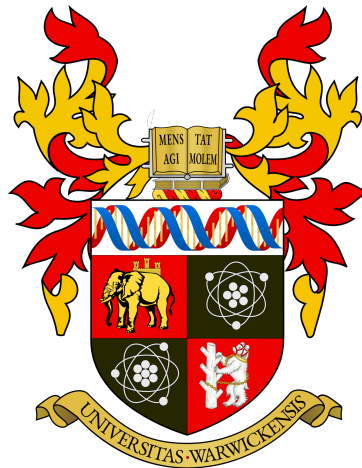


# MA4J5 Structures of Complex Systems Coursework : Modelling Reaction Kinetics of Li-ion Batteries and Solving for the Optimal Charging Strategy with a Genetic Algorithm

u1617871, u1703854, u1705902

29th April 2021



## Abstract

We propose a novel genetic algorithm to solve for the optimal charging strategy of a Li-ion battery. We discover the inability of classical stochastic and dynamical rule based systems to model battery degradation and charging effectively. Therefore, we move to an analytic setting proposed by [3] to further our analysis. We generalise the standard constant current - constant voltage (CC-CV) charging strategy to a sequence of charging elements in a charging strategy. For example, a strategy may be given by (CV, CC, CV, ...). Then, we optimise over the set of possible sequences obeying boundary conditions to find the optimal charging strategy. We show this to be the 4-sequence (CC, CV, CC, CV) offering similar degradation and a at least a 10 minute gain on charging time compared to the standard CC-CV strategy.

# 1 Introduction

In this project, we explore the processes that take place inside a Lithium-ion battery. Specifically those with a graphite anode, and a cobalt oxide cathode.

Lithium-ion batteries have been commercially available since the 1960s, however developments across multiple disciplines have seen their performance improve significantly [2]. Such developments have arisen from the field of chemistry where changes to the structure of cathodes, anodes and electrolytes can significantly improve useful qualities such as speed of discharge and ability to hold charge over long periods of time. Other developments come from modelling the battery as a system *over time* to optimise charging strategies and minimise issues such as long-term damage.

Lithium-ion batteries are versatile for a variety of applications and they offer power solutions to systems regardless of shape and size. They can be found in energy storage systems, laptops, mobile phones and a variety of common electronic devices. One of the advantages of using Lithium-ion is their high energy density. They last longer between charging cycles, while providing a high current output. This particularly makes them great for mobile phones. Furthermore, they also have a very low self-discharge rate, which is a common issue in rechargeable batteries. On the other hand, one disadvantage of Lithium-ion was that for a given capacity, they are more expensive to manufacture than other rechargeable batteries such as NiMH and NiCd batteries. However, as they are becoming more common, it costs less and less to manufacture.

The motivation for studying the optimal charging strategy is battery degradation. As an example, consumers who buy a phone would likely have to replace the battery or buy a new phone in the space of a year, because the battery loses its ability to hold charge efficiently over a long period of charging and discharging cycles. Eventhough Lithium-ion batteries are much better at holding charge, battery degradation is still a problem. This is also a problem for the environment and climate because high battery degradation means more batteries are being manufactured unnecessarily each year. Demand for Lithium ion batteries has been doubled between 2016 and 2018 as can be seen [4]. Lithium ion batteries require a lot of water to manufacture What is the most efficient charging-discharging cycle to keep battery degradation to a bare minimum?

We first focus on modelling the Lithium-Ion battery as a stochastic rule based system using the chemical reaction equations, simulated by the Gillespie algorithm. Furthermore, we will also compare it with the dynamical system equivalent of this model. We will see later that these models clearly have their limitations for finding optimal charging strategies. Therefore, we then consider the analytic model and battery degradation measure proposed by [3]. We propose a novel genetic algorithm which optimises over charging strategies to develop the optimal charging

strategy.

In order to model a complex system, it is important to understand any factors that could influence a chosen state. This allows us to select an appropriate modelling strategy and define an appropriate system boundary. In the case of this project, a background in electrochemistry is required to do this effectively.

## 2 Theory

### 2.1 Electrochemistry

The electrical *charge* on a single electron is  $-1.602 \times 10^{-19}$  coulombs. Voltage is the *energy* given to this charge which can be transferred to any other form of energy (heat, light, kinetic, ...) in an electrical component. It is important throughout to distinguish between energy (measured in *joules*) and charge (measured in *coulombs*). The following equations help to clarify,

$$\text{Voltage} = \frac{\text{Joules}}{\text{Coulomb}}, \quad \text{Current} = \frac{\text{Coulombs}}{\text{Second}}, \quad \text{Resistance} = \frac{\text{Joules}}{\text{Second}}.$$

A battery is designed to store electrochemical potential *energy* which then gets carried by the *charge*. Resistance is the extent to which this energy is lost. Newton's first law states that an object will have a constant velocity unless acted upon by an external force. Applied to the above, a current would require no voltage to move if there wasn't resistance acting against it, this idea ties resistance, voltage and current together in Ohm's law,

$$\text{Voltage} = \text{Current} \times \text{Resistance}.$$

When an electron is removed from a lithium atom, conservation of charge means the resultant  $\text{Li}^+$  ion has a positive charge identical in magnitude to that of an electron, namely  $+1.602 \times 10^{-19}$  coulombs. 0.9 grams of lithium contains roughly  $7.774 \times 10^{22}$  atoms, meaning as many lithium *ions* could create a charge of roughly 12455 coulombs. This is the same as roughly 3,459 mAh (milliamp Hours) which is the area under a charge/time graph denoting a battery's electric power over time. However, energy is required to separate these lithium ions from the electrons (charge the battery), and is released as they are reunited (discharge the battery). It is up to the user how much voltage they demand from a battery or even give it. Relative to a voltage of 3.6V, the total energy stored in the battery is 44,839 joules which is comparable to the energy stored in 1/5 of an Oreo biscuit. Whilst the maths checks out, achieving a situation like the one above requires a

touch of chemistry.

