta_n^{ct} \big|_{x=0} \right) - R_f I_{app} \end{split}$$
(1)

where $\Phi_{2,p}$ and $\Phi_{2,n}$ are the electrolyte potential and U_p and U_n are the equilibrium potential in the cathode and anode respectively. η_p^{ct} and η_n^{ct} are the charge transfer overpotential at the cathode and anode respectively. R_f is the sum of the contact resistance between the electrodes and current collectors and the ohmic resistances of the current collectors. I_{app} is the applied current and the V_{batt} is the output voltage of the cell.

The overall overpotential of the battery, η_{batt} is the described as the difference between the output voltage of the battery and the equilibrium potential of the battery and is expressed as

W.A. Appiah et al.

$$\eta_{batt} = \underbrace{\begin{bmatrix} \left(\Phi_{2,p} \left|_{x=L_{p}} - \Phi_{2,n} \right|_{x=0} \right) + \\ \left[\text{Electrolyte overpotential } (\eta_{2}) \\ \left[\left(U_{p} \left(c_{1,p}^{s} \right) \right|_{x=L_{p}} - U_{p} \left(\overline{c}_{p} \right) \left|_{x=L_{p}} \right) - \left(U_{n} \left(c_{1,n}^{s} \right) \left|_{x=0} - U_{n} \left(\overline{c}_{n} \right) \right|_{x=0} \right) \right] + \\ \left[\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=L_{p}} - U_{p} \left(\overline{c}_{p} \right) \right|_{x=L_{p}} \right) - \left(U_{n} \left(c_{1,n}^{s} \right) \left|_{x=0} - U_{n} \left(\overline{c}_{n} \right) \right|_{x=0} \right) \right] + \\ \left[\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=L_{p}} - U_{p} \left(\overline{c}_{p} \right) \right|_{x=L_{p}} \right) - \left(U_{n} \left(c_{1,n}^{s} \right) \left|_{x=0} - U_{n} \left(\overline{c}_{n} \right) \right|_{x=0} \right) \right] + \\ \left[\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=L_{p}} - \eta_{n}^{ct} \right|_{x=0} \right) - \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{p} \right) \right|_{x=0} \right) \right) \\ \left[\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=L_{p}} - \eta_{n}^{ct} \right|_{x=0} \right) - \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{p} \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - \eta_{n}^{ct} \right|_{x=0} \right) - \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{p} \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - \eta_{n}^{ct} \right|_{x=0} \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - \eta_{n}^{ct} \right|_{x=0} \right) - \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{p} \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - \eta_{n}^{ct} \right|_{x=0} \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{p} \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p}^{s} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left|_{x=0} - U_{p} \left(\overline{c}_{1,p} \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left(\overline{c}_{1,p} \right) \right) \right) \right) \\ \left(\underbrace{\left(U_{p} \left(c_{1,p} \right) \left(U_{p} \left(c_{1,p} \right)$$

The four major components of the battery overpotential are (i) the difference in the electrolyte potential between the cathode/current collector and the anode/current collector interfaces (electrolyte overpotential (η_2)), (ii) the difference between the electrode potential at the cathode/current collector and the anode/current collector interfaces due to inhomogeneity in Li concentrations in the electrode (Li concentration overpotential (η_1^c)), (iii) the potential difference due to charge-transfer limitations at the cathode/current collector and the anode/current collector and the anode/current collector interfaces (kinetic overpotential (η_1^c)) and (iv) the ohmic overpotential (η_1^{Ω}) generated by the contact and electrode ohmic resistance.

The electrolyte overpotential was derived from Eqs. (A4), (A9) and (A13), which are the electrolyte potential in the cathode, separator, and anode respectively. Integrating Eqs. (A4), (A9) and (A13) along the x-axis results in the expression

$$\eta_{2} = \Phi_{2,p}|_{x=L_{p}} - \Phi_{2,n}|_{x=0} = \begin{bmatrix} -\frac{1}{\kappa_{eff,n}} \int_{0}^{L_{n}} i_{2,n}(x,t) dx - i_{2,sep} \int_{L_{n}}^{L_{n}} \frac{dx}{\kappa_{eff,sep}} - \frac{1}{\kappa_{eff,p}} \int_{L_{n}}^{L_{p}} i_{2,p}(x,t) dx + \\ \frac{2RT}{F} \int_{0}^{L_{p}} (1 - t_{+}^{0}) dlnc_{2}(x,t) \end{bmatrix}$$
(3)

Eq. (3) can be divided into the electrolyte concentration overpotential (η_2^c) and the electrolyte ohmic overpotential (η_2^{Ω}) and are expressed as

$$\eta_2 = \eta_2^c + \eta_2^\Omega \tag{4.1}$$

$$\eta_2^c = \frac{2RT}{F} \int_0^{L_p} \left(1 - t_+^0\right) dlnc_2(x, t)$$
(4.2)

$$\eta_2^{\Omega} = -\frac{1}{\kappa_{eff,n}} \int_0^{L_n} i_{2,n}(x,t) dx - i_{2,sep} \int_{L_n}^{L_s} \frac{dx}{\kappa_{eff,sep}} - \frac{1}{\kappa_{eff,p}} \int_{L_s}^{L_p} i_{2,p}(x,t) dx$$
(4.3)

where *F* is the Faraday constant, *R* is the gas law constant, *T* is the operating temperature and i_2 is the current density in the solution phase. The thickness of the electrodes (L_p and L_n) and separator (L_s) as well as the operating temperature (*T*) are assumed to be constant.

The Li concentration overpotential (η_1^{Li}) is defined as the difference between the potential at the surface of the particles and the equilibrium potential at the current collector/electrode interface and is expressed for the anode and cathode respectively as

$$\left. \left. \int_{1,n}^{L_{i}} = U_{n}(c_{1}^{s}) \right|_{s=0} - U_{n}(\overline{c}_{1,n})$$
(5.1)

$$\eta_{1,p}^{Li} = U_n(c_1^s) \Big|_{x = L_{pos}} - U_p(\bar{c}_{1,p})$$
(5.2)

The total Li concentration overpotential can then be expressed as

$$\eta_{1}^{Li} = \left(U_{p} \left(c_{1,p}^{s} \right) \big|_{x=L_{p}} - U_{p} \left(\overline{c}_{p} \right) \big|_{x=L_{p}} \right) - \left(U_{n} \left(c_{1,n}^{s} \right) \big|_{x=0} - U_{n} \left(\overline{c}_{n} \right) \big|_{x=0} \right)$$
(5.3)

where c_1^s is the concentration of Li at the surface of the particles and

varies along the x-axis in the porous electrode, and $\bar{c}_{1,n}$ and $\bar{c}_{1,p}$ is the average concentration of the electrode under equilibrium conditions for the anode and cathode respectively.

