

Novel and systematic validity assessment of Li-ion battery lifetime predictions

E. Sarasketa-Zabala*, E. Martinez-Laserna, L.M. Rodriguez-Martinez¹, I. Gandiaga

IK4-Ikerlan, José María Arizmendiarieta Pasealekua, 2, E-20500 Arrasate-Mondragón, Spain

**E-mail: esarasketa@ikerlan.es*

Abstract

A realistic lifetime prediction approach for Li-ion batteries is presented. This paper especially focuses on the evaluation of combined calendar and cycle ageing, and proposes a stepwise validation methodology that includes complex realistic operation conditions. The ageing model developed for a LFP-based 26650-size battery cell can be used for the lifetime assessment of different Energy Storage System applications with high accuracy, as is the case for an elevator application considered as a case study. The ageing prediction root-mean-square error was just 1.35% after 180 days of battery cell testing. The model was also successfully validated for PHEV operation combined with V2G use.

Keywords: lithium battery, battery SOH (State of Health), battery calendar life, cycle life, battery model

1 Introduction

Comprehensive ageing evaluation of lithium ion (Li-ion) battery cells is demanded for this technology based Energy Storage Systems (ESS) successful integration. To identify the factors playing a key role in battery lifetime, it is necessary a complete analysis of ageing processes based on complex operation conditions of most applications: combination of cycling, rest periods at different State of Charges (SOCs), partial charging, wide range of temperatures, etc. Non-accelerated tests are highly time- and cost-intensive, but precision and applicability range of lifetime prediction models based on accelerated tests are limited. The use of the model for product development and management issues needs to be ensured.

There are numerous worldwide activities in the field of Li-ion battery ageing analysis, modelling and lifetime prediction, which are tackled from a wide range of perspectives. The overview was already presented in authors previous publications [1-3]. This investigation work enhances the results by proposing a methodology for lifetime prognosis that comprises both cycling and calendar ageing, and also their interaction in depth analysis that suits different applications. It is based on on-board measurable parameters, as it is pursued the ageing model to be integrated into a Battery Management System (BMS), and it seeks a cost-effective route for combining temperature (T), State of Charge (SOC), rest periods, Depth of Discharge (DOD), current rate (C-rate) and Ampere hours (Ah)-throughput impact factors over time with high accuracy.

The main objective of this work includes the development of ageing model validation procedures and the analysis of the applicability of the methodology adopted for lifetime analysis under realistic operation conditions. Experimental results related to different validation steps and corresponding to a lithium iron phosphate (LiFePO₄, LFP)/graphite 26650-size battery cell are discussed. The validity of the presented ageing model is assessed for two application examples: elevator application and Plug-in Hybrid Electric Vehicle (PHEV) with vehicle to grid (V2G) energy use.

¹ Present address: CIC energiGUNE, Arabako Teknologi Parkea, Albert Einstein 48,E-01510 Miñao, Spain.

2 Lifetime prediction approach

The overall methodology for battery lifetime assessment was presented in Ref. [3] and comprises the following main steps: i) investigation of single battery stress factors effects; ii) development of battery ageing calendar and cycling models; iii) thorough validation of individual cycling and calendar ageing models; and iv) complete battery ageing model development (combination of calendar and cycle ageing) and comprehensive validation. Both capacity and internal resistance were measured in order to evaluate the degradation of battery cell performance. However, for the case of the investigated LFP-based battery cell, and focusing only on the dominant ageing mechanism, Loss of Lithium Inventory (LLI), lifetime resulted to be restricted by the remaining available capacity as presented in storage and cycling ageing tests results presented in Refs. [1,2]. Therefore, the ageing model was finally developed just based on capacity loss (Q_{loss}) evolution.

