CRC Report No. SM-E-4/8

Predictive Lifetime Battery Simulations of Intra- and Inter-Cycle Degradation for V2G Use

Final Report

May 2025



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Predictive Lifetime Battery Simulations of Intra- and Inter-Cycle Degradation for V2G Use ¹

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Executive summary

Vehicle-to-grid (V2G) services, using electric vehicle (EV) batteries for grid support, are gaining attention in the research community and industry. These services enhance grid reliability, reduce peak energy demand, and aid in renewable energy integration. However, the impact of V2G on EV battery degradation has been uncertain. Previous studies based on experiments and empirical models have reported conflicting effects, from inconsequential impacts to the need for early battery pack replacements.

In our study, by utilizing a physics-based degradation model, we examine the influence of V2G activity on EV battery life. We consider various duty cycles and investigate three families of cells, each characterized by a different dominant degradation mechanism.

We introduce the V2G Throughput gained versus Days lost (TvD) ratio to quantify the impact of offering V2G services. This ratio measures the additional throughput provided to the grid relative to the loss of battery life due to increased degradation. Using the TvD ratio, we compare the effects of various degradation mechanisms on the benefits and drawbacks of V2G services. Our findings indicate that the dominant degradation mechanism, particularly the contribution of calendar aging to overall capacity loss, plays a crucial role in determining the degradation and the associated TvD ratio of V2G.

We calibrate our physics-based model using three distinct cell data sets that feature NMC chemistry: 1. Cells that experience substantial loss of electrode active material due to particle cracking during cycling, which occurs as a result of high concentration gradients across the particle. 2. Cells where the dominant degradation mechanism is the growth of the solid electrolyte interphase (SEI) layer. 3. Cells that suffer degradation from a combination of both SEI growth and active material loss. Using these models, we simulate concrete and relevant V2G and baseline lifetime scenarios while exploring the TvD ratio for each cell family.

We show that V2G is more beneficial than harmful for cell chemistries where the degradation is dominated by calendar aging; in other words, if the battery is aging substantially on its own, we might as well use it for the V2G. Conversely, if the cells are mostly aging to cycle aging, the harm of performing V2G can outweigh its benefits. This way, by considering cell families with different dominant degradation mechanisms, our work clarifies several past seemingly inconsistent results that have been reported in the literature. We also show that the timing of charging and discharging, whether late or early, within the V2G duty cycle has a secondary effect on the TvD ratio.

Our proposed TvD ratio can be extended by calculating the greenhouse gas (GHG) abated

Hamidreza Movahedi, Sravan Pannala, Jason Siegel, Stephen J. Harris, David Howey, Anna Stefanopoulou, Extra throughput versus days lost in V2G services: Influence of dominant degradation mechanism, Journal of Energy Storage, Volume 104, Part B, 2024, 114242, ISSN 2352-152X, https://doi.org/10.1016/j.est.2024.114242.

from the grid due to V2G services while also considering the extra GHG and cost of a possible early battery pack replacement. For future work, we suggest extending this study by incorporating cells with LFP chemistry, which are known for their longer lifespan. Additionally, this work emphasizes the need to estimate battery degradation states using field data to determine the impact of V2G services and whether they prove beneficial or harmful for the owners at different stages of battery life.

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List of acronyms and abrivations

BOL	Beginning of life
C_n	Negative electrode capacity
C_p	Positive electrode capacity
DOD	Depth of discharge
EOL	End of life
EV	Electric vehicle
GHG	Green house gas
HPPC	Hybrid pulse power characterization
LAM	Loss of active material
LLI	Loss of Lithium inventory
n_{Li}	Mol of Lithium
NMC	Nickel Manganese Cobalt
noV2G	Baseline duty cycle with no vehicle to grid services
OEM	Original equipment manufacturer
RPT	Reference performance test
SEI	Solid electrolyte interphase
SOC	State of charge
SOH	State of health
SPM	Single particle model
TvD	Throughput gained vs. Days lost
V2G	Vehicle to grid
x	Negative electrode stoichiometry
y	Positive electrode stoichiometry

1 Background

Personal vehicles spend a significant portion of their lives parked [2]. During this time, they can be utilized for vehicle-to-grid (V2G) services, which leverage electric vehicle (EV) batteries as extra energy storage to assist the power grid. These V2G services include bulk applications such as peak shaving and frequency regulation [3].