The charge transfer overpotential between the current collector/ electrode interfaces is represented as the kinetic overpotential, η^{ct} in Eq. (2) (η_n^{ct} and η_p^{ct}), can be obtained from the Butler Volmer kinetics, Eqs. (A5) and (A15) for the anode/electrolyte interface and cathode/electrolyte interface respectively and is expressed as

$$\eta_n^{ct} = G_{a_n, F/(RT)}^{-1} \left(\frac{Fj_n}{i_n^0} \right)$$
(6.1)

$$\eta_{p}^{ct} = G_{a_{p},F/(RT)}^{-1} \left(\frac{Fj_{p}}{l_{p}^{0}} \right)$$
(6.2)

The overall kinetic overpotential is then given as

$$\eta^{ct} = G_{a,F/(RT)}^{-1} \left(\frac{Fj_p}{i_p^0}_{x=L_p} \right) - G_{a,F/(RT)}^{-1} \left(\frac{Fj_n}{i_n^0} \right|_{x=0} \right)$$
(6.3)

where and G^{-1} is the inverse of a function G defined as

$$G = \left(exp\left(\frac{\alpha F}{RT}\eta\right) - exp\left(-\frac{(1-\alpha)F}{RT}\eta\right)\right)$$
(6.4)

The electrode ohmic overpotential, $\eta_1^{\Omega} = IR_f = I(R_{SEI} + R_{cont})$, is described as the overpotential due to the contact resistance between the composite electrode and current collector, and the ohmic resistance of the solid-electrolyte interphase. These resistances are treated as an empirical constant in this work, and it depends on the film resistance, R_f obtained during the degradation parameter estimation.

The total overpotential of the LiFePO $_4$ /graphite cell is described by the combination of all the derived overpotential expressions and is represented as

$$\eta_{batt} = V_{batt} - U_{batt} = \eta_2 + \eta_1^c + \eta_1^{ct} + \eta_1^{\Omega} = \eta_1^c + \eta_2^c + \eta_1^{ct} + \eta_1^{\Omega} + \eta_2^{\Omega}$$
(7)

The P2D model was solved using the Battery module in COMSOL Multiphysics.

4. Results and discussion

4.1. Experimental data analysis

Fig. 3a, b shows the average discharge overpotential of aged and non-aged batteries as a function of number of cycles. The absolute average discharge overpotential of the long-lived aged batteries (Battery-AL), was slightly higher than that of the non-aged battery (Battery-NL) during cycling. A similar trend was observed for batteries with medium (Battery-AM and Battery-NM) and short (Battery-AS and Battery-NS) cycle life. The absolute average discharge overpotential for the long, medium, and short-lived aged batteries increased at a slow rate for ca. 1500, ca. 1300 and ca. 700 cycles respectively and accelerated at the last stages of cycling (Fig. 3a). The absolute average discharge overpotential of the long, medium and short lived non-aged batteries increased at a relatively slower rate for the first ca. 500 cycles and accelerated until the end of their cycle life (Fig. 3b) with a faster rate of acceleration for Battery-NS than Battery NM and Battery NL.

The average charge overpotential of aged batteries (Battery-AL, Battery-AM and Battery-AS) have in common a two-staged trend of initial constant overpotential, followed by a rapid increase until the end of their cycle life (Fig. 3c). The constant overpotential stage was shorter for Battery-AS and longer for Battery-AL. These observations suggest that the cell cycle life depends on how long the constant overpotential period lasts. The average charge overpotential of the non-aged batteries



Fig. 3. Analysis of average overpotential in aged and non-aged batteries with different cycle life. Average discharge overpotential of (a) aged and (b) non-aged batteries, and average charge overpotential of (c) aged and (d) non-aged batteries. Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NL, Batte

(Fig. 3d) remained constant throughout the cycling process with those of Battery-NL and Battery-NM being lower than that of Battery-NS. To understand the various factors responsible for these complex dynamics, we adopted the P2D model to extract the various associated degradation mechanisms and categorize the overpotential into four main parts as presented in the remaining part of Section 4.

4.2. Estimation of degradation parameters

To extract the degradation mechanisms associated with the overpotential observed in Fig. 3, we estimated the parameters that changed with cycling in the P2D model by comparing the model predictions with experimental voltage profiles obtained from the aged and non-aged LiFePO₄/graphite batteries at the 1st and 630th cycle and presented the outcome in Fig. 4. The solid and symbol lines represent the model predictions and the experimental data respectively. Fig. 4a–f, show the experimental and model predictions for the aged and non-aged batteries with long, medium, and short cycle life respectively. The batteries with the shortest cycle life (Battery-AS and Battery-NS) served as the limiting battery in determining the cycle number for the in-situ analysis. This approach has been utilized in previous reports [19,63,64] and has proven to be an efficient method for estimating battery degradation mechanisms. We achieved a high correlation between the model prediction and the experimental data by using the SNOPT algorithm to fit the parameters in the P2D model for LiFePO₄/graphite battery that changed with cycling. These parameters are the film resistance, R_f (Eq. (A19)), the volume fraction of the cathode active material, $\varepsilon_{1,p}$ (Eq. (A11)) and the initial SOCs of the cathode, $x_{0,p}$ (Eq. (A10)) and anode, $x_{0,n}$ (Eq. (A1)) where $x_{0,i} = c_{1,i,suff}/c_{1,i}^0$ i = p, n.

4.3. Analysis of degradation mechanisms

The results presented in the previous Subsections 4.1 and 4.2 show that ageing had a pronounced effect on the cycling performance of the LiFePO₄/graphite batteries which was manifested in the capacity (Fig. 4) and the overpotential (Fig. 3). In this subsection we discuss the various battery degradation mechanisms constituting these effects.

Based on the studies conducted on the parameters that changed with cycling, we observed an increase in the film resistance at the 630th cycle for all the batteries (Fig. 5a). The aged batteries exhibited consistently lower film resistance than the non-aged batteries for a given lifetime category. The film resistance increased as the cycle life decreased for both the aged and non-aged batteries. There was no significant increase in the film resistance of Battery-AL. However, Battery-NL exhibited a



Fig. 4. Comparison of experimental discharge voltage profiles with the model predictions for aged and non-aged batteries during the 1st and 630th cycles. a, c, e; aged batteries, and b, d, f; non-aged batteries. Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NL, Battery-NS respectively.

significant increase in the film resistance at the 630th cycle. The film resistance is defined as the sum of the SEI resistance due to the formation of SEI, and the contact resistance within the particles of the composite electrode and between the composite electrodes and the current collector. Hence, the changes in the film resistance are mainly attributed to the increase in the SEI thickness, which was thicker for the non-aged batteries than the aged batteries at the 630th cycle for a given lifetime category. The results presented in Fig. 5a, is the increase in the film resistance at the 630th cycle with respect to the first cycle and that after

precycling was not considered.

