Battery Degradation Modelling For Implementation in PGMcpp

prepared by

Anthony Truelove MASc, P.Eng.

 $\ensuremath{\mathsf{PRIMED}}$ - Research Engineer

November 7, 2023

Drafted using \LaTeX

Contents

Co	ontents	i
Li	ist of Tables	ii
Li	st of Figures	iii
1	Motivation and Intent	1
2	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	2 3 3 5 6 8 10
3	Cycle Ageing 3.1 ODE	12 12
4		14 15 16
5	Calibrating the Total Degradation Model 5.1 Step 1: Calendar Ageing with SOC = 0	17 17 17 18 19
Re	eferences	20

List of Tables

2.1	$B_{\rm cal}$ vs SOC for the Saft VL6P (6.8 Ah), from Table 1 of [1]	6
2.2	$\widehat{B}_{\rm cal}$ vs SOC for the Saft VL6P (6.8 Ah). Italicized row is extrapolated	6
2.3	Ea _{cal} vs SOC for the A123s (2.3 Ah), from Table 1 of [1]. Italicized row is	
	extrapolated	9

List of Figures

2.1	$\widehat{B}_{\rm cal}$ vs SOC for the Saft VL6P (6.8 Ah)	7
2.2	$\widehat{B}_{\rm cal}$ vs SOC for the Saft VL6P (6.8 Ah). Least-squares model shown	8
2.3	Ea_{cal} vs SOC for the A123s (2.3 Ah)	Ć
2.4	Ea _{cal} vs SOC for the A123s (2.3 Ah). Least-squares model shown	10

1 Motivation and Intent

- In order to assess the economic viability of incorporating battery energy storage into
- microgrid designs, a general and reliable means of modelling degradation (specifically energy
- 4 capacity fade) is needed. Specifically, a model that is directly compatible with time domain
- 5 power/energy modelling is desirable. To that end, an ODE of the form

$$\frac{dSOH}{dt} = f(C, SOC, SOH)$$
 (1.1)

- 6 is sought, where SOH is state of health (dimensionless), C is C-rate (dimensionless), and
- SOC is state of charge (dimensionless). For the sake of clarity, C-rate is defined as

$$C = \frac{|P|(1 \text{ hr})}{E_0}$$

- where |P| is absolute power (charge/discharge), and E_0 is nominal energy capacity. Likewise,
- 9 for the sake of clarity, SOH is defined as

$$SOH = \frac{E}{E_0}$$

where E is time-varying energy capacity. Likewise, for the sake of clarity, SOC is defined as

$$SOC = \frac{Q}{E_0}$$

where Q is time-varying charge.

¹By definition, C=1 corresponds to the |P| needed to completely charge/discharge the battery in one hour.

2 Calendar Ageing

To begin, one might first focus on simple calendar ageing. That is, energy capacity fade that occurs in the limiting case where $|P| \equiv 0$. To that end, one might turn to the results presented in [1].

a 2.1 ODE

17

The following ODE model for calendar ageing is proposed in [1]

$$\frac{dE}{dt}_{\text{cal}} = z_{\text{cal}} B_{\text{cal}}(\text{SOC}) \exp\left[-\frac{\text{Ea}_{\text{cal}}(\text{SOC})}{RT}\right] \left(\frac{E}{B_{\text{cal}}(\text{SOC}) \exp\left[-\frac{\text{Ea}_{\text{cal}}(\text{SOC})}{RT}\right]}\right)^{1-\frac{1}{z_{\text{cal}}}}$$
(2.1)

where E is time-varying energy capacity, z_{cal} is a dimensionless constant, B_{cal} is a preexponential factor (function of SOC), E_{acal} is an activation energy (function of SOC), R is the universal gas constant, and T is absolute temperature.

Assumption 1. Value of z_{cal} : If energy capacity fade is attributable to solid electrolyte interface (SEI) growth and diffusion limitations, then

$$z_{\rm cal} \approx \frac{1}{2}$$

see [1].

Imposing assumption 1 upon (2.1), the model simplifies to

$$\frac{dE}{dt}_{\text{cal}} = \frac{1}{2E} \left(B_{\text{cal}}(\text{SOC}) \exp\left[-\frac{\text{Ea}_{\text{cal}}(\text{SOC})}{RT} \right] \right)^2$$
 (2.2)

¹Denoted by Q in the notation of [1].