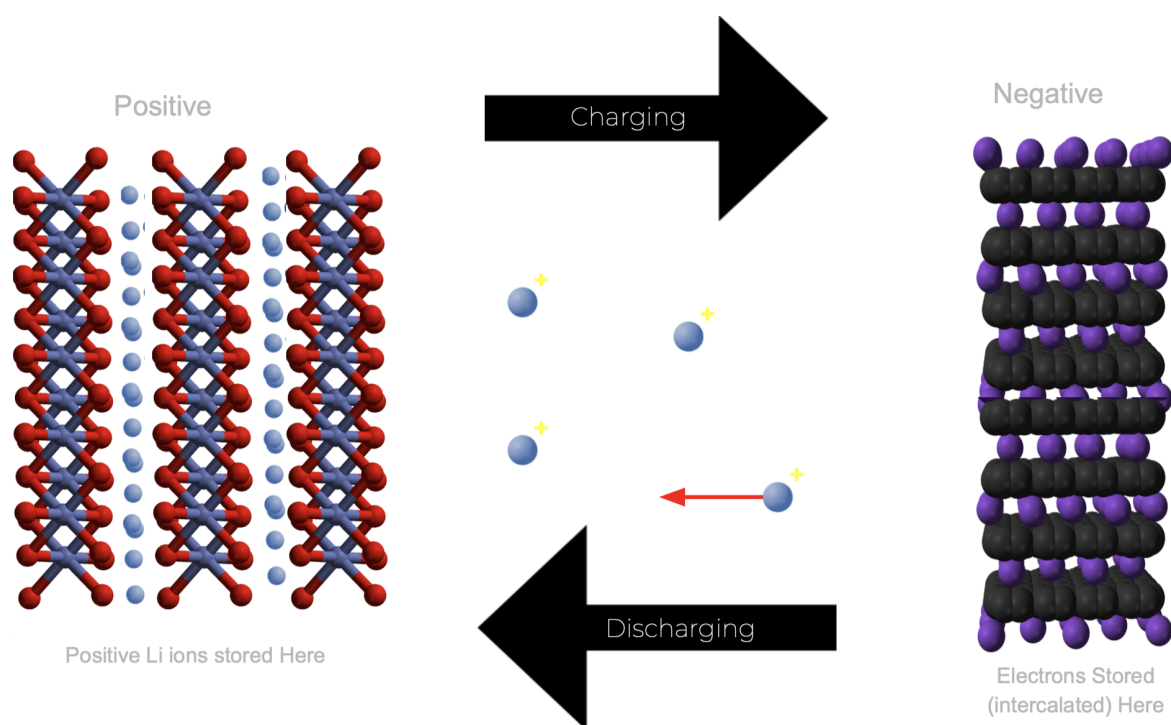
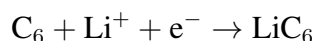
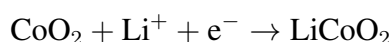


Figure 1: Simplified molecular model of ion transport in a battery

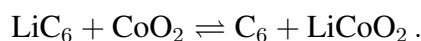
Chemical potential energy is stored in a battery by trapping charged particles in molecular lattices. Figure 1 may be used as a visual aid for the following explanation. When charging a lithium-ion battery, electrons are united with lithium ions in a graphite structure. We say the electrons are *intercalated* in the graphite structure ( $C_6$ ). This gives the *charging* equation,



*Note this equation can happen both ways but for the purpose of illustration, the preferred direction is stated.* In the charged state, the electrons are unstable in the carbon structure and ready to be liberated when a potential difference is demanded from an external circuit (discharged). This is analogous to a ball being rolled to the top of a hill, the ball can be rolled down to produce kinetic energy from gravitational potential whenever a user requires. When discharging, the ions move across the battery to the cobalt oxide structure, this is a more stable state, like the ball being at the bottom of a hill.

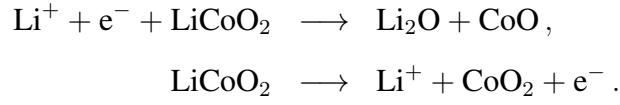


These two two-way equations can also happen simultaneously, giving the overall equation,



This is a delicate chemical system optimised to be efficient and reproducible. An unfortunate caveat of this is when a battery is overcharged, or over discharged, this causes irreversible

damage to the battery such as oxidising the valuable lithium ions or synthesising a less useful version of cobalt oxide.



These types of batteries are most commonly used in electrical appliances today such as laptops and phones. Such flaws as those stated above are a case for optimisation both chemically and as a system, we explore the latter in more depth in the next section.

## 2.2 Charging Strategies

The standard charging strategy for Li-ion batteries is the Constant Current - Constant Voltage (CC-CV) protocol. A Battery Management System (BMS) built into the battery pack controls this charging protocol. For example, the Li-ion battery that powers your laptop is a rechargeable battery pack with a built in BMS. This BMS ensures optimal charging of your laptop by

I Minimising the time taken for a full charge cycle while

II Minimising the long term battery damage

Laptop batteries typically last between two and four years, or for around 1,000 full charging cycles [? ]. From (frustrating) anecdotal experience, we are aware that the run time of our laptops decreases with time. The ability of our battery to store charge decreases with each successive charge cycle. In this paper, we propose a new charging strategy which optimises for (I) and (II) above for a general Li-ion battery via application of a simple genetic algorithm. We then compare this to the performance in terms of battery degradation and charge time of the standard CC-CV protocol. However, first we need to understand the CC-CV charging strategy and its variants.

## 2.3 CC-CV charging protocol

In the following, we briefly describe the CC-CV charging protocol and how a BMS may achieve this. As reference, Figure 2(a) (2) plots the empirical CC-CV charging profile for a Li-ion battery. We consider the CC and CV stages separately.