In addition, aged batteries with medium (Battery-AM) and short (Battery-AS) cycle life, showed an increase in the film resistance at the 630th cycle but this increase was significantly lower than those of the medium- and short-lived non aged batteries. The loss of active materials was higher in the non-aged batteries than the aged batteries for a given lifetime category and increased as the cycle life decreased for both aged and non-aged batteries (Fig. 5b). This implies that, the increase in the film resistance of the non-aged batteries as well as medium and short-



Fig. 5. Predicted degradation mechanisms for aged and non-aged batteries with long, medium, and short cycle life at the 630th cycle. a. increase in film resistance, b. increase in loss of active materials (LAM_{dePE}) and increase in loss of lithium ion (LLI). Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NS respectively.

lived aged batteries can be attributed partly to the increase in the contact resistance between the particles of the composite LiFePO₄ electrode due to the loss of active materials to inactive or dead particles.

Moreover, the formation of the SEI leads to the consumption of active Li ions in the anode [65], and the formation of the cathode electrolyte interphase (CEI) and dead particles traps Li ions [66] resulting in capacity loss during cycling. To analyze the contribution of the SEI and CEI to capacity fade and overpotential, we estimated the percentage loss of Li ions between the first cycle and the 630th cycle for all the batteries considered in this study. Such estimation was based on the values of initial and final lithium content on the active materials, fitted from the experimental data (see Table 2). For instance, during the first cycle in Battery-AS, the LiFePO₄ cathode was discharged from Li_{0.114}FePO₄ to Li_{0.990}FePO₄ and the carbonaceous anode from Li_{0.960}C₆ to Li_{0.261}C₆. During the 630th cycle there was no significant changes in the Li content in the LiFePO₄ cathode at the beginning and end of discharging (Li_{0.114}FePO₄ to Li_{0.989}FePO₄), but that of the carbonaceous anode reduced both at the beginning and end of discharging, Li_{0.844}C₆ and Li_{0.160}C₆ respectively. The percentage of Li ions loss to the formation of CEI in the cathode after the 630th cycle was (((0.99 - 0.114) - (0.989 - 0.000))) $(0.114))/(0.99 - 0.114)) \times 100\% = 0.11\%$, and that loss to the formation of the SEI in the anode was (((0.960 - 0.260) - (0.844 - 0.160)))/(0.99 - 0.114)) × 100% = 1.67%. Thus, the total loss of Li ions at the end of the 630th cycle for Battery-AS was 1.78 %. It should be acknowledged that some of the Li ions loss to the formation of CEI could potentially be attributed to the loss of active materials. However, for the purposes of this study, we assumed that all the Li ions trapped in the cathode resulted from the formation of the CEI. A similar approach was used to calculate the total loss of Li ions in the other batteries and the

results are presented in Fig. 5c. The total loss of Li ions at the end of the 630th cycle increased with decreasing cycle life for both the aged and non-aged batteries with a higher increasing rate in the non-aged batteries than the aged batteries.

4.4. Model predicted overpotentials

To illustrate the correlation between the battery degradation mechanisms and the electrolyte overpotentials, η_2 , we used the derivations from the mathematical expression in Eq. (3) to simulate the electrolyte overpotentials of the batteries considered in this work. The electrolyte concentration overpotential, η_2^c for the aged and non-aged batteries was simulated and analyzed using Eq. (4.2) and presented in Fig. 6a and b respectively. There was no significant difference between the electrolyte concentration overpotential for the aged batteries with long (Battery-AL) and medium (Battery-AM) cycle life. However, the electrolyte concentration overpotential observed in the aged battery with short cycle life (Battery-AS) was lower than those of Battery-AL and Battery-AM. The electrolyte concentration overpotential of the non-aged batteries varied with that of Battery-NS being slightly lower than those of Battery-NM and Battery-NL. From Eq. (4.2), η_2^c is function of c_2 , T, t_+ and the thickness of the cell. Since all these parameters apart from c_2 were constant, η_2^c is directly related to c_2 . Thus, the slight difference in the electrolyte concentration overpotential observed in the aged and non-aged batteries was due to the loss of the Li ions in the electrolyte.

The electrolyte ohmic overpotential (η_2^{α}) was simulated using Eq. (4.3) and the outcome is presented in Fig. 6c and d for the aged and nonaged batteries respectively. Like the electrolyte concentration overpotential (Fig. 6a and b), there was no significant difference between the



Fig. 6. Electrolyte overpotential as function of time for batteries with long, medium, and short cycle life at the 630th cycle. a, b, Electrolyte concentration overpotential, and c, d, Electrolyte ohmic overpotential of aged and non-aged batteries respectively. Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NL, Battery-NL, Battery-NL, Battery-NS respectively.

electrolyte ohmic overpotential for the long and medium-lived aged batteries (Battery-AL and Battery-AM) were slightly higher than that of the short-lived aged battery (Battery-AS). Similarly, electrolyte concentration overpotential observed in the aged battery with short cycle life (Battery-AS) was lower than those of Battery-AL and Battery-AM. The electrolyte ohmic overpotential of the non-aged batteries (Battery-NL, Battery-NM and Battery-NS) decreased with an increase in the cycle life. In other words, shorter-lived cells exhibit smaller ohmic overpotentials with those of the non-aged batteries lower than those of the aged batteries. From Eq. (3), η_2^{Ω} depends on i_2 and the effective electrolyte conductivities in the electrodes ($\kappa_{eff,n}$ and $\kappa_{eff,p}$) and the separator ($\kappa_{eff,sep}$). Since all the batteries were discharged at a constant current, there was no changes in i_2 , thus the difference in the electrolyte ohmic overpotential between the batteries with long cycle life (Battery-AL and Battery-NL) and those with short cycle life (Battery-AS and Battery-NS) is due to the slight changes in the effective electrolyte conductivities within the cathode $\kappa_{eff,p}$. This is because $\kappa_{eff,p}$ in Eq. (A13) is directly proportional to the porosity of the electrode, ε according to $\kappa_{eff,p} =$ $\kappa_p \big(\varepsilon_{2,p} \big)^{1.5}$ and $\varepsilon_{2,p}$ increases as the volume fraction of the cathode active material, $\varepsilon_{1,p}$ decreases. Hence, from Fig. 5b, the higher loss in the active materials of the non-aged batteries is reflected in the increase in the effective ionic conductivity in the electrolyte leading to the decrease in the electrolyte ohmic overpotentials. This suggests that, as the cathode loses active material, its porosity increases and with it the effective conductivity of the electrolyte filling-up such pores. However, these changes observed in Fig. 6 are quite small indicating a small or negligible contribution of the electrolyte to the difference in the overpotentials of the aged and non-aged batteries with different cycle life at the 630th cycle. The vibrating point in curves of the inserted figure corresponds to the sharp drop in the OCV of the graphite.