Eqs. (1)–(3) describe the developed ageing algorithm and correspond to the individual analysis of calendar and cycle ageing (Q_{loss_cal} and Q_{loss_cyc} , respectively) as baseline for the comprehensive lifetime prognosis approach. Calendar and cycle ageing models development and validation were thoroughly described in Refs. [1,2]. Eqs. (1,2) do not include C-rate factor but it was tested that the model also predicts accurately this ageing factor effect [2].

$$Q_{loss_cal} [\%] = \alpha_1 \cdot \exp(\beta_1 \cdot T^{-1}) \cdot \alpha_2 \cdot \exp(\beta_2 \cdot SOC) \cdot t^{0.5} \quad (1)$$

$$Q_{loss_cyc} [\%] \text{ (10\%} \leq \text{DOD} \leq \text{50\%)} = (\gamma_1 \cdot \text{DOD}^2 + \gamma_2 \cdot \text{DOD} + \gamma_3) \cdot k \cdot \text{Ah}^{0.87} \quad (2)$$

$$Q_{loss_cyc} [\%] \text{ (DOD} < \text{10\% \& DOD} > \text{50\%)} = (\alpha_3 \cdot \exp(\beta_3 \cdot \text{DOD}) + \alpha_4 \cdot \exp(\beta_4 \cdot \text{DOD})) \cdot k \cdot \text{Ah}^{0.65} \quad (3)$$

where $\alpha_1, \beta_1, \alpha_2, \beta_2, \gamma_1, \gamma_2, \gamma_3, \alpha_3, \beta_3, \alpha_4$ and β_4 are fitting parameters, and k is a complex balancing factor that is a function of Ah-throughput and deals with the cycling ageing tests acceleration [2].

The main basis for the complete algorithm are that cycle and storage ageing effects can be superimposed ($Q_{loss} = Q_{loss_cal} + Q_{loss_cyc}$), and SOC and T impact factors effects are the same during storage and cycling operation [4]. The overall approach allows simulating realistic battery cell operation for a given system through the combination of single calendar and cycling ageing models, and also predicting cycle lifetime under different T and SOC conditions. These hypotheses that aim towards reduced ageing matrixes need of comprehensive stepwise validation.

3 Ageing model validation

The first step for the complete model validation includes different storage and cycling periods (combination of multiple dynamic conditions of all stress factors). Fig. 1 (a) shows a test profile that combines different levels of SOC, T, DOD, C-rate and storage periods. Three different tests were defined for approaching battery real operation, which are referred to as Test I (profile shown in Fig. 1 (a)), Test II and Test III. The main difference between these profiles is the ambient temperature: varying from 25 to 30°C for Test I (battery cell surface temperature is plotted in Fig. 1 (a)), 35-40°C for Test II and 40-45°C for Test III. The storage periods were additionally longer for Test III. Fig. 1 (b) shows capacity change measured under such experimental conditions (open circles), and includes the predictions (dotted lines) that result from simulating the instantaneous dynamic battery cell operation. The mean prediction error was just 0.38% and the overall root-mean-square error (RMSE) was only 1.23%.