In the constant current (CC) stage, the BMS fixes the current supply to the cell. Note the phase ends when the pre-set upper limit of voltage is reached. However, note the capacity of the battery (area under red curve) is less than the maximal capacity of the battery. Hence, we continue

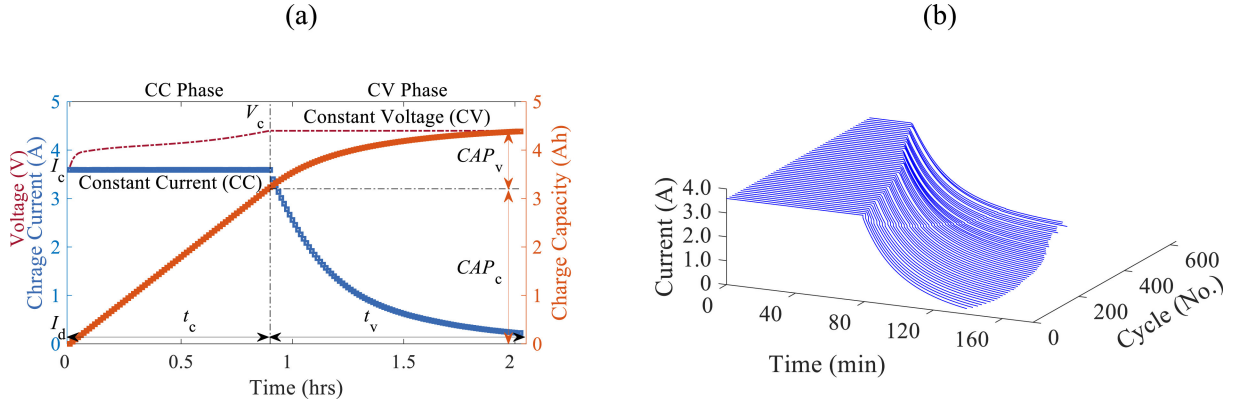


Figure 2: (a) CC-CV charging protocol curve for a typical Li-ion battery charging from a state of complete discharge, i.e zero capacity ( $CAP_{t=0} = 0$ ). (b) CC-CV plots of successive charges for a battery. Note the ratio of constant current charge time (CCCT),  $t_c$  to constant voltage charge time (CVCT),  $t_v$  decreases with successive charges. This figure is an extract from [5]

charging and move on to the next stage of the process.

This is the constant voltage (CV) charging profile. The BMS fixes the voltage supply to the cell. As such, the charging current is variable in the CV phase. We can visualise this clearly by the blue line in Figure 2(a) (2) The phase ends when the pre-set lower threshold of current  $I_d$  is reached. The capacity of the cell (area under red curve) is still not the maximal capacity of the battery but is close enough. Therefore, to save time we stop charging.

## 2.4 Alternate Charging strategies

The CC-CV charging profile is the standard strategy. However, there are multiple other strategies which may be more suitable depending on the requirements. For example:

- Boost Charge, Constant Current - Constant Voltage (BC-CC-CV)
- Multistage current charging (IPPL-CC-CV)

The above profiles are variants of the CC-CV profile, with the current and voltage held fixed at different intervals.

## 2.5 Rule Based stochastic System

Before we can proceed further, we need to describe a method to model the reactions happening within a Li-ion battery. We do this by modelling the battery charging process with a rule based

stochastic process followed by a dynamical system. In this section we assume that the Lithium-Ion battery is a stochastic rule based system. We begin by introducing the general idea of types and rules which determine how the different quantities in our system evolves.

**Definition 2.1** (Types). Consider a basic object set  $\mathcal{O}$  that makes up the system. We let  $\mathcal{T} = \{T_1, \dots, T_s\}$  for  $s \in \mathbb{N}$  define the set of types. We require at any time, that any  $o \in \mathcal{O}$  is an element of exactly one type  $T_i$ ,  $1 \leq i \leq s$ . Each  $T_i$  is a subset of the basic object set  $\mathcal{O}$  and they form a partition of  $\mathcal{O}$  such that  $T_i \cap T_j = \emptyset$  for each  $i \neq j$ .

**Definition 2.2** (Rules). Let  $\mathcal{R} = \{R_1, \dots, R_r\}$ ,  $r \in \mathbb{N}$  be a finite set of rules corresponding to the system. We define the  $j$ -th rule as,

$$(R_j) \quad \sum_{i=1}^s \alpha_{ij} T_i \xrightarrow{k_j} \sum_{i=1}^s \beta_{ij} T_i \quad (2.1)$$

where  $s$  denotes the number of types in the system and  $k_j$  corresponds to the rule rate or reaction rate of rule  $R_j$ . Here the  $\alpha_{ij}, \beta_{ij}$  represent the source and target coefficients, which describe the changes of amounts of the types  $T_i$  during the execution of rule  $R_j$ .

For each rule  $R_j$  we collect the coefficients  $\alpha_{ij}, \beta_{ij}$  into a column vector which we will call the source and target complex of rule  $R_j$ . We represent these as follows,

$$C_j^s = \begin{pmatrix} \alpha_{1j} \\ \vdots \\ \alpha_{sj} \end{pmatrix} \quad (2.2)$$

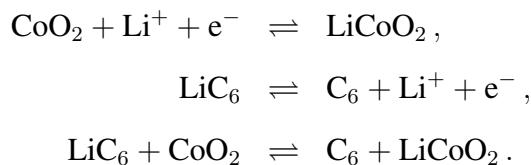
$$C_j^t = \begin{pmatrix} \beta_{1j} \\ \vdots \\ \beta_{sj} \end{pmatrix} \quad (2.3)$$

We can assemble the source and target complexes  $C_j^s, C_j^t$  into a vector  $\mathcal{N}_j = C_j^t - C_j^s$  which represents the net production of each type of objects under the execution of rule  $R_j$  a single time.