The kinetic overpotential, η^{ct} defined as the difference between the charge transfer overpotential at the cathode/current collector interface and the anode/current collector interface as expressed in Eq. (6.3) was simulated for the aged and non-aged batteries at the 630th cycle and presented in Fig. 7a and b respectively. There was no significant difference between the kinetic overpotentials for the aged batteries but those of the non-aged batteries increased at a faster rate for the shortlived battery (Battery-NS) than the medium and long-lived batteries (Battery-NM and Battery-NL). From Eq. (6.3), η^{ct} is inversely proportional to i_i^0 which is dependent on the concentration of Li in the solid phase. At the beginning of discharge, surface concentration of Li in the cathode is almost equal to the maximum concentration $(c_{1,p,surf} \approx c_{1,p,max})$ and that in the anode approaches zero $(c_{1,n,surf} \approx 0)$, hence i_i^0 is low (Fig. 7a and b). As discharge proceeds, $c_{1,p,surf}$ decreases while $c_{1,n,surf}$ increases, thus i_i^0 increases until the point where $c_{1,p,surf} =$ $c_{1,n,surf}$ and begins to decrease as observed in Fig. 7a and b. This indicates



Fig. 7. Electrode overpotentials for batteries with long, medium, and short cycle life at the 630th cycle. a, b, Kinetic overpotential, and c, d, Lithium concentration overpotential of aged and non-aged batteries respectively. Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NL, Battery-NS respectively.

that, the kinetic overpotential, η^{ct} is directly dependent on the changes in the concentration of Li in the solid phase which is affected by the distribution of Li ion concentration in the cell. At the 630th cycle, the kinetic overpotential for Battery-NS increased at a significantly faster rate than the other batteries during the later stages of discharging because of the higher amount of total Li ions loss during cycling as evidenced in Fig. 5c.

Fig. 7c and d show the Li concentration overpotential, η_1^{Li} for the aged and non-aged batteries with different cycle life simulated using Eq. (5.3). η_1^{Li} is generated due to the concentration gradient of Li ions in the particles of the electrode. η_1^{Li} increased during discharging for both aged and non-aged batteries. There was no significant difference in η_1^{Li} between the aged batteries but those of the non-aged batteries increased with a decrease in the cycle life. However, since η_1^{Li} is related to the Li concentration gradient in the particles of the cathode and anode, their values are highly influenced by the total Li ions loss during cycling and Li ions trapped in the particles of loss active materials in the cathode. Thus, the non-aged battery with short cycle life (Battery-NS) which lost most Li ions and active materials in Fig. 5b and c, also exhibited an accelerated increase in the concentration overpotential, η_1^{Li} (Fig. 7c and d). Fig. 7 illustrated the correlation between the total loss of Li ions and loss of active materials on the kinetic and the Li concentration overpotential and this was high for the non-aged batteries than the aged batteries.

The last part of Eq. (2) describes the electrode ohmic overpotential, η_1^{Ω} which is considered in this work to be due to the increase in the film resistance described in Fig. 5a. The predicted η_1^{Ω} for the aged batteries (Fig. 8a) were lower than those for the non-aged batteries (Fig. 8b) at a given lifetime category. In addition, η_1^{Ω} increased with a decreasing cycle life for both the aged and non-aged batteries at the 630th cycle. Ageing of batteries prior to cycling leads to the formation of stable SEI and prevents excessive increase in η_1^{Ω} as observed in Fig. 8a for the aged batteries (Battery-AL, Battery-AM and Battery-AS), and vice versa for non-aged batteries (Battery-NL, Battery-NM, and Battery-NS). Thus, the observations in η_1^{Ω} , can be attributed mainly to the rate of the formation of the SEI during cycling.

To quantify the contribution of the various degradation mechanisms presented in Fig. 5, we predicted the discharge profile of the aged and non-aged batteries considering each of the degradation mechanisms, calculated the percentage capacity loss at the 630th cycle and presented the outcome in Fig. 8c (aged batteries) and 8d (non-aged batteries). For both the aged and non-aged batteries, the contribution of LAM_{dePE} in each battery was higher than that of LLI at the 630th cycle. The percentage contribution of the film resistance to the capacity loss was very small in the non-aged batteries and insignificant in the aged batteries as observed in the inserted figures in Fig. 8a and b. The contribution of LAM_{dePE} increased with a decreasing cycle life at the 630th cycle with a faster rate in the non-aged batteries than the aged batteries. Similar to LAM_{dePF}, the contribution of LLI increased with a decreasing cycle life in both aged and non-aged batteries, but their contribution to the capacity loss was relatively smaller than that of LAM_{dePE}. This is because the estimation of LLI depends on the state of charge (SOC) of the anode and cathode. While the SOC of the anode at the 630th cycle changed significantly, that of the cathode remained fairly constant during constant. However, for LiFePO₄/graphite cells, the limiting electrode is the cathode, hence a change in the SOC of the anode does not significantly affect the discharge capacity of the cell. Fig. 8c and d suggest that the LAM_{dePE} is the dominating degradation mechanism at the 630th cycle. This agrees with previous works based on experiments [67] and other forms of non-invasive in-situ capacity fade analysis [68].