Peak shaving involves charging EV batteries during off-peak periods and discharging them during peak demand, optimizing energy usage and aiding the integration of renewable sources. V2G services provide an opportunity to unlock the untapped potential of EV batteries that are underutilized for driving. This is particularly beneficial for infrequently used EVs or those located in regions with high electricity tariffs. However, the increased utilization of EV batteries in V2G services raises concerns about increased degradation, which can impact the overall cost of EV ownership.

Studying this degradation is crucial to comprehensively evaluate the environmental and economic implications of widespread V2G adoption amid the broader shift to EVs. The evaluation of V2G in battery lifespan is particularly pertinent due to California's recent introduction of battery durability standards. By 2030, vehicles must maintain at least 80% of their electric range for ten years or 150,000 miles. In model year 2031, battery packs must retain 75% of their energy for eight years or 100,000 miles [4]. These specified standards can potentially include EVs utilized in V2G mode.

In previous studies on the impact of V2G on EV battery degradation, using experimental [5, 6] and empirical methods [7, 8], the findings have been inconsistent, ranging from minor effects [9, 10] to the need for early battery replacement [11, 12]. There is currently no agreement on the main factors that contribute to battery degradation. Some researchers suggest that the duration of testing, measured in days, plays a significant role [7]. Others, however, highlight a strong correlation between Ah throughput and the decrease in battery capacity [13]. Additionally, the impact of these factors can vary depending on the SOC range and the average SOC [14].

In this study, we calibrate a physics-based model based on three different NMC cell families, each with unique degradation behaviors, and fine-tune them for four distinct degradation mechanisms. Our approach aims to clarify the mixed results from previous studies and strengthen the hypotheses about observed degradation patterns.

We also introduce a new metric to quantify the impact of V2G services. This metric combines the additional Ah throughput gained with the reduction in battery lifespan, measured in days, until the battery reaches its end of life (EOL), defined as 70% capacity retention.

2 Tasks and deliverables

In quarter 1, the pseudo-2D (P2D) model degradation mechanisms were tuned and verified in some V2G experiments. This task was summarized in section 4.1 and the accompanying paper [1]. The subsequent quarter focused on extending the model with a cathode degradation mechanism for a high nickel content cathode. This model is described in section 3.2.4. In quarter 3, a surrogate SPMT (Single Particle Model and Thermal Dynamics) model was simulated for pattern exploration. The details of the surrogate model are explained in section 3.3. Finally, in quarter 4,

the detrimental sequences within the V2G duty cycle were simulated, and physical rationales for each behavior were provided. This task is performed in sections 4.3 and 4.4, and the accompanying paper [1].

3 Approach

We conduct simulations to determine the battery's lifespan under different V2G conditions and compare the results with baseline scenarios where V2G is not performed. To conduct these simulations, we model four different degradation mechanisms parallel to a single particle model (SPM), as described in the accompanying paper [1]. We calibrate these models using data collected from three sets of fast-aged cells in the University of Michigan Battery Control lab.

3.1 Battery chemistries with different degradation modes

Three different sets of pouch cells that were manufactured and had undergone calendar and cycle aging tests at the University of Michigan Battery Lab (UMBL) are considered. Each set is to represent a different dominance in degradation mechanisms:

- Loss of active material is explored by considering NMC111 cells. These cells use Magee graphite for the anode and NMC111 for the cathode and have a 5 Ah nominal capacity [14].
- Solid-Electrolyte Interphase (SEI) dominant degradation is represented by NMC622-45C cells. These cells employ Superior SLC 1520T Graphite for the anode and single crystal NMC622 for the cathode and are aged at a higher temperature of 45 ℃. The nominal capacity of these cells is 2.5 Ah.
- To represent a mixed degradation case, we consider cells with comparable loss of active material due to mechanical degradation associated with particle fracture in both the anode and cathode (*LAM*_{p,n}), as well as the SEI. In this cell family, we use the same materials as NMC622 cells but age at 25 °C denoted from now on as NMC622-25C cells [15].

3.2 Aging mechanisms

In this work, we built upon the previous model developed by our team and considered the following degradation mechanisms:

- Solid-electrolyte-interphase (SEI) layer growth
- Mechanical degradation due to particle cracking in the electrodes
- Lithium plating
- Transition metal dissolution in the cathode

During normal operation, Li-ion batteries are commonly assumed to degrade due to these specific mechanisms, although other degradation mechanisms can also be taken into account [16]. A detailed model, based on the SPM, is presented in Figure.1. A more detailed figure is shown in the accompanying paper [1].