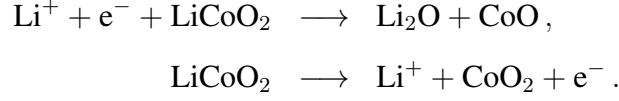
Let  $n_{ij} = \beta_{ij} - \alpha_{ij}$ , define the stoichiometric matrix using each  $\mathcal{N}_j$  as,

$$\mathcal{N} = (\mathcal{N}_1, \dots, \mathcal{N}_r) = \begin{pmatrix} n_{11} & \dots & n_{1r} \\ \vdots & \ddots & \vdots \\ n_{s1} & \dots & n_{sr} \end{pmatrix} \quad (2.4)$$

In this project we consider a Li-Ion battery which can be modelled as the following series of reversible chemical reactions,



There are two more irreversible reactions which account for the overdischarging and overcharging of the battery respectively. These can be formulated as,



For this specific example we have eight reactions, therefore we will assign a reaction rate  $k_i$ ,  $1 \leq i \leq 8$ , together with the set of rules  $\mathcal{R} = \{R_1, \dots, R_8\}$ . Similarly we have eight types, therefore we can write down the set of chemical substances as,

$$\mathcal{T} = \{\text{CoO}_2, \text{Li}^+, \text{e}^-, \text{LiCoO}_2, \text{LiC}_6, \text{C}_6, \text{Li}_2\text{O}, \text{CoO}\} \quad (2.5)$$

The stoichiometric matrix  $\mathcal{N}$  for the lithium ion battery is given by,

$$\mathcal{N} = \begin{pmatrix} -1 & 1 & 0 & 0 & -1 & 1 & 0 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 & -1 & 1 \\ -1 & 1 & 1 & -1 & 0 & 0 & -1 & 1 \\ 1 & -1 & 0 & 0 & 1 & -1 & -1 & -1 \\ 0 & 0 & -1 & 1 & -1 & 1 & 0 & 0 \\ 0 & 0 & 1 & -1 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \end{pmatrix} \quad (2.6)$$

We will pay special attention to the movement of electrons and how it evolves under the execution of all the rules. We set up the rows of  $\mathcal{N}$  in the same ordering as the type set  $\mathcal{T}$ , therefore the stoichiometric coefficients for the number of electrons is given by the third row of  $\mathcal{N}$ . To simulate how the different quantities in this system evolves, we use the Gillespie Algorithm. First, calculate the propensities for every rule. These can be generally defined as,

$$\mathcal{R}_j(n) := k_j h_j(n), \quad (2.7)$$

$$h_j(n) := \prod_{i=1}^s \binom{n_i}{\alpha_{ij}} \quad (2.8)$$

Here  $\alpha_{ij}$  is the  $i$ -th entry of the source complex  $C_j^s$  for rule  $R_j$  as defined above and  $n = (n_1, \dots, n_s)$  is the current number of objects of any type in the system. We are now ready to solve this system using the following algorithm. The intuition behind the Gillespie algorithm is that at each time step we calculate the reaction that is most likely to occur and update the system quantities accordingly.

Note the stochastic electron update curve in Figure 3 (3) is non-differentiable at multiple points. This poses an issue since we would like to determine the current as the rate of change of electron flow, which is the time derivative of the above graph. Motivated by the need for a smooth electron-time curve, we model the system as a dynamical system.



---

**Algorithm 1:** Gillespie Algorithm

---

- 1 Initialize  $n = n_0$ ,  $t = t_0$  and final time  $T$
  - 2 **while**  $t < T$  **do**
  - 3     Generate  $r_1, r_2$  uniformly distributed in the interval  $[0, 1]$
  - 4     Calculate  $\mathcal{R}_0 = \sum_{j=1}^r \mathcal{R}_j(n)$
  - 5     Calculate  $\tau = \frac{1}{\mathcal{R}_0} \ln(\frac{1}{r_1})$
  - 6     Update the time  $t \rightarrow t + \tau$
  - 7     Compute the most likely rule to be executed at  $t + \tau$ . Find  $j$  such that,
$$\frac{1}{\mathcal{R}_0} \sum_{i=1}^{j-1} \mathcal{R}_i(n) < r_2 < \frac{1}{\mathcal{R}_0} \sum_{i=1}^j \mathcal{R}_i(n),$$
  - 8     Execute rule  $R_j$  and update the system quantities.
- 

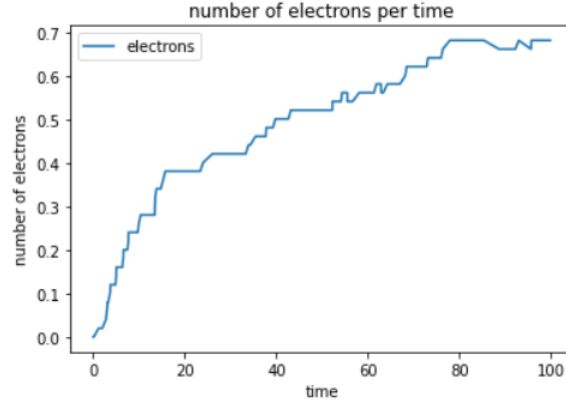


Figure 3: The number of electrons  $e^-$  as a function of time simulated as a stochastic rule based system.

## 2.6 Dynamical Systems

The definition of a dynamical system is composed of the following ideas. Let  $\mathbb{S}$  denote the state space and  $T$  be an ordered time set. Given an operator  $\varphi_t$ ,  $t \in T$ , we denote the set  $\varphi_t(s) \in \mathbb{S}$ ,  $t \in T$  as the trajectory which passes through the element  $s$  at time  $t = 0$ . For the lithium ion battery we consider a one sided discrete time set  $T = \mathbb{Z}_{\geq 0}$  where the update size  $\Delta t$  will be specified. For all  $s \in \mathbb{S}$  we can define a forward and backward existence time  $t^+(s), t^-(s) \in \mathbb{S}$ . This is convenient because it tells us how long the trajectory will exist inside the state space  $\mathbb{S}$ . We denote  $J(s) = (t^-(s), t^+(s))$  as the existence time of the element  $s$  together with the convention that  $\varphi_0(s) = s$ .