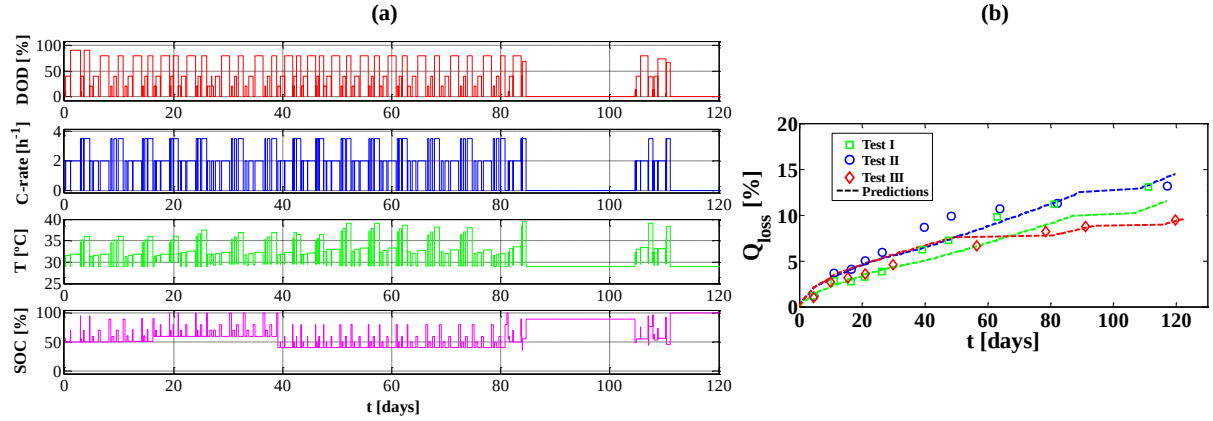


Fig. 1. (a) Validation Test I approaching real operation (ageing model input factors). (b) Capacity loss (Q_{loss}) results for the three validation test profiles (markers) and the corresponding predictions (dotted lines)

In real applications, the cycling profiles are not usually symmetric, as the one shown in Fig. 1. (a), and it is not operated in battery charge sustaining (CS) mode continuously. The next validation step should be therefore non-symmetric cycling profiles evaluation. Lastly, it is proposed to carry out tests under complex operating conditions, *i.e.* realistic profiles, combining partial SOC cycling (micro-cycles), charge depleting (CD) cycling (macro-cycles), rest periods at different SOC, incomplete charging and battery cell temperature change over time.

A CS cycling profile was tested changing the charge and discharge C-rates within the same DOD condition, as it is shown in Fig. 2 (a) and (b). This validation test represents most power demanding battery traction and regenerative events of a residential elevator, including the charge from the grid in order to implement a CS profile [3]. It was assumed that the elevator would be in continuous operation so as to accelerate the ageing process. The inset in Fig. 2 (a) indicates the test repetition unit (a complete cycle) that was performed continuously at 35°C. Fig 2 (c) shows the measured capacity loss for three tested battery cells under the same profile (open circles) and the lifetime model prediction (dotted line). These results prove that the model is applicable to different operation modes with high accuracy (0.58% RMSE).

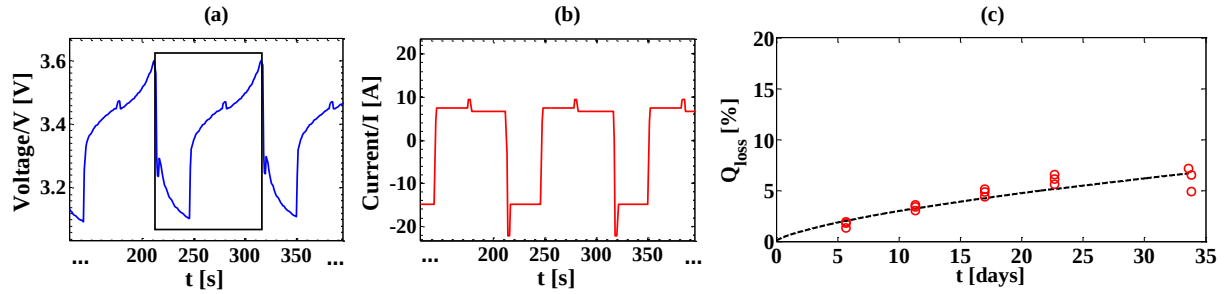


Fig. 2. Elevator operation. (a) Voltage and (b) current profiles (repetition unit indicated with the box) carried out at 35°C. (c) Capacity loss (Q_{loss}) results for the three tested battery cells (open circles) and the corresponding prediction (dotted line)