Figure 1: SPM and the degradation models.

In the following sections, a brief description of the model of each degradation mechanism is provided, highlighting specific improvements to the baseline models from the literature. The SEI growth model remains unchanged, but an optimal experiment design for modeling and parametrization of the model was developed during this project[17]. The model for particle cracking, which was previously introduced in [18], remains unchanged. The Lithium plating model is enhanced to include concentration dynamics in the electrolyte. A cathode dissolution model has also been added to our existing framework.

3.2.1 SEI growth model

When the electrolyte and negative electrode react, they produce a layer of reaction products at the interface of the solid electrode. This layer leads to a decrease in the cell's capacity since it consumes Lithium. In addition, this layer elevates the internal resistance of the cell. The SEI model utilized in this work is similar to those previously developed and extensively studied [19]. The equations of this model are presented in the upper left window of Figure 1. As part of our work, we focused on sensitivity analysis and optimal experiment design for calendar aging tests to accurately estimate SEI degradation parameters [17]. This parameterization helps to make more precise predictions of the Li-ion battery's EOL. To this end, a physics-based model of the SEI layer is used to develop a closed-form solution for the loss of Lithium inventory during calendar aging. This model is shown to match experimental data. Further, the developed model is used to find the

sensitivity of loss of Lithium inventory to SEI parameters in diffusion-limited and kinetically limited SEI patterns.

Through this sensitivity analysis, we show that in the kinetically limited case, performing calendar aging tests at high SOC levels provides the most accurate results. For the diffusion-limited case, we have to use optimal experiment design techniques to find the optimal calendar aging SOCs that are non-trivial. It is also shown that these optimal SOC values result in higher accuracy estimations compared to sub-optimal SOCs [17].

3.2.2 Mechanical degradation due to particle cracking

Cell electrodes undergo expansion during Li-ion intercalation and contraction during deintercalation, causing alternating stresses. This leads to crack initiation, active material loss, and Li-ion entrapment, resulting in capacity fade and resistance increase. We use a material fatigue model to simulate this crack growth [20]. The equations used in this model are presented in the upper right window of Figure 1.

3.2.3 Modified Lithium plating model

Lithium plating is the deposition of metallic Lithium on the particle surface, causing cyclable Lithium loss and capacity fade. Modeling this phenomenon commonly involves Tafel or Bulter-Volmer kinetics, reflecting the thermodynamic conditions favoring metallic Lithium formation over intercalation reactions. The plating current density j_{pl} is usually modeled using the Tafel equation

$$j_{pl} = -i_{0,pl} \exp\left(\frac{-\alpha_{c,pl}F}{RT}\eta_{pl}\right) \tag{1}$$

$$i_{0,pl} = k_{0,pl} c_e F \tag{2}$$

$$\frac{\partial c_{pl}}{\partial t} = \frac{a_s \, j_{pl}}{F} \tag{3}$$

where $i_{0,pl}$ is the exchange current density of Li deposition, c_{pl} is concentration of accumulated plating, $\alpha_{c,pl}$ is charge transfer coefficient, $k_{0,pl}$ is the Li-plating kinetic rate constant, and c_e is concentration of Li in electrolyte. The overpotential of Li-plating η_{pl} can be calculated as:

$$\eta_{pl} = \eta^- + U^- \left(c_{ss}^- \right). \tag{4}$$

where $U^{-}(.)$ is the negative OCP function. It is known that using these equations based on SPM performs poorly in modeling Li-plating. This limitation arises from assuming a uniform intercalation current across the electrode.

Since SPM does not consider the concentration dynamics of the electrolyte, we modified the Li-plating model to include the non-uniformity of the concentration in this domain. As a result, the plating overpotential during charging remains positive and will not translate to any notable rate dependence or charge/ discharge dependence of Li-plating. To address this issue, we adjust [21] the exchange current density in equation 2 to:

$$i_{0,pl} = k_{0,pl} c_e (c_{ss} - c_{s,avg}) F$$
(5)

where c_s is the surface concentration and $c_{s,avg}$ is the average concentration of the anode. It is apparent that the term $(c_{ss} - c_{s,avg})$ represents the concentration gradient in the anode.