**Definition 2.3** (Dynamical System). Let  $(\mathbb{S}, T, \varphi)$  be a triple where the symbols have their usual meaning as introduced before. Here  $\varphi$  can be interpreted as the shift operator which acts on

elements  $s \in \mathbb{S}$  and is indexed by the time set  $T$ . Assume the following hold,

1.  $\Omega = \bigcup_{s \in \mathbb{S}} J(s) \times \{s\}$  is open in  $T \times \mathbb{S}$ ,
2.  $\varphi : \Omega \longrightarrow \mathbb{S}$  is continuous,
3.  $\varphi_0(s) = s$  for all  $s \in \mathbb{S}$ ,
4. for  $s \in \mathbb{S}$ ,  $t' \in J(s)$  and  $t \in J(\varphi_{t'}(s))$ , we have  $t + t' \in J(s)$ , and
5.  $\varphi_t(\varphi_{t'}(s)) = \varphi_{t+t'}(s)$ .

then  $(\mathbb{S}, T, \varphi)$  is called a dynamical system.

To be able to solve the system, we need to define what the reaction velocities are. We assemble the different types in the system into a concentration vector  $\mathbf{x}$ . The simplest way to think about this is to define  $\mathbf{x}$  as,

$$\mathbf{x} = (x_1, \dots, x_8) = (\text{CoO}_2, \text{Li}^+, \text{e}^-, \text{LiCoO}_2, \text{LiC}_6, \text{C}_6, \text{Li}_2\text{O}, \text{CoO}).$$

The reaction velocities for the  $j$ -th rule is given by,

$$v_j(k_j, \mathbf{x}) = k_j \prod_{i=1}^8 x_i^{\alpha_{ij}} \quad (2.9)$$

here  $x_i$  denotes the  $i$ -th entry of the vector  $\mathbf{x}$  and  $\alpha_{ij}$  is the stoichiometric coefficient on the source side for reaction  $R_j$ . If a certain chemical substance is not present in reaction  $R_j$ , then  $\alpha_{ij} = 0$  and therefore  $x_i^{\alpha_{ij}} = 1$ . The ODE describing the dynamical system is then given by,

$$\frac{d\mathbf{x}}{dt} = \mathcal{N}\mathbf{v}(\mathbf{k}, \mathbf{x}) \quad (2.10)$$

where  $\mathbf{v} = (v_1, \dots, v_8)$  for the lithium ion battery reaction equations. Fig. 4 illustrates how

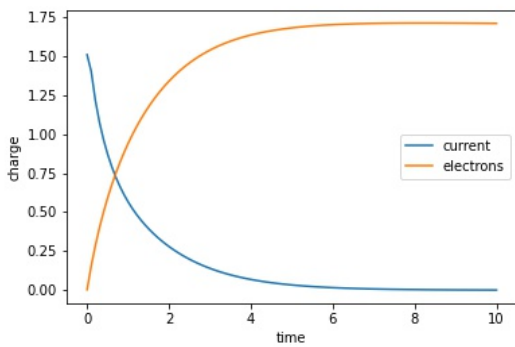


Figure 4: Simulation of the quantity of  $\text{e}^-$  and the current  $I = \frac{dC}{dt}$  (shown in yellow and blue respectively)

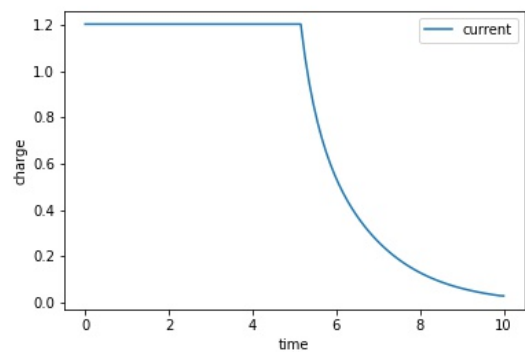


Figure 5: Simulation of the different charging phases, constant current then constant voltage

the number of electrons evolves under the execution of the system of ODE's. The current  $I$ , which is the rate of change of the number of electrons at any given time decreases exponentially and it eventually hits zero. This is consistent with the second charging phase of the battery,

corresponding to constant voltage (CV). Fig 5 has been created by first considering the constant current phase which is a straight line in the interval  $t \in [0, 5]$  and from  $t \in [5, 10]$  we solve the system of ODE's to calculate how the current  $I$  varies as a function of time. This model clearly has its limitations. Modelling a battery based on reaction kinetics is essentially just moving the electrons  $e^-$  from anode to cathode. Simply simulating the reaction kinetic equations is not enough to fully capture the charge and discharge phases of the battery. However, we would like to investigate optimal charging strategies for the Lithium-Ion battery using a genetic algorithm. Even though it is possible to calculate quantities such as charge  $C$  or the current  $I = \frac{dC}{dt}$ , using explicit solutions for the battery will allow us to calculate the more interesting properties such as power, capacity and charging time. In the next section we consider an analytical model for the CC-CV charging profile proposed by [3] who also provide a single measure of battery degradation which simplifies our setting.

### 3 Analytical model for the CC-CV charge profile

The following section is an analytical model proposed by [3] which is a good complementary reference. Throughout the charging process, the input charging current  $I(t)$  and charging voltage  $V(t)$  is controlled by the BMS. The charging current and voltage are interdependent hence we can only control one variable at a given time. Consider the standard CC-CV charging profile. Given  $I(t)$  and a time interval  $[t_0, t_1]$ , we can calculate the increase in capacity  $CAP$  of the battery by integrating  $I(t)$  with respect to time. Formally,  $CAP = \int I(t)dt$ .

We begin with the constant current charging stage during which  $I(t) = I_c$  for  $t \in [0, t_c]$  where  $t_c$  is the constant current charge time (CCCT). The total charged capacity from the CC charging phase is given by:

$$CAP_c = \int_0^{t_c} I_c dt = I_c t_c \quad (3.1)$$

This linear relationship between capacitance and time is in agreement with empirical data. As shown in Figure 2(a) (2),  $CAP_c$  is linearly proportional to  $t_c$ .