The assessment of the applicability of the ageing model for different realistic profiles firstly focused on the analysis of another residential elevator operation profile. Fig 3 (a) shows the SOC profile (assessed Ah-based and referred to the nominal capacity) that was performed at 30 and 40°C. The testing profile consisted of 3 h of continuous cycling followed by a pause of 2 h at different SOC each day. The overall daily trips were performed one after the other and the overnight elevator stop was shortened in order to accelerate the ageing test. The macro-discharging was composed of a series of CD micro-discharging cycles and the macro-charging, representing the recharge from the grid, was a single charge up to 90% SOC. Fig 3 (b) and (c) show measured capacity loss results (open circles) and predictions (dotted lines) for the battery cell of the ESS integrated in the described elevator application operating at 30 and 40°C, respectively. The model follows the complex ageing phenomena evolution and predictions yielded an overall 1.35% RMSE. Predictions biases were different depending on the ambient temperature: estimated capacity loss values at 40°C showed more deviation from the corresponding observations. However, not

only did the predictions show a temperature factor related issue but also the experimental results. The capacity loss was very similar (9.5-11%) for the cells tested at any of the considered temperatures for *ca.* 120 days. This was also the case for the cells tested under the operation conditions corresponding to the first validation step shown in Fig 1 (the main difference between Test I and Test II was the ambient temperature, while the cells tested under both conditions underwent the same capacity loss, 11.2%, after 82 days of operation). J. Groot *et al.* [8] also concluded that higher temperature do not always accelerate ageing. These overall results indicate that combined effects of complex operation conditions influence on the ageing processes due to temperature. In conclusion, the ageing analysis of the considered reference battery cell under the elevator operation profile demonstrated that, on the one hand, the Arrhenius law followed for temperature effect modelling depends on the operation conditions. On the other hand, it also revealed that the rule of thumbs "the reaction rate doubles with $\Delta T = 10^\circ\text{C}$ increase" is just valid for the case of calendar ageing investigated individually in Ref. [1], in which specific conditions of SOC and T also play a role.

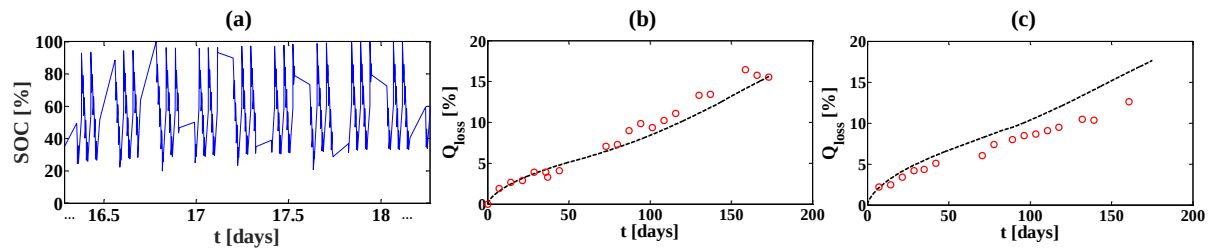


Fig. 3. (a) SOC profile of the validation test simulating elevator operation. (b) and (c) Capacity loss (Q_{loss}) results (open circles) and the corresponding predictions (dotted lines) of the tests carried out at (b) 30°C and (c) 40°C ambient temperature

The validation stage using complex operation profiles was complemented by the evaluation of PHEV operation combined with V2G use. The operation current profile from Peterson *et al.* [6] was replicated. This profile is based on Urban Dynamometer Driving Schedule (UDDS) (US EPA vehicle test) [7] and includes different V2G periods under 0.5C constant discharge current. Four different Test Cycles (TC) were evaluated, each of them representing a day of operation, and the current profiles were assessed at cell level (the TC specifications are described in Ref. [6]). Every TC starts with the fully charged battery cell and the overall DODs are *ca.* 35%, 48%, 59% and 73% for TC 1, TC 2, TC 3 and TC 4, respectively. As an example, Fig. 4 (a) shows the TC 4 current profile, which is composed of four driving sections, two parking periods and two V2G phases.