5. Conclusion

We have conducted a non-invasive in-situ analysis on the capacity



Fig. 8. Electrode ohmic overpotential for (a) aged batteries and, (b) non-aged batteries, with long, medium, and short cycle life at the 630th cycle. Percentage contribution of the various degradation mechanisms to the capacity loss for the (c) aged and (d) non-aged batteries. The electrode ohmic overpotential is assumed to be due to an increase in the solid-electrolyte-interphase (SEI) film resistance. Aged batteries with long, medium, and short cycle life, are labelled as Battery-AL, Battery-AM and Battery-AS respectively. Non-aged batteries with long, medium, and short cycle life, are labelled as Battery-NS respectively.

fading of aged and non-aged commercial lithium-ion phosphate (LiFePO₄/graphite) cells with different cycle life based on the first 630 cycles and examined the correlation between them and the different types of overpotential using an experimentally validated P2D-model. Based on a rigorous parametric analysis, we observed that the dominant degradation mechanism in both the aged and non-aged batteries at the 630th is cycle is associated to the loss of active material in the positive electrode, which is especially severe for the non-aged batteries with a short cycle life. By decomposing the overpotential into four parts, we found out that, the increase in the electrode ohmic overpotential (η_1^{Ω}) is due to the increase in the film resistance and the increase in the electrode concentration overpotentials (kinetic overpotential (η^{ct}) and Li ion concentration overpotential (η_1^{Li}) is due to the increase in both loss of active materials (LAM_{dePE}) and loss of Li ions (LLI) during cycling. In addition, we observed that the difference between the overpotential in the aged and non-aged batteries is mainly due to the increase in the electrode ohmic overpotential (η_1^{Ω}) while the increase in the kinetic overpotential (η^{ct}) and Li concentration overpotential (η^{ct}) was responsible for the difference in the overpotential between the batteries with different lifetime category. Lastly, the electrolyte overpotential (η_2) did not have any significant effect on the overall overpotential of both aged and non-aged batteries. Based on our analysis, the cycle life of batteries can be prolonged by optimizing the ageing time to form a robust SEI, proper calendaring to reduce loss of active materials and optimizing the charging regimes during cycling. In a broader context, this work highlights the importance of using physics-based models to identify the

failure mechanisms in commercial Li ion batteries, accelerating experimental design and production.

List of symbols

AM	medium-lived aged batteries
AL	long-lived aged batteries
AS	short-lived aged batteries
а	specific surface area, m^{-1}
c_1	concentration of Li in the solid phase, $mol m^{-3}$
$c_{1,surf}$	surface concentration of Li in the solid phase, $\mathrm{mol}\ \mathrm{m}^{-3}$
$c_{1,max}$	maximum concentration of Li in the solid phase, $mol m^{-3}$
c_2	electrolyte concentration $mol m^{-3}$
D_2	electrolyte diffusion coefficient, m ² s ⁻¹
$D_{1,i}$	diffusion coefficient in the solid phase, $m^2 s^{-1}$
F	Faraday's constant, 96487 $ m C \ mol^{-1}$
I _{app}	applied current density, $A m^{-2}$
i_1	current density in the solid phase, $A m^{-2}$
i_2	current density in the solution phase, $A m^{-2}$
i_{1}^{0}	exchange current density in the solid phase, $A m^{-2}$
j	pore wall flux of lithium ions, $mol m^{-2} s^{-1}$
L	thickness of battery component, m
Μ	molecular weight, $mol kg^{-1}$
NL	long-lived non-aged batteries
NM	medium-lived non-aged batteries

- NS short-lived non-aged batteries
- *r* radial coordinate, m
- R ideal gas constant, 8.3143 J mol⁻¹ K⁻¹
- R_f film resistance at the electrode/electrolyte interface, $\Omega \text{ m}^2$
- t time, s
- *t*₊ cation transference number
- T temperature, K
- U equilibrium potential, V
- *x* main dimension across the cell sandwich
- ε volume fraction
- η local over potential, V
- κ electrolyte conductivity, S m⁻¹
- σ electrode conductivity, S m⁻¹
- ρ density of active material, kg m⁻³
- Φ electric potential, V

Subscript

solid	phase
	solid

- 2 solution phase
- e electrolyte
- eff effective
- n negative electrode
- p positive electrode

CRediT authorship contribution statement

Williams Agyei Appiah: Writing – review & editing, Writing – original draft, Validation, Methodology, Formal analysis, Data curation, Conceptualization. Laura Hannemose Rieger: Writing – review & editing, Methodology, Formal analysis, Data curation, Conceptualization. Eibar Flores: Writing – review & editing, Data curation, Conceptualization. Tejs Vegge: Writing – review & editing, Supervision, Project administration, Funding acquisition. Arghya Bhowmik: Writing – review & editing, Supervision, Funding acquisition, Conceptualization, Funding acquisition, Conceptualization, Funding acquisition, Funding acquisition, Funding acquisition, Funding acquisition, Funding acquisition, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgement

The authors acknowledge the European Union's Horizon 2020 research and innovation program under grant agreement No 957189 (BIG-MAP) and No 957213 (BATTERY2030PLUS).

References

- [1] W.A. Appiah, J. Park, S. Song, S. Byun, M.H. Ryou, Y.M. Lee, Design optimization of LiNi0.6Co0.2Mn0.2O2/graphite lithium-ion cells based on simulation and experimental data, J. Power Sources 319 (2016) 147–158, https://doi.org/ 10.1016/j.jpowsour.2016.04.052.
- [2] B. Nykvist, M. Nilsson, Rapidly falling costs of battery packs for electric vehicles, Nat. Clim. Chang. 54 (5) (2015) 329–332, https://doi.org/10.1038/nclimate2564 (2014).
- [3] R. Schmuch, R. Wagner, G. Hörpel, T. Placke, M. Winter, Performance and cost of materials for lithium-based rechargeable automotive batteries, Nat. Energy 34 (3) (2018) 267–278, https://doi.org/10.1038/s41560-018-0107-2.
- J. Kasnatscheew, U. Rodehorst, B. Streipert, S. Wiemers-Meyer, R. Jakelski, R. Wagner, I.C. Laskovic, M. Winter, Learning from overpotentials in lithium ion batteries: a case study on the LiNi 1/3 Co 1/3 Mn 1/3 O 2 (NCM) cathode,