We now move our attention to the CV charging phase. Note that in the CV phase,  $I(t)$  is no longer constant. Instead,  $I(t)$  is a function of the controlled voltage. This can be seen as a direct consequence of Ohm's law. Formally, [1] propose the charging current  $I_v(t)$  during the

constant voltage phase to be  $I_v(t) = Ae^{-Bt} + C$  where  $A$ ,  $B$  and  $C$  are constants chosen to fit experimental data. Therefore, the relationship between  $CAP_v$  and the current  $I_v(t)$  within the time interval  $t \in [0, t_v]$  where  $t_v$  is the constant voltage charge time (CVCT) is given by:

$$CAP_v = \int_0^{t_v} I_v(t) dt = \int_0^{t_v} (Ae^{-Bt} + C) dt = \frac{A}{B} (1 - e^{-Bt_v}) + Ct_v \quad (3.2)$$

The total increase in capacitance can be calculated as the sum of (3.1) and (3.2):

$$\begin{aligned} CAP &= CAP_c + CAP_v \\ &= I_c t_c + \frac{A}{B} (1 - e^{-Bt_v}) + Ct_v \end{aligned} \quad (3.3)$$

We simplify this expression by considering boundary conditions and the asymptotic limit as  $t \rightarrow \infty$ . In most practical implementations of the CC-CV charging protocol, both the constant current  $I_c$  and the cut-off current  $I_d$  are predetermined. Note that the CV stage starts just when the CC stage ends. Therefore, at the start of the CV phase, the current  $I = I_c$ . Consider the expression  $I_v(t) = Ae^{-Bt} + C$  from before. Using this notation, the time at which the CV stage begins is  $t = 0$ . At  $t = 0$ ,  $I_c = A + C$ . As  $t \rightarrow \infty$ ,  $I \rightarrow I_\infty = C$ . Although the CV stage has a finite cut off time, it is a reasonable approximation to set  $C = I_\infty = I_d$ . Therefore,  $A = I_c - I_d$ . As a result of this analysis, we can simplify the analytical model to:

$$\begin{aligned} CAP &= I_c t_c + (I_c - I_d) B^{-1} (1 - e^{-Bt_v}) + I_d t_v \\ &\approx I_c t_c + (I_c - I_d) B^{-1} + I_d t_v \end{aligned} \quad (3.4)$$

Note that from the expression  $A = I_c - I_d$  we can approximate  $t_v$  given  $I_c$ ,  $I_d$  and  $B$  by:

$$t_v = -\frac{1}{B} \ln \left( \frac{I_d - C}{I_c - C} \right), \quad (3.5)$$

Typically (and ideally)  $I_d$  has a small value, we can make the approximation below, realising a linear relationship between  $t_v$  and  $B^{-1}$ .

$$t_v \approx -\frac{1}{B} \ln \left( \frac{I_d}{I_c} \right) \quad (3.6)$$

Therefore, we may consider the parameters  $t_v$  and  $t_c$  for the degradation analysis. We refer to

[3] who experimentally show the CCCT and CVCT ratio,  $t_c/t_v$  is a measure of degradation. Degradation occurs when the CCCT-CVCT ratio decreases. This can be clearly seen in Figure 2(b) (2) where the CCCT-CVCT ratio decreases with successive charging cycles.

In the following section, motivated by the knowledge that multiple charging strategies exist and the CC-CV charging profile is the standard mainly due to its practical simplicity, we ask the question of what charging strategy, in general is the most optimal. We introduce the setting of a genetic algorithm to solve this problem. We track battery degradation by the CCCT-CVCT ratio.

## 4 Genetic Algorithm Preamble

Genetic algorithms are based on the well established evolutionary strategy of natural selection which has lead us to the top of the food chain. Genetic algorithms have been shown to outperform traditional optimisation algorithms in electronics, engineering and computer science when large state spaces are involved. [6] Confidence in genetic algorithms arise from their ability to to reduce the complexity of state space optimisation.

The general setting of a genetic algorithm is described in the pseudo-code below. Briefly, a genetic algorithm simulates natural selection where the most fit individuals of a population breed and spread their good genes while the less fit individuals are removed from the gene pool. Breeding is simulated by the crossover function and the mutation function ensures diversity of solutions, ensuring good solutions are not neglected in favour of good yet less optimal solutions. Note each individual in this setting is associated with an internal state space. The parameters of this internal state space are fed into the fitness function which determines the fitness of an individual relative to other individuals in a population. Note that it is convention to assume lower fitness is better. [9]

---

**Algorithm 2:** General Genetic Algorithm

---

- 1 Input: fitness function  $fitness()$ , number of epochs  $epochs$ , population size  $popsiz$ e, mutation rate  $0 < m < 1$ , rate of survival  $0 < r < 1$ , mutation function  $mutate()$  and crossover function  $crossover()$ ;
  - 2 Result: charging profile optimising the fitness function;
  - 3  $epoch = 0$ ;
  - 4 Generate initial population -  $pop(epoch = 0)$  by generating  $popsiz$ e many random individuals;
  - 5 **for** iterations in epochs **do**
  - 6     Rank *individuals* within  $pop(epoch)$  in decreasing order of fitness.
  - 7     **for**  $individual_1, individual_2$  in the top  $r \times pop$  charging profiles **do**
  - 8          $crossover(individual_1, individual_2)$
  - 9          $mutate(crossover(individual_1, individual_2))$  with rate  $r$
  - 10     Delete the lower  $(1 - r) \times pop$  individuals from  $pop(epoch)$
  - 11     Generate  $(1 - r) \times pop$  random *individuals* and add it to  $pop(epoch)$
  - 12      $pop(epoch + 1) = pop(epoch)$
  - 13 Return: highest ranked individual in the final epoch population  $pop(epoch)$
- 

## 5 Genetic Algorithm for Optimal Charging Strategy

We describe the setting for a genetic algorithm to solve for an optimal charging strategy. We first describe the internal structure for a charging strategy which defines the system boundary followed by the fitness, crossover and mutation function.

