

Battery Degradation Modelling For Implementation in PGMcpp

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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 capacity fade) is needed. Specifically, a model that is directly compatible with time domain power/energy modelling is desirable. To that end, an ODE of the form

$$\frac{d\text{SOH}}{dt} = f(C, \text{SOC}, \text{SOH}) \quad (1.1)$$

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.¹ Likewise, for the sake of clarity, SOH is defined as

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

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

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

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].

2.1 ODE

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

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

where E is time-varying energy capacity,¹ z_{cal} is a dimensionless constant, B_{cal} is a pre-exponential factor (function of SOC), $E a_{\text{cal}}$ 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

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

see [1].

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

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

¹Denoted by Q in the notation of [1].

2.2 Translating into SOH

By definition

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

and so

$$\frac{d\text{SOH}}{dt}_{\text{cal}} = \frac{1}{2E_0 E} \left(B_{\text{cal}}(\text{SOC}) \exp \left[-\frac{E_{\text{a}_{\text{cal}}}(\text{SOC})}{RT} \right] \right)^2$$

But then, by definition,

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

and so

$$\frac{d\text{SOH}}{dt}_{\text{cal}} = \frac{1}{2E_0^2 \text{SOH}} \left(B_{\text{cal}}(\text{SOC}) \exp \left[-\frac{E_{\text{a}_{\text{cal}}}(\text{SOC})}{RT} \right] \right)^2 \quad (2.3)$$

2.3 Dimensional Analysis

Recall the base dimensions of dimensional analysis [2]

1. T: time

2. L: length

3. M: mass

4. I: electric current

5. Θ : absolute temperature

6. N: amount of substance

7. J: luminous intensity

37 By definition

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

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

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

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

41 then it is necessary that

$$[T] = [\text{K}] \quad \text{AND} \quad [\text{E}_{\text{cal}}] = [\text{J/mol}]$$

42 This is reflected in [1], which reports temperatures in terms of [K], and activation energies
43 in terms of [J/mol].

44 Now, (2.3) is dimensionally

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

45 where the base dimensions of energy [E] are

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

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

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

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

$$[B_{\text{cal}}] = \left[\frac{\text{Ah}}{\sqrt{\text{s}}} \right]$$

48 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

$$\frac{d\text{SOH}}{dt}_{\text{cal}} = \frac{1}{2\text{SOH}} \left(\frac{B_{\text{cal}}(\text{SOC})}{E_0} \exp \left[-\frac{E_{\text{a}_{\text{cal}}}(\text{SOC})}{RT} \right] \right)^2 \quad (2.4)$$

and then introduces

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

such that

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

From this, it follows that

$$\frac{d\text{SOH}}{dt}_{\text{cal}} = \frac{1}{2\text{SOH}} \left(\hat{B}_{\text{cal}}(\text{SOC}) \exp \left[-\frac{E_{\text{a}_{\text{cal}}}(\text{SOC})}{RT} \right] \right)^2 \quad (2.5)$$

2.5 Modelling \hat{B}_{cal}

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

1. \hat{B}_{cal} is minimum if and only if $\text{SOC} = 0$. That is, calendar ageing is minimized only when the battery has no charge.
2. \hat{B}_{cal} is maximum if and only if $\text{SOC} = 1$. That is, calendar ageing is maximum only when the battery is fully charged.
3. \hat{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_{cal} [Ah/ $\sqrt{\text{s}}$]
0.30	2.78×10^5
0.65	3.80×10^5
1.00	5.43×10^5

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

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

SOC []	\hat{B}_{cal} [1/ $\sqrt{\text{s}}$]
<i>0.00</i>	<i>3.28×10^4</i>
0.30	4.09×10^4
0.65	5.59×10^4
1.00	7.99×10^4

Plotting the data in Table 2.2 then yields Figure 2.1.

²Curiously, the B_{cal} data presented in [1] for the A123s (2.3 Ah) contradicts assumption 2 by instead suggesting that B_{cal} is maximum as $\text{SOC} \rightarrow 0$, and minimum as $\text{SOC} \rightarrow 1$. 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.).