22 2.2 Translating into SOH

24 By definition

$$\frac{d}{dt} [SOH] = \frac{d}{dt} \left[\frac{E}{E_0} \right] = \frac{1}{E_0} \frac{dE}{dt}$$

and so

$$\frac{dSOH}{dt}_{cal} = \frac{1}{2E_0E} \left(B_{cal}(SOC) \exp \left[-\frac{Ea_{cal}(SOC)}{RT} \right] \right)^2$$

26 But then, by definition,

$$E = E_0 SOH$$

27 and so

$$\frac{dSOH}{dt}_{cal} = \frac{1}{2E_0^2SOH} \left(B_{cal}(SOC) \exp\left[-\frac{Ea_{cal}(SOC)}{RT} \right] \right)^2$$
 (2.3)

2.3 Dimensional Analysis

- Recall the base dimensions of dimensional analysis [2]
- 30 1. T: time
- 2. L: length
- 3. M: mass
- 4. I: electric current
- $5. \Theta$: absolute temperature
- 6. N: amount of substance
- 7. J: luminous intensity

37 By definition

$$\left[\frac{d\text{SOH}}{dt}\right] = \left[\frac{1}{\text{T}}\right]$$

and so, the right-hand side of (2.3) must be commensurate.

First, the argument of exp[] must always be dimensionless (as exp[] itself is), and so if one chooses the usual

$$R \cong 8.31446 \text{ J/mol.K}$$

then it is necessary that

$$[T] = [K]$$
 AND $[Ea_{cal}] = [J/mol]$

- This is reflected in [1], which reports temperatures in terms of [K], and activation energies in terms of [J/mol].
- Now, (2.3) is dimensionally

$$\left[\frac{1}{T}\right] = \left[\frac{1}{E^2}\right] ([x])^2$$

where the base dimensions of energy [E] are

$$[E] = \left[\frac{M.L^2}{T^2}\right]$$

and x is the unknown dimensions of B_{cal} . Solving for x then reveals

$$[B_{\rm cal}] = \left[\frac{\rm E}{\sqrt{\rm T}}\right]$$

This remains largely consistent with the dimensions presented in [1], wherein

$$[B_{\rm cal}] = \left\lceil \frac{\rm Ah}{\sqrt{\rm s}} \right\rceil$$

- although Ah is technically not a measure of energy, but rather of the amp-hour capacity of
- 49 a given battery.

2.4 Re-Factoring the ODE

Since expressing energy capacity in terms of Ah (as is the case in [1]) is not directly compatible with time domain power/energy modelling (as this implicates the modelling of voltages, currents, and resistances), suppose one instead re-factors (2.3) as follows

$$\frac{dSOH}{dt}_{cal} = \frac{1}{2SOH} \left(\frac{B_{cal}(SOC)}{E_0} \exp\left[-\frac{Ea_{cal}(SOC)}{RT} \right] \right)^2$$
 (2.4)

and then introduces

$$\widehat{B}_{\text{cal}} = \frac{B_{\text{cal}}}{E_0}$$

55 such that

$$\left[\widehat{B}_{\mathrm{cal}}\right] = \left[\frac{1}{\sqrt{\mathrm{T}}}\right]$$

56 From this, it follows that

$$\frac{dSOH}{dt}_{cal} = \frac{1}{2SOH} \left(\widehat{B}_{cal}(SOC) \exp \left[-\frac{Ea_{cal}(SOC)}{RT} \right] \right)^2$$
 (2.5)

7 **2.5** Modelling $\widehat{B}_{ exttt{cal}}$

Assumption 2. Properties of \widehat{B}_{cal} :

- 1. \widehat{B}_{cal} is minimum if and only if SOC = 0. That is, calendar ageing is minimized only when the battery has no charge.
- 2. \widehat{B}_{cal} is maximum if and only if SOC = 1. That is, calendar ageing is maximum only when the battery is fully charged.
- 3. \widehat{B}_{cal} is continuous and monotonic.
- From Table 1 of [1], the data presented in Table 2.1 is extracted.²

Table 2.1: B_{cal} vs SOC for the Saft VL6P (6.8 Ah), from Table 1 of [1].