Intervals of CC and CV charging are used to build up more complex charging strategies, as this is most practical for a BMS to implement. Therefore, we consider the structure of a charging profile as a sequence of CC and CV charge elements until the battery is charged to full capacity (or almost full). The CC-CV charging protocol expressed as a sequence is (CC, CV) for example. In general, a sequence can have any length and any sequence of CC, CV combinations.

Note that for a CC charge, it is necessary to describe the charging current  $I_c$ . To ensure continuity of the charging profile,  $I_c$  is set to match the final current of the previous element in the sequence. Therefore, the only independent variable for a CC charge is the time of charging,  $t_c$ .

For a CV charge, we need to specify the initial and final current  $I_v^i$  and  $I_v^f$  respectively where  $I_v^i$  is set to be the final current of the previous element. Note we can then find the CV charge time  $t_v = -\frac{1}{B} \ln(I_v^f/I_v^i)$  from (3.6). We take values of B from [3] which have been found by empirically fitting the analytic model in for CC-CV charging to experimental data. Note the values of B obtained here (by regression) are for a CC-CV charging profile with preset  $I_c$  and  $I_d$ . There are significantly less degrees of freedom in such a model compared to a general sequence. Therefore, this can only be regarded as a theoretical model which has to be experimentally validated.

Formally a charging strategy is a sequence  $\{X_i\}_{i \geq 0}$  such that  $X_i = (x_{1,i}, x_{2,i}, x_{3,i}, x_{4,i}) \forall i = 0, \dots$  where  $x_{1,i} \in \{CC, CV\}$  represents the charging strategy,  $x_{2,i} \in (0, 10]$  represents the final current of the previous charge element and  $x_{3,i} \in (0, 10]$  represents the final current of the current charge element. Note we set 10A to be the cutoff charging current. If  $i = 0$ , we are free to set  $x_{2,i}$  as there is no previous charging element. Due to current boundary conditions we have the recurrence relation  $x_{2,i} = x_{3,i-1}$  for  $i \geq 1$ . For CC,  $x_{2,i} = x_{3,i}$  since the charging current is constant. For CV  $x_{3,i}$  will be the final current which is an independent variable.  $x_{4,i} \in \mathbb{R}_{\geq 0}$  represents the charging time. For CC,  $x_{4,i}$  is an independent variable while for CV,  $x_{4,i}$  is depends on the final current  $x_{3,i}$  and initial current in the element  $x_{2,i}$ . From (3.6), if  $x_{1,i} = CV$ , this relationship is given by  $x_{4,i} = -\frac{1}{B} \ln(x_{3,i}/x_{2,i})$ . Note this is in fact an approximate relationship which we take to be exact for simplicity. This may be a source of error.

To generate a random charging strategy we randomly select all 4 entries of  $X_0$ . Then we randomly generate independent entries of the following charging elements filling in the dependent entries of a charging element from the recurrence relation and also the CV time equation above. We keep on generating strategies until the capacity of the battery is full (3459 mAh - see electrochemistry section). If the last element of the sequence charges the battery above this capacitance we remove it from the sequence and take the shorter sequence as a charging profile. We keep track of the capacitance increase throughout a charging strategy this with (3.1) and (3.2).

The fitness function is taken to be the ratio of the total time spent in CC charging to the total time spent CV charging. That is  $fitness(\{X_i\}_{i \geq 0}) = \sum_i \mathbb{I}\{x_{1,i} = CC\} / \sum_i \mathbb{I}\{x_{1,i} = CV\}$ . Note we do not attempt to minimise charging time to simplify the setting.

Given two charging strategies,  $\{X_i\}_{i \geq 0}$  and  $\{Y_j\}_{j \geq 0}$  the *crossover* function selects a random index  $i$  from a uniform distribution  $i \sim U(0, \min\{\text{length}(X_i), \text{length}(Y_j)\})$  and generates the

sequence  $\{Z_k\}_{k \geq 0} = \text{crossover}(\{X_i\}, \{Y_j\}) = \begin{cases} X_k & \text{if } k < i \\ Y_k & \text{if } k > i \end{cases}$ . Note that at the crossover index  $i$  we fix the boundary conditions so that the the current profiles matches ( $x_{3,i} = y_{2,i+1}$ ) and also the capacity of the battery is the cumulative capacity of the charges  $\{X_j\}_{0 \leq j \leq i}$ .

The *mutate* function  $\text{mutate}(\{X_i\}_{i \geq 0})$  randomly selects an index for a charging profile and changes the charging element from CC to CV or vice versa, preserving boundary conditions. It is important to ensure boundary conditions are preserved to ensure the process represents an actual charging process.

## 6 Results

We perform the genetic algorithm (2). From [3] we consider the constant  $B^{-1} = 1.2$  which is the value obtained by fitting the model to experimental data for a lithium ion battery charging continuously at 45 Celcius with  $I_c = 3.5A$ ,  $I_c = 0.2A$  We perform the genetic algorithm with parameters  $epochs = 200$ ,  $popsiz = 100$ ,  $r = 0.25$ ,  $m = 0.25$ . These parameters are considered to perform well for genetic algorithms across multiple applications [7].

It is important to note that in this setting we consider only the degradation of the battery from a single charge. In practice, this degradation would be negligible as degradation only becomes noticeable over the course of many successive charge cycles. Ideally, the setting should be generalised to the case of having multiple successive charges (with possibly different charging strategies each) of order  $\sim 1000$ , the average lifespan of a battery [8]. In this case the constant B would be a function of number of total charges up to that charge cycle. However, our analysis was limited by the available data. Data in existing literature does allow us to calculate empirical estimates of the constant B over successive charges, but only for the CC-CV charging protocol [3]. It is unclear as to whether this would allow us to accurately predict the capacity charging profile of general charging strategies. This is because we generalise from a two sequence strategy (CC, CV) to a general length sequence strategy. We would need to empirically test this as to the best of our knowledge this topic has not been studied, at least in our (fairly general) setting. This is a possible avenue for further research; further data collection and experimental validation.