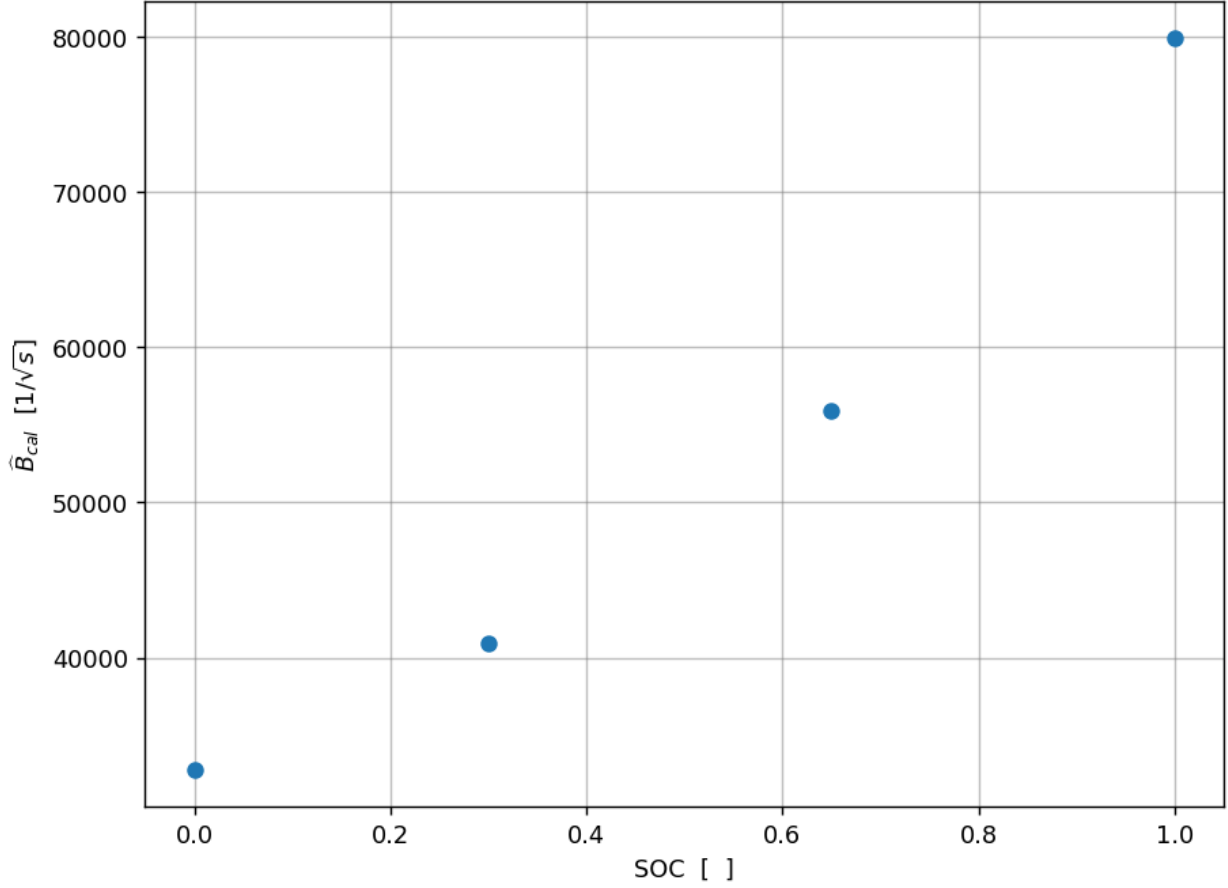


Figure 2.1: \hat{B}_{cal} vs SOC for the Saft VL6P (6.8 Ah).