SOC []	$B_{\rm cal} \left[{\rm Ah}/\sqrt{\rm s} \right]$
0.30	2.78×10^{5}
0.65	3.80×10^{5}
1.00	5.43×10^5

- 60 Dividing the right-hand column of Table 2.1 by the nominal 6.8 Ah capacity of the Saft
- VL6P, and then extrapolating the SOC = 0 row, yields Table 2.2.

Table 2.2: \widehat{B}_{cal} vs SOC for the Saft VL6P (6.8 Ah). *Italicized row is extrapolated*.

SOC []	$\widehat{B}_{\rm cal} \left[1/\sqrt{\rm s} \right]$
0.00	3.28×10^{4}
0.30	4.09×10^{4}
0.65	5.59×10^4
1.00	7.99×10^4

62 Plotting the data in Table 2.2 then yields Figure 2.1.

²Curiously, the $B_{\rm cal}$ data presented in [1] for the A123s (2.3 Ah) contradicts assumption 2 by instead suggesting that $B_{\rm cal}$ is maximum as SOC \rightarrow 0, and minimum as SOC \rightarrow 1. Unclear why this is, as logically it seems that the opposite should be true (i.e., the more energy in the battery, the more potential to drive the degradation process(es), etc.).

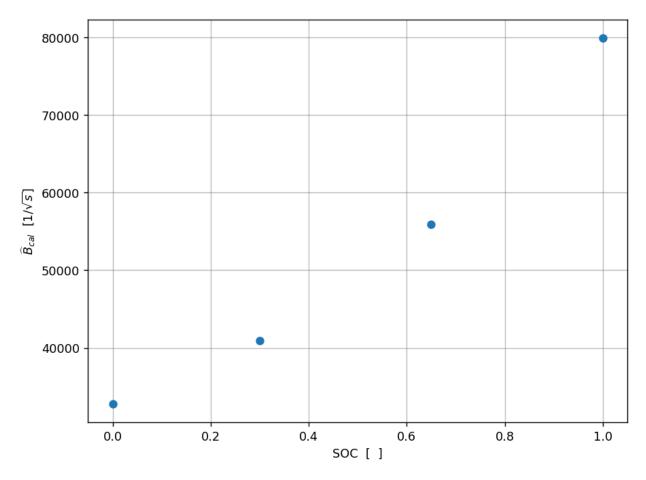


Figure 2.1: $\widehat{B}_{\rm cal}$ vs SOC for the Saft VL6P (6.8 Ah).

Given the data illustrated in Figure 2.1, one might make the following proposition

Proposition 1. Form of \widehat{B}_{cal} : In general, \widehat{B}_{cal} can be modelled as

$$\widehat{B}_{\rm cal}({\rm SOC}) \cong \widehat{B}_{\rm cal}(0) \exp\left[r_{\rm cal}{\rm SOC}\right]$$

where $\widehat{B}_{\rm cal}(0) > 0$ is the base value of $\widehat{B}_{\rm cal}$ (when SOC = 0), and $r_{\rm cal} \geq 0$ is a dimensionless constant.

- For example, performing a least squares fit of proposition 1 to the data in Table 2.2 yields
- the results illustrated in Figure 2.2.

63

64

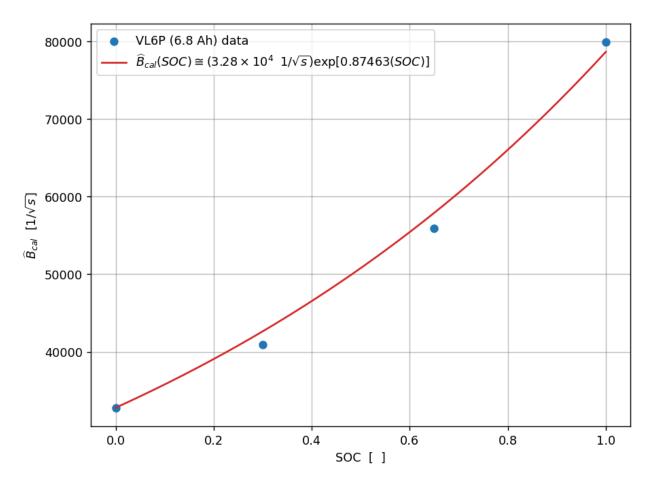


Figure 2.2: \widehat{B}_{cal} vs SOC for the Saft VL6P (6.8 Ah). Least-squares model shown.