As a result of this modification, the η_{pl} curve for higher currents reaches lower values, thus leading to a higher magnitude of the Tafel-driven kinetics $\exp(\frac{-\alpha_{c,pl}F}{RT}\eta_{pl})$ term in equation 1 which determines the plating current. A more detailed explanation of this modified model can be found in [21].

3.2.4 Cathode metal dissolution

As proposed in task 2, we incorporate cathode dissolution into our existing model for this project. The positive electrode experiences capacity fade due to acid attack on the active material, which results in the dissolution of transition metal ions into the electrolyte. This phenomenon is especially pronounced in the delithiated state of the cathode (at high cell voltages) [22]. We model this mechanism by reducing the active material ratio in the cathode [23]. The equations for the dissolution model are shown in the middle right window of Figure 1.

3.3 Adaptive inter- and Intra- cycle reformulation for fast simulation of battery lifetime

As was proposed in task 3, we have implemented an adaptive extrapolation algorithm that dynamically chooses step sizes based on degradation rates. This algorithm speeds up simulation times, allowing for quick model tuning using the least squares method. Additionally, it enables fast simulation of various V2G and non-V2G scenarios.

Battery cycling involves several timescales, with some states, such as SOC, changing over hours and slow states, such as SOH, spanning months. This observation leads to a simple extrapolation algorithm: conduct one cycle, measure state changes, and extrapolate for subsequent simulations. However, the direct extrapolation algorithm is suboptimal as it requires extrapolation of rapidly changing variables that can fluctuate constantly. Instead, only slowly changing variables evolving over longer timescales can be considered. The slowly changing degradation states in our model include active material ratios of positive and negative electrodes, SEI layer thickness, Lithium moles lost due to Li-plating, and dissolved mols of transition metal from the cathode:

$$y = [\varepsilon^+, \varepsilon^-, \delta_{SEI}, n_{diss}]$$
(6)

On the other hand, the inter-cycle extrapolation algorithm should take smaller steps when degradation rates change rapidly and larger steps when rates remain constant, rather than using constant time steps. Therefore, instead of a fixed number of cycles for each extrapolation, we use an adaptive algorithm where the step size depends on the rate of degradation change (Figure 2). To this end, we define the problem as

$$\frac{dy}{dt} = \Delta y \tag{7}$$

A fixed-step extrapolation technique is tantamount to solving ODE in equation 7 with first-order Euler's method. Instead, here we use an adaptive numerical method (3(2) Rongue Kutta) to reach

an adaptive inter-cycle extrapolation and simulation. A more detailed explanation of this technique is described in [24].



Figure 2: Schematic of the inter-cycle extrapolation algorithm [24]

This method facilitates simulating the V2G and noV2G scenarios, and based on these simulations, we can define a new metric, as will be discussed in the following subsection.

3.4 Throughput gained vs. Days lost (TvD) ratio

To assess the damage and benefits of V2G services for each cell family, we quantify them by defining the V2G Throughput gained vs. Days lost (TvD) ratio. We define the throughput gained in terms of normalized extra Ah from performing V2G compared to the baseline noV2G and the harm as the normalized life lost in days due to V2G compared to the baseline noV2G. The ratio will be :

$$TvD ratio = \frac{\text{Life gain in use } Ah/Ah \%}{\text{Life lost in days \%}}$$
(8)

This metric holds a large value when the additional extracted Ah throughput due to V2G operations is substantial, and the battery life is not significantly affected. Conversely, if V2G services result in a significant loss of battery life without providing a considerable amount of extra throughput Ah for the same capacity fade, the V2G TvD ratio will be small.

4 Results

Using the tuned models, we can simulate V2G and noV2G duty cycles for each cell mentioned earlier.

4.1 Verifying of the model with existing experimental studies

To validate the tuned model, we first examine the patterns in our simulation outcomes in relation to those from earlier reported experiments. Cycle-aging experiments carried out by Dubarry et al. [6] involved the utilization of 51 Panasonic graphite/(NCA) 18650B cylindrical battery cells, each with a capacity of 3350 mAh, and included diverse V2G scenarios. Two of these scenarios that we focused on for validation consist of the following duty cycles in each equivalent day (12 hours).