J. Electrochem. Soc. 163 (2016) A2943–A2950, https://doi.org/10.1149/ 2.0461614JES/XML.

- [5] P. Oh, H. Lee, S. Park, H. Cha, J. Kim, J. Cho, Improvements to the overpotential of all-solid-state lithium-ion batteries during the past ten years, Adv. Energy Mater. 10 (2020) 2000904, https://doi.org/10.1002/AENM.202000904.
- [6] Z. Chen, D.L. Danilov, L.H.J. Raijmakers, K. Chayambuka, M. Jiang, L. Zhou, J. Zhou, R.A. Eichel, P.H.L. Notten, Overpotential analysis of graphite-based Li-ion batteries seen from a porous electrode modeling perspective, J. Power Sources 509 (2021) 230345, https://doi.org/10.1016/J.JPOWSOUR.2021.230345.
- [7] L.H.J. Raijmakers, D.L. Danilov, R.A. Eichel, P.H.L. Notten, A review on various temperature-indication methods for Li-ion batteries, Appl. Energy 240 (2019) 918–945, https://doi.org/10.1016/J.APENERGY.2019.02.078.
- [8] W. Waag, C. Fleischer, D.U. Sauer, Critical review of the methods for monitoring of lithium-ion batteries in electric and hybrid vehicles, J. Power Sources 258 (2014) 321–339, https://doi.org/10.1016/J.JPOWSOUR.2014.02.064.
- [9] V. Ramadesigan, P.W.C. Northrop, S. De, S. Santhanagopalan, R.D. Braatz, V. R. Subramanian, Modeling and simulation of lithium-ion batteries from a systems engineering perspective, J. Electrochem. Soc. 159 (2012) R31, https://doi.org/ 10.1149/2.018203JES.
- [10] L. Lu, X. Han, J. Li, J. Hua, M. Ouyang, A review on the key issues for lithium-ion battery management in electric vehicles, J. Power Sources 226 (2013) 272–288, https://doi.org/10.1016/J.JPOWSOUR.2012.10.060.
- [11] W.A. Appiah, M.P. Stockham, J. Maria, G. Lastra, Towards understanding the variation of electrode design parameters on the electrochemical performance of aluminum graphite batteries: an experimental and simulation study, Batter. Supercaps (2023) e202300258, https://doi.org/10.1002/BATT.202300258.
- [12] S.F. Schuster, T. Bach, E. Fleder, J. Müller, M. Brand, G. Sextl, A. Jossen, Nonlinear aging characteristics of lithium-ion cells under different operational conditions, J. Energy Storage 1 (2015) 44–53, https://doi.org/10.1016/J.EST.2015.05.003.
- [13] S.J. Harris, D.J. Harris, C. Li, Failure statistics for commercial lithium ion batteries: a study of 24 pouch cells, J. Power Sources 342 (2017) 589–597, https://doi.org/ 10.1016/J.JPOWSOUR.2016.12.083.
- [14] S.F. Schuster, M.J. Brand, P. Berg, M. Gleissenberger, A. Jossen, Lithium-ion cellto-cell variation during battery electric vehicle operation, J. Power Sources 297 (2015) 242–251, https://doi.org/10.1016/J.JPOWSOUR.2015.08.001.
- [15] W. Waag, D.U. Sauer, Adaptive estimation of the electromotive force of the lithium-ion battery after current interruption for an accurate state-of-charge and capacity determination, Appl. Energy 111 (2013) 416–427, https://doi.org/ 10.1016/J.APENERGY.2013.05.001.
- [16] D.M. Bernardi, J.Y. Go, Analysis of pulse and relaxation behavior in lithium-ion batteries, J. Power Sources 196 (2011) 412–427, https://doi.org/10.1016/J. JPOWSOUR.2010.06.107.
- [17] L. Pei, T. Wang, R. Lu, C. Zhu, Development of a voltage relaxation model for rapid open-circuit voltage prediction in lithium-ion batteries, J. Power Sources 253 (2014) 412–418, https://doi.org/10.1016/J.JPOWSOUR.2013.12.083.
- [18] A. Barai, K. Uddin, W.D. Widanage, A. McGordon, P. Jennings, A study of the influence of measurement timescale on internal resistance characterisation methodologies for lithium-ion cells, Sci. Rep. 81 (8) (2018) 1–13, https://doi.org/ 10.1038/s41598-017-18424-5 (2017).
- [19] W.A. Appiah, D. Kim, J. Song, M. Ryou, Y.M. Lee, Understanding the effect of polydopamine interlayer on the long-term cycling performance of silicon anodes: a multiphysics-based model study, Batter. Supercaps 2 (2019) batt.201900019, https://doi.org/10.1002/batt.201900019.
- [20] W.A. Appiah, Y. Roh, C.B. Dzakpasu, M.-H. Ryou, Y.M. Lee, Design of thin-film interlayer between silicon electrode and current collector using a chemomechanical degradation model, J. Electrochem. Soc. 167 (2020) 080542, https:// doi.org/10.1149/1945-7111/ab9382.
- [21] A.K. Hjelm, G. Lindbergh, Experimental and theoretical analysis of LiMn2O4 cathodes for use in rechargeable lithium batteries by electrochemical impedance spectroscopy (EIS), Electrochim. Acta 47 (2002) 1747–1759, https://doi.org/ 10.1016/S0013-4686(02)00008-7.
- [22] W.A. Appiah, J. Park, S. Byun, I. Cho, A. Mozer, M.-H. Ryou, Y.M. Lee, A coupled chemo-mechanical model to study the effects of adhesive strength on the electrochemical performance of silicon electrodes for advanced lithium ion batteries, J. Power Sources 407 (2018) 153–161, https://doi.org/10.1016/J. JPOWSOUR.2018.06.079.
- [23] R. Chandrasekaran, Quantification of contributions to the cell overpotential during galvanostatic discharge of a lithium-ion cell, J. Power Sources 262 (2014) 501–513, https://doi.org/10.1016/J.JPOWSOUR.2014.03.124.
- [24] Y. Li, F. El Gabaly, T.R. Ferguson, R.B. Smith, N.C. Bartelt, J.D. Sugar, K.R. Fenton, D.A. Cogswell, A.L.D. Kilcoyne, T. Tyliszczak, M.Z. Bazant, W.C. Chueh, Currentinduced transition from particle-by-particle to concurrent intercalation in phaseseparating battery electrodes, Nat. Mater. 1312 (13) (2014) 1149–1156, https:// doi.org/10.1038/nmat4084.
- [25] L.W. Juang, P.J. Kollmeyer, T.M. Jahns, R.D. Lorenz, Improved modeling of lithium-based batteries using temperature-dependent resistance and overpotential, 2014 IEEE Transp. Electrif. Conf. Expo Components, Syst. Power Electron. - From Technol. to Bus. Public Policy, ITEC 2014. (2014). https://doi.org/10.1109/ITEC. 2014.6861800.
- [26] K. Onda, T. Ohshima, M. Nakayama, K. Fukuda, T. Araki, Thermal behavior of small lithium-ion battery during rapid charge and discharge cycles, J. Power Sources 158 (2006) 535–542, https://doi.org/10.1016/J. JPOWSOUR.2005.08.049.
- [27] K. Singh, T. Tjahjowidodo, L. Boulon, M. Feroskhan, Framework for measurement of battery state-of-health (resistance) integrating overpotential effects and entropy

changes using energy equilibrium, Energy 239 (2022) 121942, https://doi.org/10.1016/J.ENERGY.2021.121942.