$_{\scriptscriptstyle 67}$ 2.6 $_{\scriptscriptstyle 60}$ Modelling $\mathrm{Ea_{cal}}$

68

Assumption 3. Properties of Ea_{cal}:

- 1. Ea_{cal} is maximum if and only if SOC = 0. That is, the required energy to activate the degradation process(es) is maximum only when the battery has no charge.
- 2. Ea_{cal} is minimum if and only if SOC = 1. That is, the required energy to activate the degradation process(es) is minimum only when the battery is fully charged.
- 3. Ea_{cal} is continuous and monotonic.

From Table 1 of [1], the data presented in Table 2.3 is extracted. The SOC = 0 row was extrapolated.

Table 2.3: Ea_{cal} vs SOC for the A123s (2.3 Ah), from Table 1 of [1]. *Italicized row is extrapolated*.

SOC []	Ea _{cal} [J/mol]
0.00	7.43×10^4
0.30	7.34×10^4
0.65	6.98×10^4
1.00	5.69×10^4

71 Plotting the data in Table 2.3 then yields Figure 2.3.

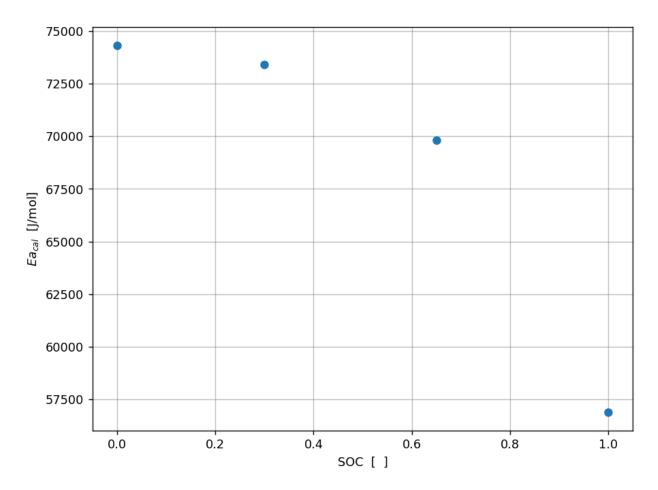


Figure 2.3: Ea_{cal} vs SOC for the A123s (2.3 Ah).

Given the data illustrated in Figure 2.3, one might make the following proposition

Proposition 2. Form of Ea_{cal} : In general, Ea_{cal} can be modelled as

73

$$\operatorname{Ea_{cal}}(\operatorname{SOC}) \cong \operatorname{Ea_{cal}}(0) - a_{\operatorname{cal}}(\exp[s_{\operatorname{cal}}\operatorname{SOC}] - 1)$$

where $\text{Ea}_{\text{cal}}(0) > 0$ is the base value of Ea_{cal} (when SOC = 0), $a_{\text{cal}} \geq 0$ is a pre-exponential factor [J/mol], and $s_{\text{cal}} \geq 0$ is a dimensionless constant.

For example, performing a least squares fit of proposition 2 to the data in Table 2.3 yields the results illustrated in Figure 2.4.

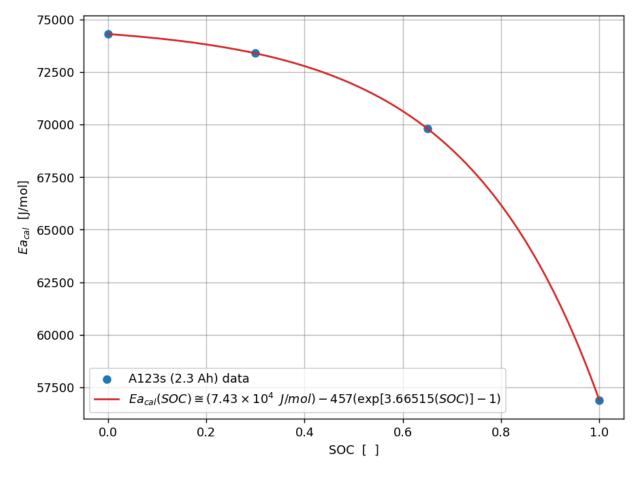


Figure 2.4: Ea_{cal} vs SOC for the A123s (2.3 Ah). Least-squares model shown.