Fig. 4 (b) shows the ageing analysis under all the considered PHEV-V2G testing profiles (TC 1-4). Experimental data from Peterson *et al.* [6] was used for the ageing model validation, as they tested the same battery cell reference as the one used within this work. The grey area in Fig. 4 (b) shows the whole set of TC 1-4 ageing results measured at 25°C ambient temperature, which are plotted as capacity based SOH evolutions as a function of total Ampere hours (Ah)-throughput. Peterson *et al.* [6] used energy (in Wh) like ageing metric, but those data may be equal to the capacity because, as mentioned in section 2, the internal resistance change of the investigated battery cell could be neglected within the operation framework considered for model development [1,2]. Capacity loss prediction results for each TC are shown with dotted lines and follow the performance fade evolutions reported by Peterson *et al.* [6], even if the tendencies of observations and estimations are different at the beginning (linear against a power law relationship). The model overestimates the ageing under TC 1 and TC 2 operation profiles, but TC 3 and TC 4 simulation results fit with the experimental results under the grey area. The deviations are in line with the model characteristics at TC1 and TC2 tests maximum operating range: 30-50% DOD at the end of the driving day. The analysis of cycle ageing modelling residuals in Ref. [2] showed the largest median values for 50% DOD fitting and already indicated the need of model improvement at middle DODs. However, it needs to be taken into account that rough ageing results from Ref. [6] were used for predictions evaluation and, therefore, this validation step did not aim at evaluating the accuracy of the presented lifetime prognosis approach for this specific application scenario. Overall, regardless the deviations observed, the ageing analysis under PHEV combined with V2G use supported that the ageing model developed for the investigated LFP-based reference battery cell is valid to estimate the capacity degradation under different applications operation profiles.

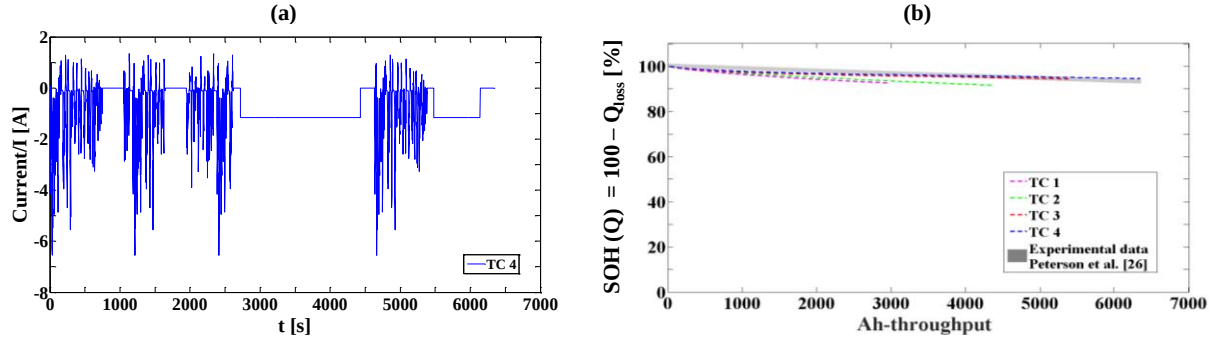


Fig. 4. (a) Representative combined urban commute driving duty cycle for PHEV, based on the Urban Dynamometer Driving Schedule (UDDS) (US EPA vehicle test) [7], and vehicle-to-grid (V2G) usage profile. A simulated test current regime (Test Cycle 4 from Peterson *et al.* [6]).
 (b) Ageing analysis under the defined PHEV-V2G operation. Grey area represents capacity loss (Q_{loss}) evolution as a function of processed Ampere-hours (Ah) at 25°C ambient testing temperature from Peterson *et al.* [6] for different Test Cycles (TC 1-4). Dotted lines show the ageing predictions for each of the TCs using the lifetime prognosis approach presented in this paper