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

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

$$\hat{B}_{cal}(SOC) \cong \hat{B}_{cal}(0) \exp[r_{cal}SOC]$$

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

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

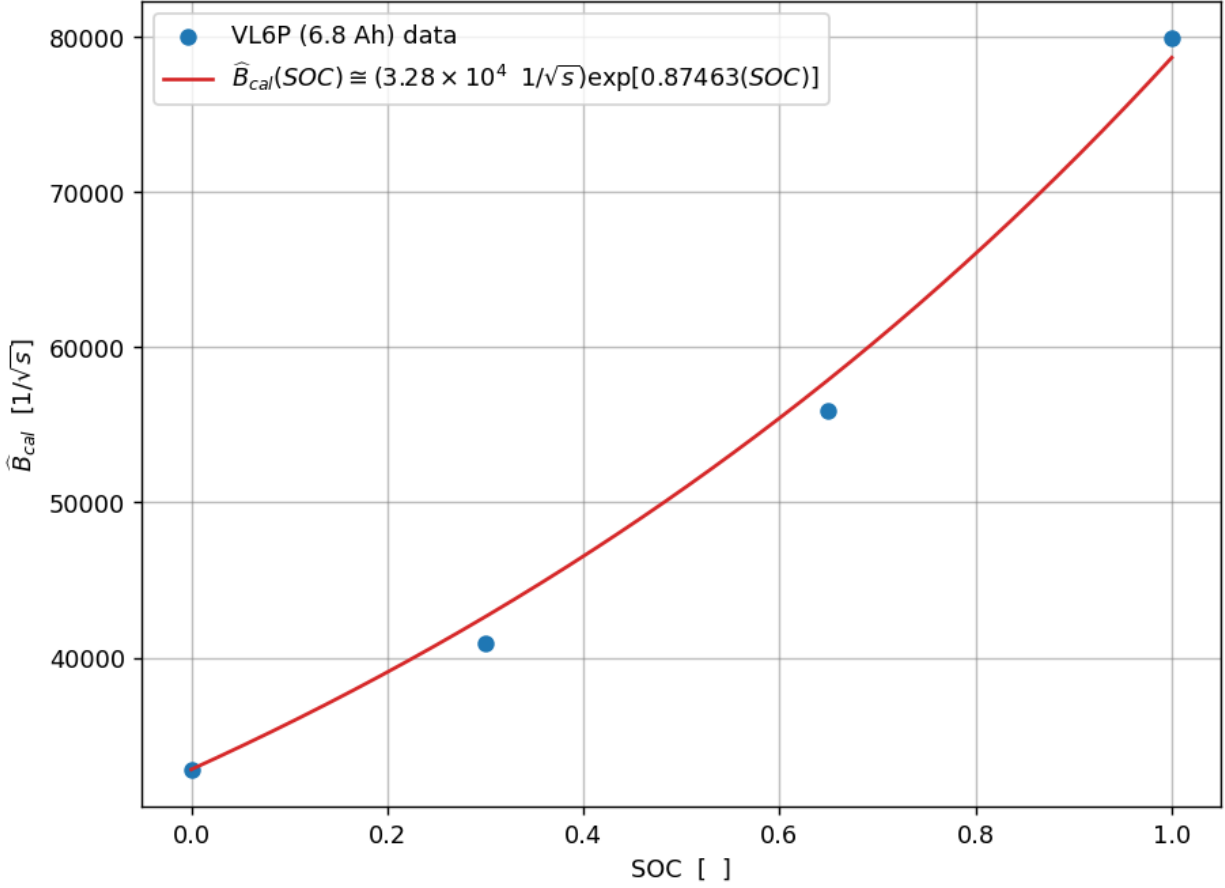


Figure 2.2: \hat{B}_{cal} vs SOC for the Saft VL6P (6.8 Ah). Least-squares model shown.

2.6 Modelling Ea_{cal}

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

SOC [%]	$E_{a_{cal}}$ [J/mol]
<i>0.00</i>	<i>7.43×10^4</i>
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.

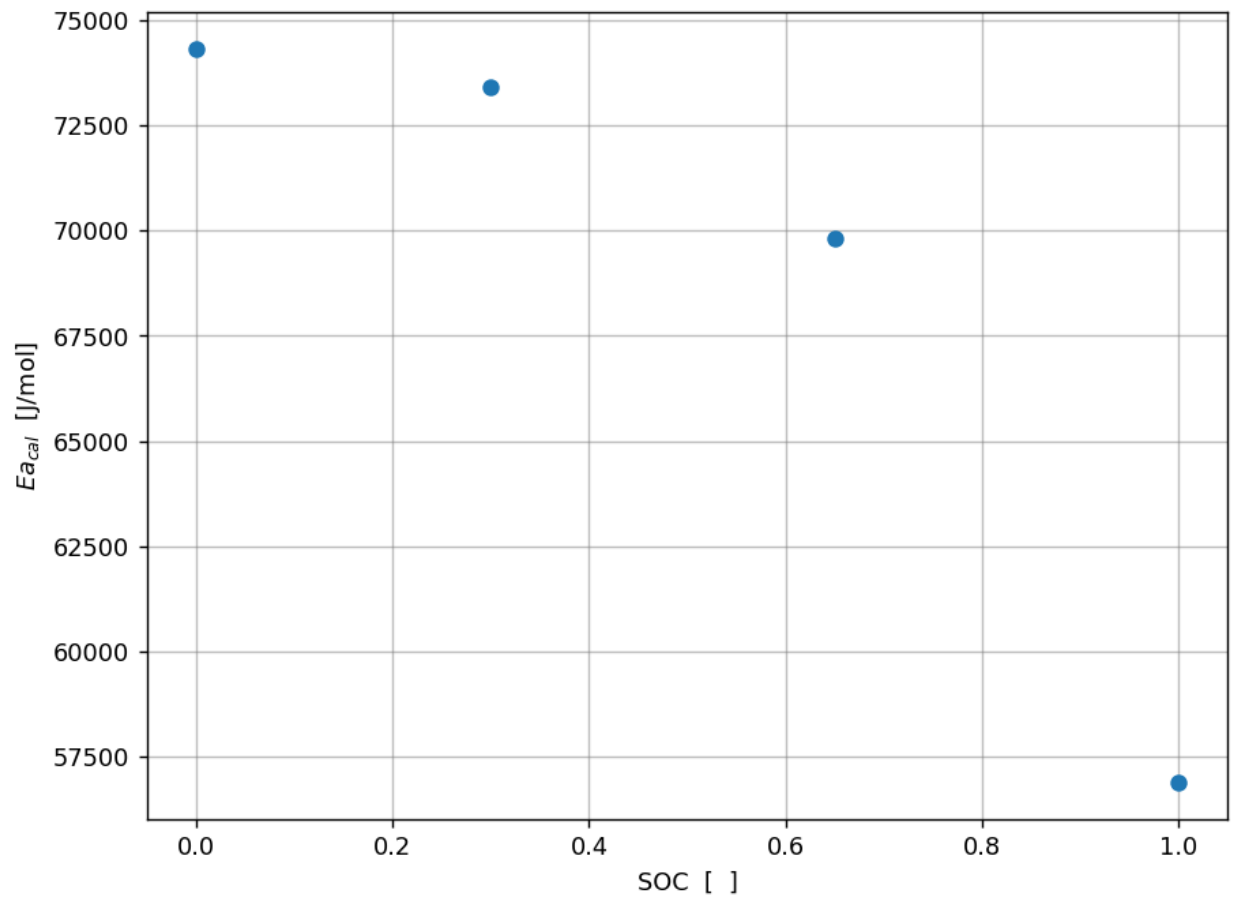


Figure 2.3: $E_{a_{cal}}$ vs SOC for the A123s (2.3 Ah).