$_{\scriptscriptstyle{76}}$ 2.7 Final Calendar Ageing ODE

Imposing propositions 1 and 2 upon (2.5) then yields, after simplifying,

$$\frac{dSOH}{dt}_{cal} = \frac{1}{2SOH} \left(\widehat{B}_{cal}(0) \exp \left[r_{cal}SOC - \frac{Ea_{cal}(0) - a_{cal} (\exp \left[s_{cal}SOC \right] - 1)}{RT} \right] \right)^{2}$$
 (2.6)

- which constitutes a five parameter model for calendar ageing which is directly compatible with time domain power/energy modelling. The five parameters are
- 1. $\widehat{B}_{\rm cal}(0)$: the base value for $\widehat{B}_{\rm cal}$, which has dimensions $\left[\frac{1}{\sqrt{\rm T}}\right]$.
- $r_{\rm cal}$: a dimensionless constant.
- 3. $Ea_{cal}(0)$: the base value for Ea_{cal} , which has units [J/mol].
- 4. a_{cal} : a pre-exponential factor, which has units [J/mol].
- s_{cal} : a dimensionless constant.

3 Cycle Ageing

Of course, energy capacity fade is accelerated by cycling the battery (i.e., $|P| \neq 0$), with the magnitude of the acceleration being dependent upon how the battery is cycled (i.e., C-rate, depth of discharge, etc.). This is cycle ageing. Here again, one might turn to the results presented in [1].

₀ 3.1 ODE

91

96

The following ODE model for cycle ageing is proposed in [1]

$$\frac{dE}{dt}_{\text{cyc}} = \frac{|I|}{3600} z_{\text{cyc}} B_{\text{cyc}}(I) \exp\left[\frac{\alpha |I| - \text{Ea}_{\text{cyc}}(\text{SOC})}{RT}\right] \left(\frac{E}{B_{\text{cyc}}(I) \exp\left[\frac{\alpha |I| - \text{Ea}_{\text{cyc}}(\text{SOC})}{RT}\right]}\right)^{1 - \frac{1}{z_{\text{cyc}}}} \tag{3.1}$$

where E is time-varying energy capacity, I is battery current, $z_{\rm cyc}$ is a dimensionless constant, $B_{\rm cyc}$ is a pre-exponential factor (function of current), α is an ageing acceleration coefficient, $Ea_{\rm cyc}$ is an activation energy (function of SOC), R is the universal gas constant, and T is absolute temperature.

Imposing a similar $z_{\rm cyc} \approx \frac{1}{2}$ assumption (see assumption 1, also stated in [1]) then yields

$$\frac{dE}{dt}_{\text{cyc}} = \frac{|I|}{7200E} \left(B_{\text{cyc}}(I) \exp\left[\frac{\alpha |I| - \text{Ea}_{\text{cyc}}(\text{SOC})}{RT}\right] \right)^2$$
(3.2)

 $_{97}$ a notable simplification from (3.1).

¹Denoted by Q in the notations of [1].

However, recall that the motivation of this work is to find a general and reliable means of modelling degradation that is directly compatible with time domain power/energy modelling. Unfortunately, the dependence of (3.1) and (3.2) upon current means that the only way to translate this ODE into something of the form

$$\frac{d\text{SOH}}{dt}_{\text{cyc}} = f(C, \text{ SOC}, \text{ SOH})$$

is by involving the voltages and resistances particular to each use case (i.e., power law, Ohm's law, etc.). But then, this is a departure from time domain power/energy modelling, and so (3.1) is not going to be workable like (2.1) was.