Despite the flaws of our study, the optimal charging strategies given as the output of the genetic algorithm do reveal insights into the impact of charging profile on battery degradation. In



particular, although sequences of arbitrary length were allowed, only relatively short sequences were produced as output. By running the algorithm (with the same parameters) 10 times over, the mean sequence length was given to be 5 with variance 1.3. The charging strategies are ranked in decreasing order of charge time and degradation (measured by CCCT-CVCT ratio). The experimental observations for the best three charging strategies are collected in the table below. We note each of the sequences produced were alternating sequences of CC and CV elements. The average time for a full charge for these protocol is 1.9 hr which is better than the average charging time of 2 to 3 hours [10] and average CCCT-CVCT ratio was 2.3 which is comparable to observed CCCT-CVCT ratio from [3] with similar constant  $B^{-1} = 1.2$ . This shows that sequences of CC followed by CV of average length 5 can be viewed as comparable to CC-CV charging. It is curious to note that while we only optimise to minimise degradation via the CCCT-CVCT ratio, the optimal solutions offer shorter charging times compared to the standard CC-CV protocol.

Results	Parameters	CC	CV	CC	CV
charge time: 2.51hr CCCT-CVCT ratio: 2.40	Initial Current (A)	3.42	3.42	0.47	0.47
	Final Current (A)	3.42	0.47	0.47	0
	Charging time (hr)	0.51	0.63	1.27	0.1
Results	Parameters	CC	CV	CC	CV
Charge time: 1.51hr CCCT-CVCT ratio: 2.30	Initial Current (A)	4.27	4.27	0.97	0.97
	Final Current (A)	4.27	0.97	0.97	0
	Charging time (hr)	0.13	0.41	0.32	0.05
Results	Parameters	CC	CV	CC	CV
Charge time: 1.7hr CCCT-CVCT ratio: 2.15	Initial Current (A)	6.21	6.21	0.85	0.85
	Final Current (A)	6.21	0.85	0.85	0
	Charging time (hr)	0.28	0.52	0.88	0.02

Table 1: Top 3 charging strategies given by the genetic algorithm.

## 7 Conclusions

Motivated by the widespread use of Li-ion batteries, we propose a novel genetic algorithm to solve for the optimal charging strategy of a Li-ion battery. We note that considering the reaction kinetics within a Li-ion battery as a mass action system (interpreting the battery as a stochastic and dynamic rule based system) is insufficient to describe the complexities of battery degradation as a result of overheating and over-discharge. Therefore, we turn to the analytic model proposed

by [3] and the CCCT-CVCT ratio as a measure of degradation. We apply this analytical model to predict the CCCT-CVCT ratio (degradation) of a random charging strategy; a sequence of CC and CV charging elements. The genetic algorithm we propose supports the standard CC-CV charging strategy as the top-3 optimal results are of the type CC-CV-CC-CV. The charge times predicted by these strategies offer at least a 10 minute shorter charge. This is a curious result considering the genetic algorithm seeks to minimise degradation, not charging time. Future work would involve exploring this further, evaluating the factors contributing to this. We note our results are purely theoretical and need to be experimentally validated. It is important to note we consider only the degradation of a battery over a single charge. In addition, we make the (strong) assumption that the constant  $B$  from the analytical model fit to CC-CV curves will fit general length charging strategies. Therefore it is best to view this study as the introduction of a novel genetic algorithm which should be extended and empirically validated in the future. Genetic algorithms studied in the context of batteries tend to focus on optimising the physical parameters of the battery for example the length of anode, cathode etc. Therefore, this paper does succeed in providing new insight, despite its flaws. Future work would extend this technique to multiple charge cycles and also to different batteries.

## References

- [1] Akram Eddahech, Olivier Briat, and Jean-Michel Vinassa. Determination of lithium-ion battery state-of-health based on constant-voltage charge phase. *Journal of Power Sources*, 258:218–227, 2014.
- [2] V. Reddy et al. Brief history of early lithium-battery development. 2020.
- [3] FajiaLi ChengliangLiu NedaShafiei YulongLi MichaelPecht' 'Haining Liu, Ijaz HaiderNaqvi. 'an analytical model for the cc-cv charge of li-ion batteries with application to degradation analysis'.
- [4] Amit Katwala. The spiralling environmental cost of our lithium battery addiction, wired.co.uk.
- [5] Haining Liu, Ijaz Haider Naqvi, Fajia Li, Chengliang Liu, Neda Shafiei, Yulong Li, and Michael Pecht. An analytical model for the cc-cv charge of li-ion batteries with application to degradation analysis. *Journal of Energy Storage*, 29:101342, 2020.
- [6] K.F. Man, K.S. Tang, and S. Kwong. Genetic algorithms: concepts and applications [in engineering design]. *IEEE Transactions on Industrial Electronics*, 43(5):519–534, 1996.

- [7] I. Rojas, J. Gonzalez, H. Pomares, J.J. Merelo, P.A. Castillo, and G. Romero. Statistical analysis of the main parameters involved in the design of a genetic algorithm. *IEEE Transactions on Systems, Man, and Cybernetics, Part C (Applications and Reviews)*, 32(1):31–37, 2002.
- [8] 'Mostafa Sabbaghi'. 'reusability assessment of lithium-ion laptop batteries based on consumers actual usage behavior'. '2016'.
- [9] Lothar M. Schmitt. Theory of genetic algorithms. *Theoretical Computer Science*, 259(1-2):1–61, may 2001.
- [10] Anna Tomaszewska, Zhengyu Chu, Xuning Feng, Simon O'Kane, Xinhua Liu, Jingyi Chen, Chenzhen Ji, Elizabeth Endler, Ruihe Li, Lishuo Liu, Yalun Li, Siqi Zheng, Sebastian Vetterlein, Ming Gao, Jiuyu Du, Michael Parkes, Minggao Ouyang, Monica Marinescu, Gregory Offer, and Billy Wu. Lithium-ion battery fast charging: A review. *eTransportation*, 1:100011, 2019.