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

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

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

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

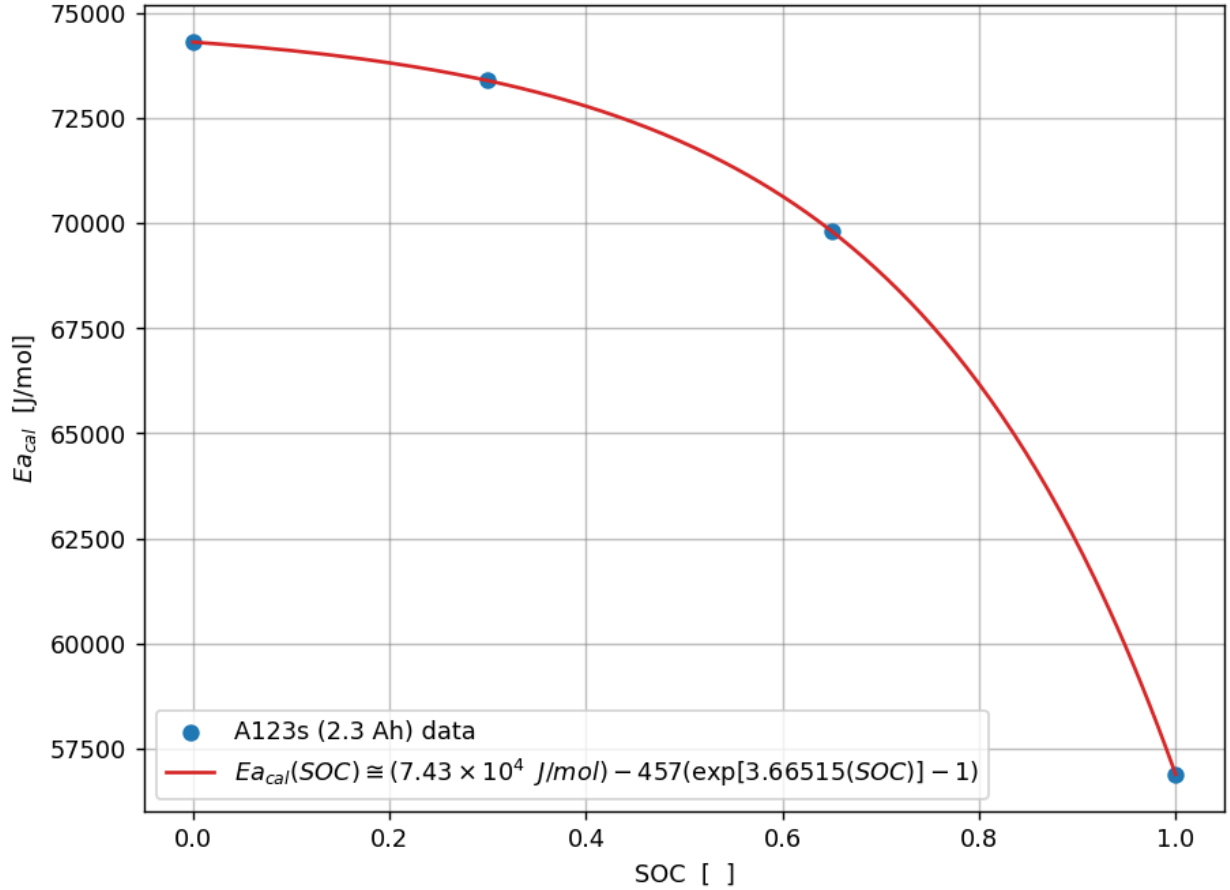


Figure 2.4: $E_{a_{cal}}$ vs SOC for the A123s (2.3 Ah). Least-squares model shown.

2.7 Final Calendar Ageing ODE

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

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

78 which constitutes a five parameter model for calendar ageing which is directly compatible
79 with time domain power/energy modelling. The five parameters are

- 80 1. $\hat{B}_{\text{cal}}(0)$: the base value for \hat{B}_{cal} , which has dimensions $\left[\frac{1}{\sqrt{T}}\right]$.
- 81 2. r_{cal} : a dimensionless constant.
- 82 3. $Ea_{\text{cal}}(0)$: the base value for Ea_{cal} , which has units [J/mol].
- 83 4. a_{cal} : a pre-exponential factor, which has units [J/mol].
- 84 5. 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].