4 Total Degradation Rate

With (3.1) not being workable like (2.1) was, an alternative means of capturing cycle ageing within the constraints of time domain power/energy modelling needs to be developed. To begin, one might make some modelling assumptions regarding total degradation rate; namely

Assumption 4. Superposition: Total degradation rate is the superposition of calendar ageing and cycle ageing. That is

$$\frac{dSOH}{dt} = \frac{dSOH}{dt}_{cal} + \frac{dSOH}{dt}_{cyc}$$

Assumption 5. Proportionality: Cycle ageing can be modelled as being proportional to calendar ageing. That is

$$\frac{d\text{SOH}}{dt}_{\text{cyc}} = \Phi(C) \frac{d\text{SOH}}{dt}_{\text{cal}}$$

where $\Phi \geq 0$ is a function of C-rate.

106

108

110

111

112

Assumption 6. Symmetry: Total degradation rate is the same whether the battery is charging or discharging.

From assumptions 4 - 6, it follows that

$$\frac{d\text{SOH}}{dt} = (1 + \Phi(C)) \frac{d\text{SOH}}{dt_{\text{cal}}}$$
(4.1)

And so, substitution of (2.6) into (4.1) yields¹

$$\frac{dSOH}{dt} = \frac{1 + \Phi(C)}{2SOH} \left(\widehat{B}_{cal}(0) \exp \left[r_{cal}SOC - \frac{Ea_{cal}(0) - a_{cal} (\exp \left[s_{cal}SOC \right] - 1)}{RT} \right] \right)^{2}$$
(4.2)

With (4.2), one arrives at the desired

$$\frac{dSOH}{dt} = f(C, SOC, SOH)$$

All that remains is to determine a suitable form for Φ .

$_{ au}$ 4.1 Modelling Φ

118

120

Assumption 7. Properties of Φ :

1. $\Phi = 0$ if and only if C = 0. That is to say

$$\frac{d \text{SOH}}{dt} \rightarrow \frac{d \text{SOH}}{dt}_{\text{cal}}$$

if and only if |P| = 0.

2. Φ is continuous and monotonic increasing.

From assumption 7, it follows that one might make the following proposition

Proposition 3. Form of Φ : In general, Φ can be modelled as

$$\Phi(C) = \alpha C^{\beta}$$

where $\alpha > 0$ is a dimensionless acceleration coefficient, and $\beta > 0$ is a dimensionless acceleration exponent.

¹ It is interesting to note the curious similarities in structure between (4.2) and (3.2), especially when $r_{\text{cal}} = 0$.

4.2 Final Total Degradation ODE

Imposing proposition 3 upon (4.2) then yields

$$\frac{dSOH}{dt} = \frac{1 + \alpha C^{\beta}}{2SOH} \left(\widehat{B}_{cal}(0) \exp \left[r_{cal}SOC - \frac{Ea_{cal}(0) - a_{cal} (\exp [s_{cal}SOC] - 1)}{RT} \right] \right)^{2}$$
(4.3)

which constitutes a seven parameter model for total degradation (i.e., calendar ageing + cycle ageing) which is directly compatible with time domain power/energy modelling. The seven parameters are

- 1. $\widehat{B}_{\rm cal}(0)$: the base value for $\widehat{B}_{\rm cal}$, which has dimensions $\left[\frac{1}{\sqrt{T}}\right]$.
- r_{cal} : a dimensionless constant.
- 3. $Ea_{cal}(0)$: the base value for Ea_{cal} , which has units [J/mol].
- 4. a_{cal} : a pre-exponential factor, which has units [J/mol].
- s_{cal} : a dimensionless constant.
- 6. α : a dimensionless constant.
- 7. β : a dimensionless constant.

5 Calibrating the Total Degradation Model

Recall (4.3)

134

138

142

147

$$\frac{dSOH}{dt} = \frac{1 + \alpha C^{\beta}}{2SOH} \left(\widehat{B}_{cal}(0) \exp \left[r_{cal}SOC - \frac{Ea_{cal}(0) - a_{cal} (\exp \left[s_{cal}SOC \right] - 1)}{RT} \right] \right)^{2}$$

To calibrate the model parameters (to either given data or a choice of desired behaviour), one can apply a divide-and-conquer approach according to the following steps

- 1. Calibrate under calendar ageing with SOC = 0; then,
- 2. Calibrate under calendar ageing with SOC = 1; then,
- 3. Calibrate under some prescribed cycle ageing.