- [28] S.K. Pradhan, B. Chakraborty, Battery management strategies: an essential review for battery state of health monitoring techniques, J. Energy Storage 51 (2022) 104427, https://doi.org/10.1016/J.EST.2022.104427.
- [29] V.J. Ovejas, A. Cuadras, State of charge dependency of the overvoltage generated in commercial Li-ion cells, J. Power Sources 418 (2019) 176–185, https://doi.org/ 10.1016/J.JPOWSOUR.2019.02.046.
- [30] A.G. Li, K. Mayilvahanan, A.C. West, M. Preindl, Discrete-time modeling of Li-ion batteries with electrochemical overpotentials including diffusion, J. Power Sources 500 (2021) 229991, https://doi.org/10.1016/J.JPOWSOUR.2021.229991.
- [31] K. Märker, C. Xu, C.P. Grey, Operando NMR of NMC811/graphite lithium-ion batteries: structure, dynamics, and lithium metal deposition, J. Am. Chem. Soc. 142 (2020) 17447–17456, https://doi.org/10.1021/JACS.0C06727/ASSET/ IMAGES/LARGE/JA0C06727_0004.JPEG.
- [32] K. Gotoh, T. Yamakami, I. Nishimura, H. Kometani, H. Ando, K. Hashi, T. Shimizu, H. Ishida, Mechanisms for overcharging of carbon electrodes in lithium-ion/ sodium-ion batteries analysed by operando solid-state NMR, J. Mater. Chem. A 8 (2020) 14472–14481, https://doi.org/10.1039/D0TA04005C.
- [33] Y. Jin, N.J.H. Kneusels, C.P. Grey, NMR study of the degradation products of ethylene carbonate in silicon-lithium ion batteries, J. Phys. Chem. Lett. 10 (2019) 6345–6350, https://doi.org/10.1021/ACS.JPCLETT.9B02454/ASSET/IMAGES/ LARGE/JZ9B02454_0003.JPEG.
- [34] C.M. Wang, W. Xu, J. Liu, D.W. Choi, B. Arey, L.V. Saraf, J.G. Zhang, Z.G. Yang, S. Thevuthasan, D.R. Baer, N. Salmon, In situ transmission electron microscopy and spectroscopy studies of interfaces in Li ion batteries: challenges and opportunities, J. Mater. Res. 25 (2010) 1541–1547, https://doi.org/10.1557/JMR.2010.0198.
- [35] F. De Giorgio, N. Laszczynski, J. von Zamory, M. Mastragostino, C. Arbizzani, S. Passerini, Graphite//LiNi0.5Mn1.5O4 cells based on environmentally friendly made-in-water electrodes, ChemSusChem 10 (2017) 379–386, https://doi.org/ 10.1002/CSSC.201601249.
- [36] Y. Li, G.M. Veith, K.L. Browning, J. Chen, D.K. Hensley, M.P. Paranthaman, S. Dai, X.G. Sun, Lithium malonatoborate additives enabled stable cycling of 5 V lithium metal and lithium ion batteries, Nano Energy 40 (2017) 9–19, https://doi.org/ 10.1016/J.NANOEN.2017.07.051.
- [37] C.K. Kim, K. Kim, K. Shin, J.J. Woo, S. Kim, S.Y. Hong, N.S. Choi, Synergistic effect of partially fluorinated ether and fluoroethylene carbonate for high-voltage lithium-ion batteries with rapid chargeability and dischargeability, ACS Appl. Mater. Interfaces 9 (2017) 44161–44172, https://doi.org/10.1021/ ACSAMI.7B12352/ASSET/IMAGES/LARGE/AM-2017-123526 0005.JPEG.
- [38] L. Yang, B. Ravdel, B.L. Lucht, Electrolyte reactions with the surface of high voltage LiNi 0.5Mn1.5O4 cathodes for lithium-ion batteries, Electrochem. Solid-State Lett. 13 (2010) A95, https://doi.org/10.1149/1.3428515/XML.
- [39] B.J. Tremolet de Villers, S.M. Bak, J. Yang, S.D. Han, In situ ATR-FTIR study of the cathode–electrolyte interphase: electrolyte solution structure, transition metal redox, and surface layer evolution, Batter. Supercaps 4 (2021) 778–784, https:// doi.org/10.1002/BATT.202000259.
- [40] S. Watanabe, M. Kinoshita, K. Nakura, Capacity fade of LiNi(1-x-y)CoxAlyO2 cathode for lithium-ion batteries during accelerated calendar and cycle life test. I. Comparison analysis between LiNi(1-x-y)CoxAlyO2 and LiCoO2 cathodes in cylindrical lithium-ion cells during long term storage test, J. Power Sources 247 (2014) 412–422, https://doi.org/10.1016/J.JPOWSOUR.2013.08.079.
- [41] X. Wang, Y. Li, Y.S. Meng, Cryogenic electron microscopy for characterizing and diagnosing batteries, Joule 2 (2018) 2225–2234, https://doi.org/10.1016/J. JOULE.2018.10.005.
- [42] P. Iurilli, C. Brivio, V. Wood, On the use of electrochemical impedance spectroscopy to characterize and model the aging phenomena of lithium-ion batteries: a critical review, J. Power Sources 505 (2021) 229860, https://doi.org/ 10.1016/J.JPOWSOUR.2021.229860.
- [43] D. Andre, M. Meiler, K. Steiner, C. Wimmer, T. Soczka-Guth, D.U. Sauer, Characterization of high-power lithium-ion batteries by electrochemical impedance spectroscopy. I. Experimental investigation, J. Power Sources 196 (2011) 5334–5341, https://doi.org/10.1016/J.JPOWSOUR.2010.12.102.
- [44] J. Huang, Z. Li, J. Zhang, Dynamic electrochemical impedance spectroscopy reconstructed from continuous impedance measurement of single frequency during charging/discharging, J. Power Sources 273 (2015) 1098–1102, https://doi.org/ 10.1016/J.JPOWSOUR.2014.07.067.
- [45] H.P.G.J. Beelen, L.H.J. Raijmakers, M.C.F. Donkers, P.H.L. Notten, H.J. Bergveld, A comparison and accuracy analysis of impedance-based temperature estimation methods for Li-ion batteries, Appl. Energy 175 (2016) 128–140, https://doi.org/ 10.1016/J.APENERGY.2016.04.103.
- [46] I. Babaeiyazdi, A. Rezaei-Zare, S. Shokrzadeh, State of charge prediction of EV Liion batteries using EIS: a machine learning approach, Energy 223 (2021) 120116, https://doi.org/10.1016/J.ENERGY.2021.120116.