- RC-RC (No V2G): Drive- Rest- Charge, Drive-Rest-Charge
- DCR-DCR (V2G): Drive-Discharge-Charge-Rest, Drive-Discharge-Charge-Rest

In both scenarios, the battery is charged at C/4 rate at work and C/8 at home. For the V2G case, the discharge to the grid is at C/4 for one hour after each driving period to simulate bulk grid services. Two different US06 Drive cycles were taken into account for each duty cycle. One was derived from simulations conducted by Kollmeyer et al. (referred to as KPy) [25], and the other was supplied by an Original Equipment Manufacturer (OEM). The OEM drive cycle encompasses greater Ah throughput and depth of discharge. The resulting range of state of charge is outlined as follows:

- State of Charge for V2G: 100-45% for OEM drive cycle and 100-55% for KPy drive cycle.
- State of Charge for no V2G: 100-70% for OEM drive cycle and or 100-80% for KPy drive cycle.



Figure 3: Capacity fade versus cycle number and versus charge throughput based on (a) Dubarry et al. [6] and (b) our simulations.

The resulting Ah throughput per cycle for each scenario is:

- Kpy: DCR-DCR: 10.91 Ah
- OEM: DCR-DCR: 12.62 Ah
- Kpy: RC-RC (No V2G): 5.91 Ah
- OEM: RC-RC (No V2G): 7.62 Ah

The results based on the model tuned for cell NMC111 are illustrated in Figure 3. As depicted in this figure, our model indicates a 50% increase in the degradation rate per day (cycle) when V2G is included in the duty cycle. Additionally, we observe consistent trends with those presented by Dubarry et al. [6]. Specifically, duty cycles without V2G exhibit superior performance (slower degradation) with regard to cycle number but perform worse (faster degradation) when evaluating results based on Ah throughput.

4.2 Effect of calendar aging contribution on the TvD ratio

Using the tuned models and duty cycles that have been extensively described in the accompanying paper [1], the contribution of each degradation mechanism to the capacity fade is determined. We show that engaging in V2G bulk services will increase the contribution of particle cracking and Li-plating to capacity fade for all three cell families. This observation is sensible, given that these

degradation mechanisms amplify with higher Ah throughput as the battery reaches its end of life (EOL). Performing V2G also reduces the contribution of calendar aging mechanisms (SEI growth and cathode dissolution).

When examining each cell family separately, it is observed that under V2G, the cell dominated by LAM_{Neg} degradation, labeled as NMC111, experiences more rapid degradation due to V2G. This results in a significant loss of battery life without a substantial increase in Ah throughput. Conversely, the calendar aging-dominant NMC622-45C cell experiences slightly accelerated degradation but shows significantly higher throughput when subjected to V2G. This highlights the risk of wasted mileage if not utilized for V2G. Positioned as a midpoint, the NMC622-25C cells show moderate life loss and increased Ah throughput, striking a balance between the extreme cases.

Based on the TvD definition, it becomes evident in Figure 4 that with the rise in the calendar aging component of degradation, V2G bulk services become more advantageous, tapping into the unused potentials of the cells.

As proposed in task 4, we alter the SOC window and average SOC of the duty cycles to identify the detrimental sequences for the battery. We then analyze their impact on the battery degradation during V2G.



Figure 4: TvD ratio based on the portion of calendar aging on the capacity degradation for three cell families. The driving here is assumed to be one hour to work and one hour back.

4.3 SOC window effect

To examine the effects of different SOC windows while maintaining the same ΔSOC s, we conducted additional simulations at various levels of maximum SOC values, as illustrated in Figure 5. The dark color shows the high-voltage windows, and the bright color shows the low-voltage windows.



Figure 5: Different SOC levels with the same Ah throughput. The low SOC level case ranges between 35-55%, and the high SOC falls within 80-100%. The duty cycle shown here is assumed to be for one day.

The resulting capacity degradation simulations are presented in Figure 6. The terminal voltage output at BOL and EOL is illustrated in Figure 7 for NMC111 cells. The results for NMC622-45c cells are presented in Figure 8.

In both V2G and noV2G cases, lowering the operating voltage reduces the degradation rate in both cells. However, it can be seen that this reduction is larger in NMC111 cells compared to NMC622-45C for both V2G and noV2G scenarios. This difference can be explained by considering equation 9.

$$\frac{dn_{Li,LAM}}{dt} = \frac{3600}{F} \left(x \frac{dC_n}{dt} + y \frac{dC_p}{dt} \right)$$
(9)

Reducing the operating voltage reduces the SOC of the negative electrode (x) and increases the SOC of the positive electrode (y). Therefore, the effect of lowering the operating voltage on the LLI in the negative electrode $(x\frac{dC_n}{dt})$ is increasing the degradation rate, and that effect on the LLI in the positive electrode $(y\frac{dC_p}{dt})$ is mitigating the degradation.