3.1 ODE

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

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

where E is time-varying energy capacity,¹ I is battery current, z_{cyc} is a dimensionless constant, B_{cyc} is a pre-exponential factor (function of current), α is an ageing acceleration coefficient, $E a_{\text{cyc}}$ is an activation energy (function of SOC), R is the universal gas constant, and T is absolute temperature.

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

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

a notable simplification from (3.1).

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

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

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

102 is by involving the voltages and resistances particular to each use case (i.e., power law, Ohm's
 103 law, etc.). But then, this is a departure from time domain power/energy modelling, and so
 104 (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

$$\frac{dSOH}{dt}_{cyc} = \Phi(C) \frac{dSOH}{dt}_{cal}$$

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

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

From assumptions 4 - 6, it follows that

$$\frac{dSOH}{dt} = (1 + \Phi(C)) \frac{dSOH}{dt_{cal}} \quad (4.1)$$

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

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

115 With (4.2), one arrives at the desired

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

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

117 4.1 Modelling Φ

Assumption 7. Properties of Φ :

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

$$\frac{d\text{SOH}}{dt} \rightarrow \frac{d\text{SOH}}{dt}_{\text{cal}} \quad (118)$$

if and only if $|P| = 0$.

2. Φ is continuous and monotonic increasing.

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

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

$$\Phi(C) = \alpha C^\beta \quad (120)$$

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

¹It 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

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

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

5 Calibrating the Total Degradation Model

Recall (4.3)

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

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.

5.1 Step 1: Calendar Ageing with SOC = 0

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

$$\frac{d\text{SOH}}{dt} = \frac{1}{2\text{SOH}} \left(\hat{B}_{\text{cal}}(0) \exp \left[-\frac{\text{Ea}_{\text{cal}}(0)}{RT} \right] \right)^2 \quad (5.1)$$

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

$$\frac{d\text{SOH}}{dt} = \frac{1}{2\text{SOH}} \left(\hat{B}_{\text{cal}}(0) \exp \left[r_{\text{cal}} - \frac{\text{Ea}_{\text{cal}}(0) - a_{\text{cal}} (\exp [s_{\text{cal}}] - 1)}{RT} \right] \right)^2 \quad (5.2)$$

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

1. $\hat{B}_{\text{cal}}(0)$

2. $\text{Ea}_{\text{cal}}(0)$

3. r_{cal}

4. a_{cal}

5. s_{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_{cal} , a_{cal} , and s_{cal} are free parameters, and $\hat{B}_{\text{cal}}(0)$ and $\text{Ea}_{\text{cal}}(0)$ 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 $\text{SOC} = 0$ and then placed on a shelf at 20°C , the BESS would degrade (i.e., calendar age) to $\text{SOH} = 0.8$ in ten years;
2. If a new BESS is charged to $\text{SOC} = 1$ and then placed on a shelf at 20°C , the BESS would degrade (i.e., calendar age) to $\text{SOH} = 0.8$ 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 $\text{SOC} = 0.5$ at 20°C , then the BESS would degrade (i.e., cycle age) to $\text{SOH} = 0.8$ in 3,000 cycles.

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

- 176 1. $\hat{B}_{\text{cal}}(0) = 5.222 \times 10^6 \text{ 1}/\sqrt{\text{hr}}$
- 177 2. $E_{\text{a}_{\text{cal}}}(0) = 5.279 \times 10^4 \text{ J/mol}$
- 178 3. $r_{\text{cal}} = 0.350$
- 179 4. $a_{\text{cal}} = 108.5 \text{ J/mol}$
- 180 5. $s_{\text{cal}} = 1.895$
- 181 6. $\alpha = 10$
- 182 7. $\beta = 1.1$

183 It is interesting to note that when this particular model is applied to a range of charge/dis-
 184 charge policies, with both the discharge C-rate and depth of discharge (DoD) being varied,
 185 the model degradation results illustrated in Figures 5.1 - 5.4 emerge.