$_{\scriptscriptstyle{141}}$ 5.1 Step 1: Calendar Ageing with SOC = 0

For calendar ageing (i.e., C = 0) with SOC = 0, (4.3) simplifies to

$$\frac{dSOH}{dt} = \frac{1}{2SOH} \left(\widehat{B}_{cal}(0) \exp\left[-\frac{Ea_{cal}(0)}{RT} \right] \right)^2$$
 (5.1)

and thus the number of free parameters is reduced to two; namely $\widehat{B}_{\rm cal}(0)$ and ${\rm Ea}_{\rm cal}(0)$.

Therefore, given either data or a choice of desired behaviour, the parameters remaining after reduction can be determined by way of setting up and solving an optimization problem.

5.2 Step 2: Calendar Ageing with SOC = 1

For calendar ageing (i.e., C=0) with SOC = 1, (4.3) simplifies to

$$\frac{dSOH}{dt} = \frac{1}{2SOH} \left(\widehat{B}_{cal}(0) \exp \left[r_{cal} - \frac{Ea_{cal}(0) - a_{cal} (\exp \left[s_{cal} \right] - 1)}{RT} \right] \right)^2$$
 (5.2)

and thus the number of free parameters is reduced to five; namely

```
1. \widehat{B}_{\rm cal}(0)
```

150 2.
$$Ea_{cal}(0)$$

$$r_{\rm cal}$$
 3. $r_{\rm cal}$

$$a_{\text{cal}}$$
 4. a_{cal}

153 5.
$$s_{\rm cal}$$

Therefore, given either data or a choice of desired behaviour, the parameters remaining after reduction can be determined by way of setting up and solving an optimization problem. Furthermore, this can be implemented as a constrained optimization problem wherein only $r_{\rm cal}$, $a_{\rm cal}$, and $s_{\rm cal}$ are free parameters, and $\widehat{B}_{\rm cal}(0)$ and ${\rm Ea}_{\rm cal}(0)$ take the values determined in step 1.

5.3 Step 3: Cycle Ageing

For cycle ageing, one would use the entirety of (4.3); that is, all seven parameters are in play. However, like in step 2, the parameters can be determined by way of setting up and solving a constrained optimization problem wherein only α and β are free parameters, and all other parameters take the values determined in steps 1 and 2.

5.4 Example Calibration

Suppose one wishes a model battery energy storage system (BESS) to exhibit the following degradation dynamics

- 1. If a new BESS is discharged to SOC = 0 and then placed on a shelf at 20° C, the BESS would degrade (i.e., calendar age) to SOH = 0.8 in ten years;
- 2. If a new BESS is charged to SOC = 1 and then placed on a shelf at 20°C, the BESS would degrade (i.e., calendar age) to SOH = 0.8 in three years; and,
- 3. If a new BESS was subjected to a repeating 1C/1C charge/discharge policy, with an 80% depth of discharge about SOC = 0.5 at 20°C, then the BESS would degrade (i.e., cycle age) to SOH = 0.8 in 3,000 cycles.¹

These desired dynamics are reproduced by the following model parameter values (expressing time here in terms of hours rather than seconds)

1.
$$\widehat{B}_{cal}(0) = 5.22226 \times 10^6 \text{ 1/}\sqrt{\text{hr}}$$

2.
$$Ea_{cal}(0) = 5.279 \times 10^4 \text{ J/mol}$$

$$r_{\rm cal} = 0.4361$$

$$a_{\rm cal} = 100 \text{ J/mol}$$

$$s_{cal} = 2$$

$$\alpha = 8.935$$

7.
$$\beta = 1$$

 $^{^1}$ Assuming the BESS power capacity \geq energy capacity, so that a 1C/1C policy is feasible.

References

- [1] M. Petit, E. Prada, and V. Sauvant-Moynot, "Development of an empirical aging model for Li-ion batteries and application to assess the impact of Vehicle-to-Grid strategies on Battery Lifetime," *Applied Energy*, vol. 172, p. 398–407, 2016. [Online]. Available: https://www.sciencedirect.com/science/article/abs/pii/S0306261916304500
- [2] J.D. Logan, Applied Mathematics, 4th ed. John Wiley & Sons, Inc., 2013, ISBN-13:
 978-1-118-47580-5.