Furthermore, from Table 4 of the accompanying paper [1], it is visible that for NMC111 cell LAM in the negative electrode is much more significant in the positive electrode $\left(\frac{dC_n}{dt} \gg \frac{dC_p}{dt}\right)$. This relationship is reversed for the NMC622-45C cell.



Figure 6: V2G and noV2g duty cycles simulated at different voltage levels for NMC111 cell. The dark color shows the high-voltage windows, and the bright color shows the low-voltage windows. The change in EOL days and Ah is shown by arrows.



Figure 7: NMC111 cell voltage at Beginning of Life (BOL) and End of Life (EOL). As the cell ages, the capacity fades, and the voltage hits the minimum voltage for the lower voltage window.

Hence, in the NMC111 cell we have $|x\frac{dC_n}{dt}| \gg |y\frac{dC_p}{dt}|$ and reducing the voltage will decrease the LLI_{LAM} in total. Therefore, both SEI and LAM will mitigate the capacity fade when the operating voltage is decreased. In the NMC622-45C cell, we have $|y\frac{dC_p}{dt}| \gg |x\frac{dC_n}{dt}|$ so the SEI and LLI_{LAM} have opposing effects. Hence, in this case, lowering the operating voltage window will decrease the SEI and increase LLI_{LAM} . However, in total, lowering the average SOC still reduces capacity fade, albeit slightly.



Figure 8: V2G and noV2g duty cycles simulated at different voltage levels for NMC622-45C cell. The dark color shows the high-voltage windows, and the bright color shows the low-voltage windows. The change in EOL days and Ah is shown by arrows.

4.3.1 Power denial

While lowering the operating voltage reduces the overall degradation for both NMC111 and NMC622-45C cells, the power denial must be considered in lower voltages. Figure 7 shows the voltage profile for the beginning of life (BOL) and EOL for NMC111 cells at high and low operating voltages. As the cell degrades, the capacity decreases, so the same current load will result in reaching the cell minimum voltage (3 V). This results in the cell not being capable of performing the duty cycle even though the capacity has not reached the 70% end of warranty threshold, as can be seen in Figure 6. Reducing the SOC window can be combined with an algorithm performed by a smart BMS to shift the voltage window to higher values after 80% retention. This way, reducing the degradation and postponing power denials is possible.

4.4 Average SOC effect

In a similar analysis, the effect of different average values of SOC on the degradation is also studied for a specific voltage window. This is done by considering early charging of the battery right after arrival at the destination and late charging right before leaving.

As is expected, late-charging (lower average SOC) reduces the degradation rate, and earlycharging (higher average SOC) will increase the degradation. However, the amount of this change is dissimilar for each cell family. This effect is more visible in NMC622-25C cells and less evident in the NMC111 cells. The reasoning is detailed in the accompanying paper [1], Subsection 5.2.

5 Conclusions

In this work, we used a physics-based model to investigate the degradation of Li-ion batteries due to V2G usage. To this end, we tuned a SPM model with SEI, mechanical degradation due to particle cracking, Li-plating, and cathode dissolution for three NMC cell families. The primary degradation mechanisms varied among the cells: the first cell experienced particle cracking, the second one exhibited mostly SEI growth degradation, and the third one involved a combination of these two mechanisms. We also introduced the TvD ratio to compare the performance of each case. We demonstrate through simulations of various V2G and no V2G duty cycles that in cases where the cell chemistries and conditions contribute significantly to calendar aging, V2G offers more potential benefits than drawbacks. We also demonstrate that the sequence of charging and discharging in the V2G scenarios can have a secondary role in the TvD ratio.

This work can also be enhanced by factoring in the reduction in greenhouse gas (GHG) emissions from the grid due to V2G services, weighed against the extra cost of early battery pack replacement. For future research, we also recommend extending the study to include LFP cells, retuning the model accordingly, and possibly taking into account the degradation mechanisms commonly observed in these chemistries. Moreover, we suggest expanding this work by online estimation of battery degradation and assessing whether V2G services are beneficial or harmful for owners in different stages of the battery life.

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