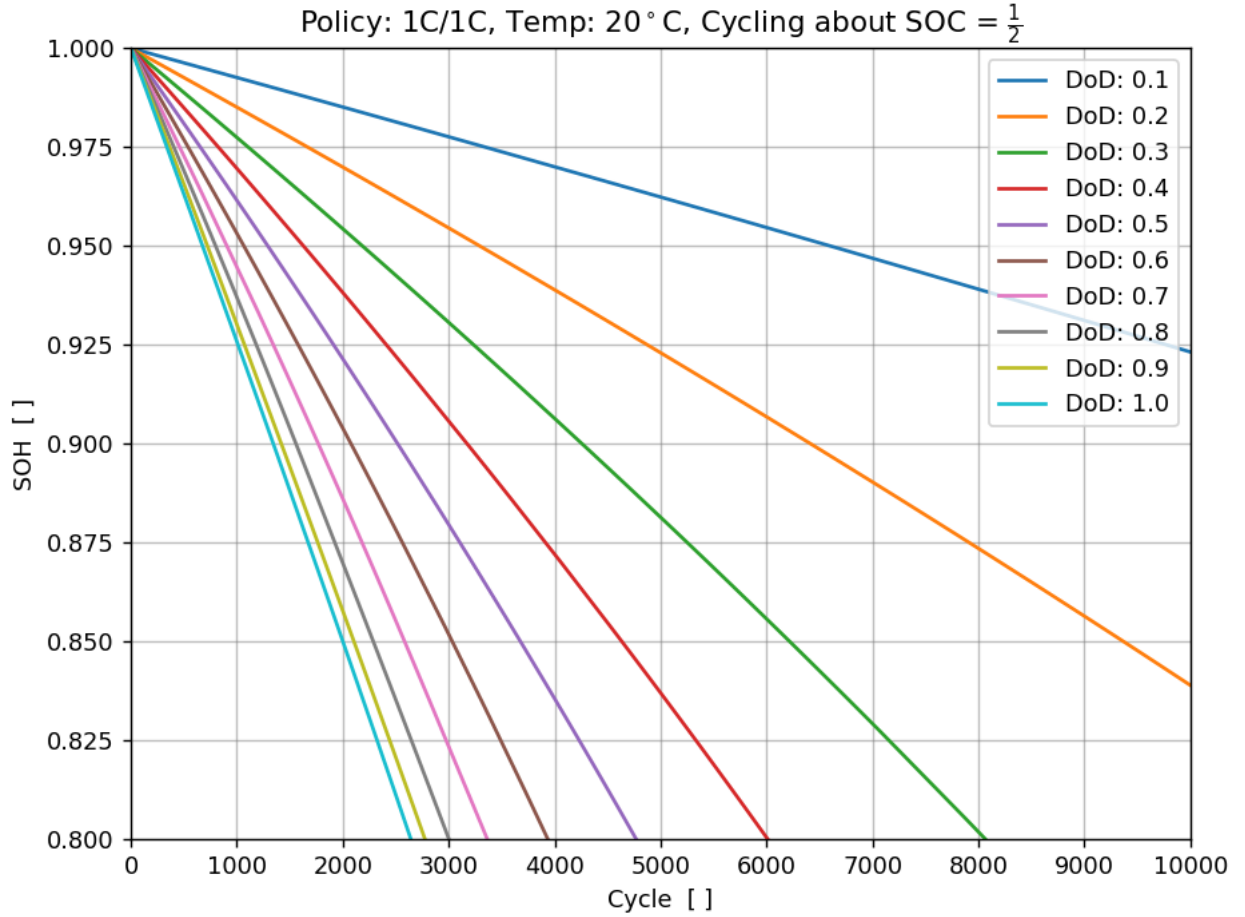


Figure 5.1: Model degradation curves for 1C/1C cycling about SOC = 0.5 at 20°C.