In summary, comprehensive and stepwise model validation results showed that the developed model can predict accurately the lifetime of the considered LFP battery cell under different realistic operation conditions. Different validation steps enabled gaining insight into critical modelling issues (*e.g.* influence of temperature on cycle ageing and 30-50% DOD effect), which has become the proposed validation methodology essential for the model improvement process. Another limitation of the developed ageing model is that it serves for a single degradation mode (LLI). However, validation results showed that predictions match with cell overall ageing behaviour. Validation results also confirmed that, for the investigated LFP-based cell, calendar and cycle ageing impact factors effects can be combined for ageing prediction under dynamic and complex operation conditions. K. Smith *et al.* [9] and B. Lunz *et al.* [10] also used this premise for NCA (LiNiCoAlO_2) and NCM ($\text{Li}(\text{NiMn})_2\text{O}_4$)-based battery technologies, respectively. It was additionally demonstrated the initial hypothesis that SOC and T effects could be considered equal during battery storage or cycling, although complex operation tests results showed that temperature effect during cycling should be further investigated. C. Günther *et al.* [11] also assumed this hypothesis for NCA and NCM-based battery technologies. What all this means is that the presented approach enables reducing significantly the ageing tests matrixes and it therefore provides a cost-effective route for combining temperature, SOC, rest periods, DOD and C-rate impact factors with high accuracy.

4 Conclusions

The overall scope of this research work was to develop a lifetime prognosis methodology that combines both calendar and cycle ageing and covers a wide range of realistic operation conditions. A novel systematic approach for evaluating calendar and cycle ageing complex interactions was proposed. Different validation steps showed that developed ageing model and the presented approach is suitable for evaluating accelerated real applications battery lifetime with 1.35% RMSE. It makes possible to simplify several specific models for different applications into a single one, which minimises experimental and computing work related time and costs significantly. An additional benefit of the proposed methodology is that the overall model can be also used for analysing single calendar and cycling ageing. Moreover, the ageing model is based on real applications operation parameters (field measures are straightforward converted into ageing model inputs) and can be easily integrated into BMS for online capacity fade estimations.

The lifetime prognosis methodology will be further improved when applying it to other battery technologies. This will also enable investigating more in depth the achievable coverage and advantages of the presented approach, and the real reduction of testing time will be also yielded.

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Authors



Dr. Eng. Elixabet Sarasketa-Zabala received her M. Sc. degree in Chemical Engineering from the Faculty of Engineering of Bilbao (ETSI de Bilbao, Spain) and Master in Energy Systems from the University of Gävle (HIG, Sweden) in 2009, and Ph.D in Engineering with International mention from Mondragon University (Spain) in 2014. She has been working at the Energy Business Unit of IK4-Ikerlan Technology Research Centre since 2009. Her research interests include reliability, safety and lifetime assessment of Li-ion battery technologies and advanced characterisation of batteries and EDLC approaching different industrial application needs.



Egoitz Martinez-Laserna received his M.Sc in Electronic Engineering from the University of Mondragon in 2013. He joined the Energy Business Unit of IK4-Ikerlan Technological Research Centre in 2013. Currently he is pursuing a Ph. D degree in IK4-Ikerlan focused on second life batteries performance, sizing and integration. His research interests are in the field of electric vehicles, renewable energy and energy management.



Dr. Lide M. Rodriguez-Martinez is since January 2015, the Group Leader of Li based and responsible for the Strategic Research Line in Li-S technology at CIC Energigune. Before that (2001-2014), she was a senior researcher at IK4-Ikerlan Technological Research Centre working on novel technology development of tubular SOFC, battery ageing and testing for specific applications and the development of new energy storage concepts. PhD in Solid State Chemistry (1999, Cambridge University) and at Berkeley laboratory for tech transfer (2001).



Iñigo Gandiaga received a Diploma in Physics from the University of the Basque Country, UPV-EHU (Spain) in 2010. He joined the Energy Business Unit of IK4-Ikerlan Technology Research Centre in 2010. His research interests include different electrochemical energy storage technologies (EDLC, Li-ion and NiMH), particularly the lifetime and sizing of batteries for transport and stationary applications.