- [47] M.F. Ng, J. Zhao, Q. Yan, G.J. Conduit, Z.W. Seh, Predicting the state of charge and health of batteries using data-driven machine learning, Nat. Mach. Intell. 23 (2) (2020) 161–170, https://doi.org/10.1038/s42256-020-0156-7.
- [48] C. Lyu, Y. Song, J. Zheng, W. Luo, G. Hinds, J. Li, L. Wang, In situ monitoring of lithium-ion battery degradation using an electrochemical model, Appl. Energy 250 (2019) 685–696, https://doi.org/10.1016/J.APENERGY.2019.05.038.
- [49] Q. Zhang, R.E. White, Calendar life study of Li-ion pouch cells: part 2: simulation, J. Power Sources 179 (2008) 785–792, https://doi.org/10.1016/J. JPOWSOUR.2007.12.022.
- [50] J. Li, K. Adewuyi, N. Lotfi, R.G. Landers, J. Park, A single particle model with chemical/mechanical degradation physics for lithium ion battery State of Health (SOH) estimation, Appl. Energy 212 (2018) 1178–1190, https://doi.org/10.1016/ J.APENERGY.2018.01.011.
- [51] J. Li, R.G. Landers, J. Park, A comprehensive single-particle-degradation model for battery state-of-health prediction, J. Power Sources 456 (2020) 227950, https:// doi.org/10.1016/J.JPOWSOUR.2020.227950.
- [52] S. Santhanagopalan, Q. Guo, P. Ramadass, R.E. White, Review of models for predicting the cycling performance of lithium ion batteries, J. Power Sources 156 (2006) 620–628, https://doi.org/10.1016/J.JPOWSOUR.2005.05.070.
- [53] M. Doyle, T.F. Fuller, J. Newman, Modeling of galvanostatic charge and discharge of the lithium/polymer/insertion cell, J. Electrochem. Soc. 140 (1993) 1526–1533.
- [54] W.A. Appiah, J. Park, S. Byun, M.-H. Ryou, Y.M. Lee, A mathematical model for cyclic aging of spinel LiMn 2 O 4/graphite lithium-ion cells, J. Electrochem. Soc. 163 (2016) 2757–2767, https://doi.org/10.1149/2.1061613jes.
- [55] F. Yang, Y. Qiao, B. Gao, P. Duan, Y. Zhu, Investigation on Li-ion battery charging polarization characteristics and influence factors, Ionics (Kiel) 22 (2016) 1603–1610, https://doi.org/10.1007/S11581-016-1694-1/FIGURES/12.
- [56] E. Prada, D. Di Domenico, Y. Creff, J. Bernard, V. Sauvant-Moynot, F. Huet, Simplified electrochemical and thermal model of LiFePO 4 -graphite Li-ion batteries for fast charge applications, J. Electrochem. Soc. 159 (2012) A1508–A1519, https://doi.org/10.1149/2.064209JES/XML.
- [57] W.A. Appiah, A. Stark, S. Lysgaard, J. Busk, P. Jankowski, J.H. Chang, A. Bhowmik, B. Gollas, J.M. Garcia-Lastra, Unveiling the plating-stripping mechanism in aluminum batteries with imidazolium-based electrolytes: a hierarchical model based on experiments and ab initio simulations, Chem. Eng. J. 472 (2023) 144995, https://doi.org/10.1016/J.CEJ.2023.144995.
- [58] A. Nyman, T.G. Zavalis, R. Elger, M. Behm, G. Lindbergh, Analysis of the polarization in a Li-ion battery cell by numerical simulations, J. Electrochem. Soc. 157 (2010) A1236, https://doi.org/10.1149/1.3486161/XML.
- [59] V. Srinivasan, J. Newman, Discharge model for the lithium iron-phosphate electrode, J. Electrochem. Soc. 151 (2004) A1517, https://doi.org/10.1149/ 1.1785012/XML.
- [60] K.A. Severson, P.M. Attia, N. Jin, N. Perkins, B. Jiang, Z. Yang, M.H. Chen, M. Aykol, P.K. Herring, D. Fraggedakis, M.Z. Bazant, S.J. Harris, W.C. Chueh, R. D. Braatz, Data-driven prediction of battery cycle life before capacity degradation, Nat. Energy 45 (4) (2019) 383–391, https://doi.org/10.1038/s41560-019-0356-8.
- [61] No Title, (n.d.). https://github.com/laura-rieger/in-situ-analysis.
- [62] J. Park, W.A. Appiah, S. Byun, D. Jin, M.H. Ryou, Y.M. Lee, Semi-empirical longterm cycle life model coupled with an electrolyte depletion function for largeformat graphite/LiFePO4 lithium-ion batteries, J. Power Sources 365 (2017) 257–265, https://doi.org/10.1016/J.JPOWSOUR.2017.08.094.
- [63] Q. Zhang, R.E. White, Capacity fade analysis of a lithium ion cell, J. Power Sources 179 (2008) 793–798.
- [64] W.A. Appiah, M.-H. Ryou, Y.M. Lee, A physics-based model capacity fade analysis of LiMn 2 O 4/graphite cell at different temperatures, J. Electrochem. Soc. 166 (2019) 5109–5116, https://doi.org/10.1149/2.0161903jes.
- [65] D. Diddens, W.A. Appiah, Y. Mabrouk, A. Heuer, T. Vegge, A. Bhowmik, D. Diddens, Y. Mabrouk, A. Heuer, W.A. Appiah, T. Vegge, A. Bhowmik, Modeling the solid electrolyte interphase: machine learning as a game changer? Adv. Mater. Interfaces 9 (2022) 2101734 https://doi.org/10.1002/ADMI.202101734.
- [66] K. Edström, T. Gustafsson, J.O. Thomas, The cathode–electrolyte interface in the Li-ion battery, Electrochim. Acta 50 (2004) 397–403, https://doi.org/10.1016/J. ELECTACTA.2004.03.049.
- [67] M. Dubarry, C. Truchot, M. Cugnet, B.Y. Liaw, K. Gering, S. Sazhin, D. Jamison, C. Michelbacher, Evaluation of commercial lithium-ion cells based on composite positive electrode for plug-in hybrid electric vehicle applications. Part I: initial characterizations, J. Power Sources 196 (2011) 10328–10335, https://doi.org/ 10.1016/J.JPOWSOUR.2011.08.077.
- [68] M. Dubarry, C. Truchot, B.Y. Liaw, Synthesize battery degradation modes via a diagnostic and prognostic model, J. Power Sources 219 (2012) 204–216, https:// doi.org/10.1016/J.JPOWSOUR.2012.07.016.