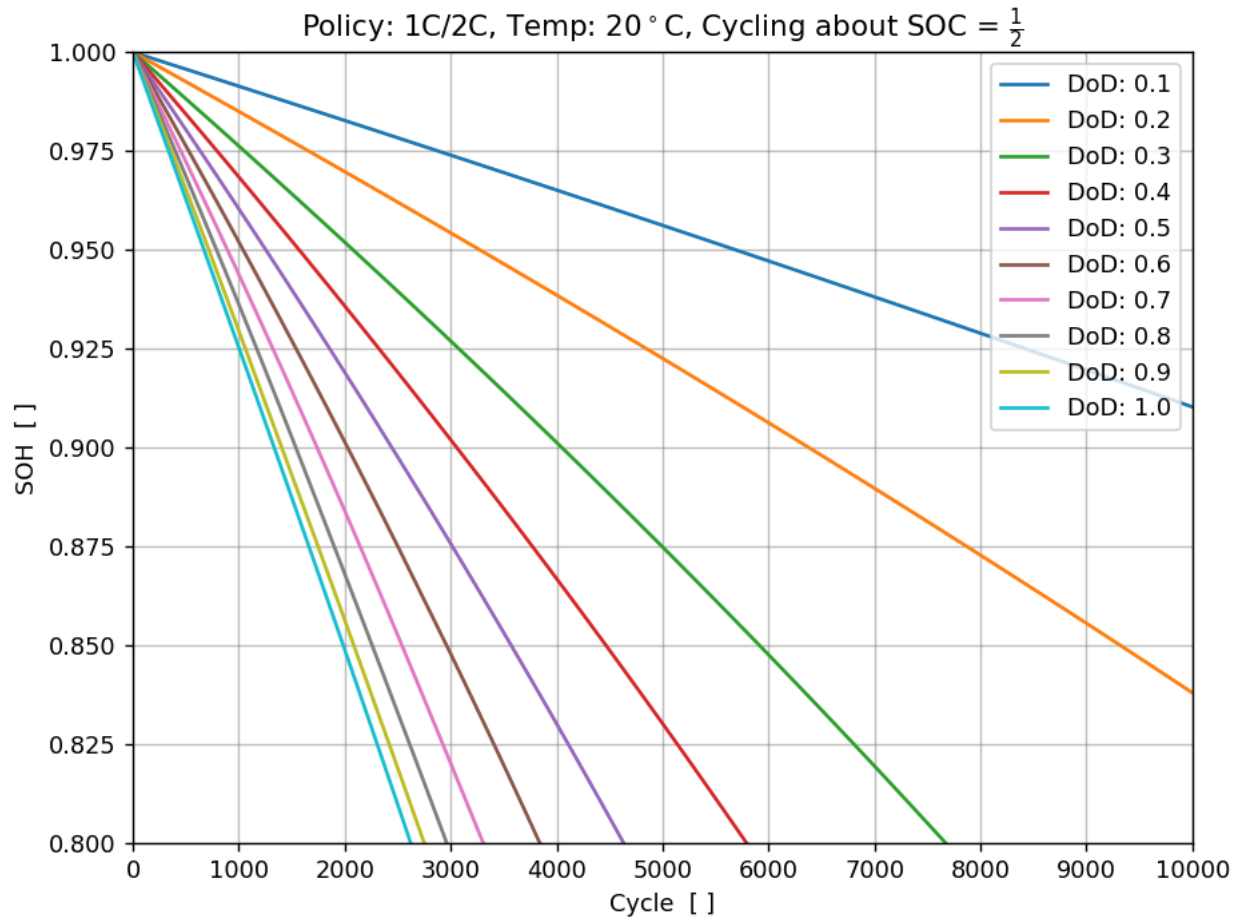


Figure 5.2: Model degradation curves for 1C/2C cycling about SOC = 0.5 at 20°C.

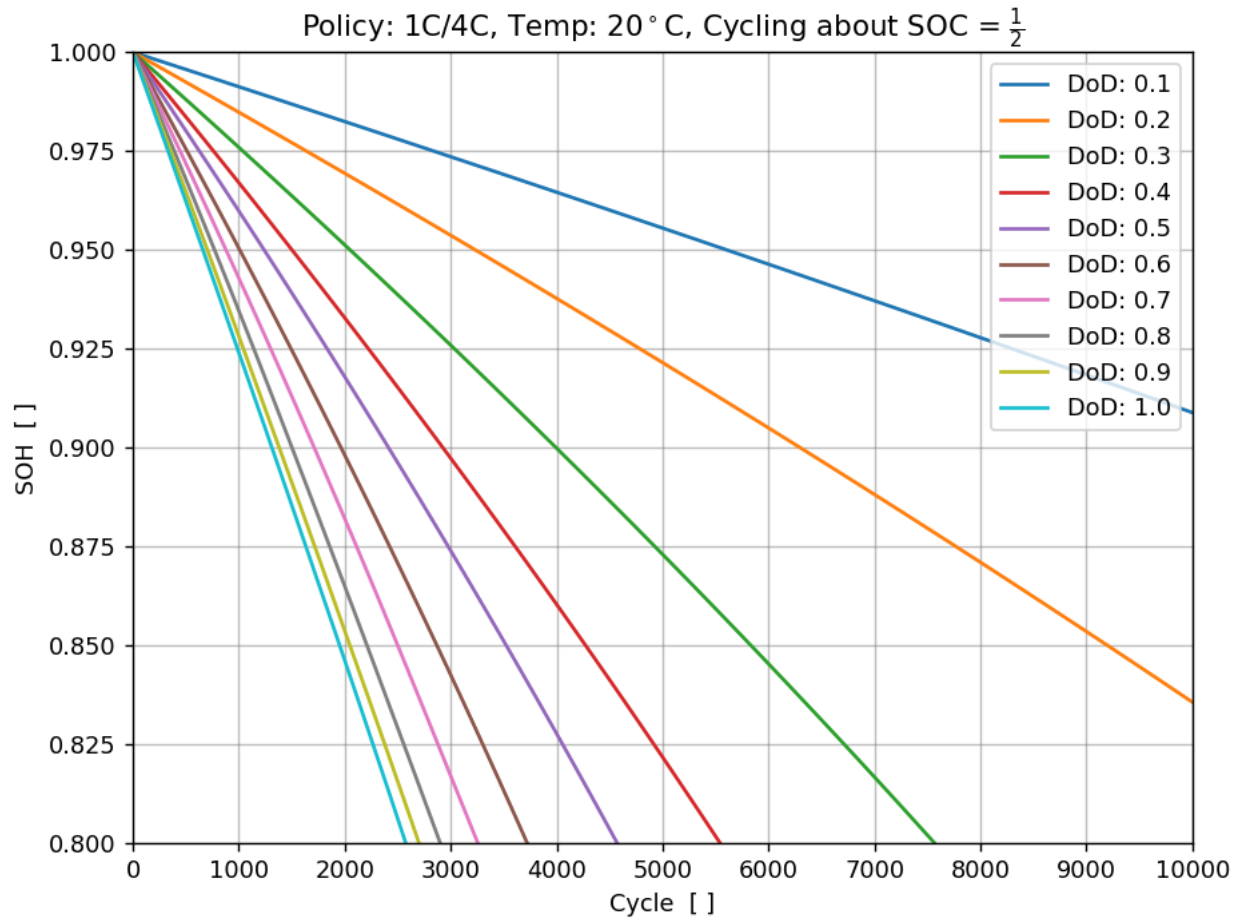


Figure 5.3: Model degradation curves for 1C/4C cycling about SOC = 0.5 at 20°C.

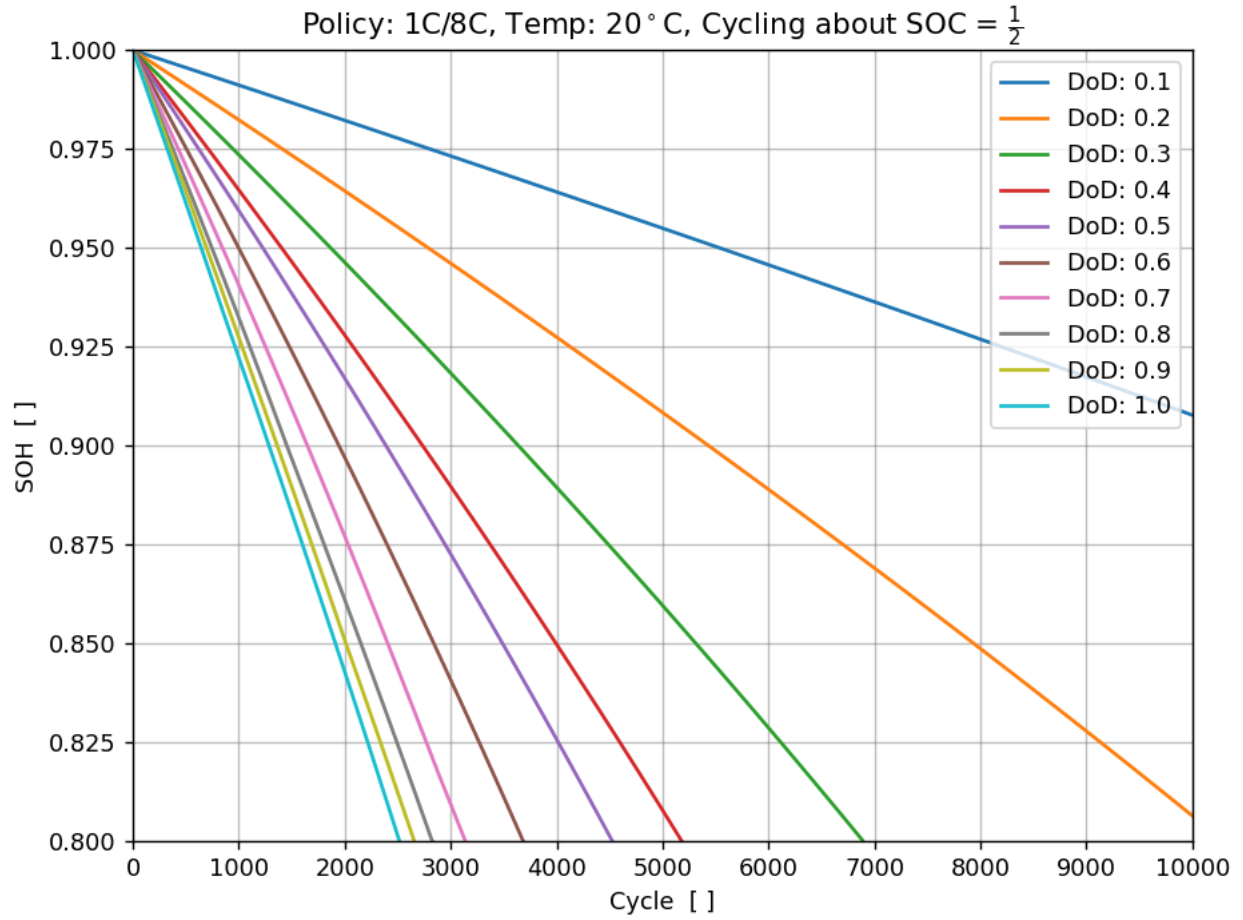


Figure 5.4: Model degradation curves for 1C/8C cycling about SOC = 0.5 at 20°C.

Of note in Figures 5.1 - 5.4 is

1. Increasing C-rates accelerate degradation, as one might logically expect; and
2. Increasing depth of discharge accelerates degradation, as one might logically expect.

Furthermore, it is apparent that changes in depth of discharge are modelled, in this case, as having a far more significant impact on degradation than changes in C-rates. This is consistent with findings in the literature (see, for example, [3]).

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