

Modeling battery cells under discharge using kinetic and stochastic battery models

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Abstract

In this paper we review several approaches to mathematical modeling of simple battery cells and develop these ideas further with emphasis on charge recovery and the response behavior of batteries to given external load. We focus on models which use few parameters and basic battery data, rather than detailed reaction and material characteristics of a specific battery cell chemistry, starting with the coupled ODE linear dynamics of the kinetic battery model. We show that a related system of PDE with Robin type boundary conditions arises in the limiting regime of a spatial kinetic battery model, and provide a new probabilistic representation of the solution in terms of Brownian motion with drift reflected at the boundaries on both sides of a finite interval. To compare linear and nonlinear dynamics in kinetic and stochastic battery models we study Markov chains with states representing available and remaining capacities of the battery. A natural scaling limit leads to a class of nonlinear ODE, which can be solved explicitly and compared with the capacities obtained for the linear models. To indicate the potential use of the modeling we discuss briefly comparison of discharge profiles and effects on battery performance.

Keywords: battery lifetime; state-of-charge; charge recovery; probabilistic solution of PDE; Robin boundary condition; nonlinear ODE

1. Introduction

The subject of this work is mathematical modeling of state-of-charge in simple battery cells, such as a non-rechargeable 3 Volts Lithium coin battery. The goal is to understand the response of the battery, and ultimately to predict battery lifetime, as energy is consumed under a given discharge usage pattern. The main incentive for our work is the battery usage in Wireless Sensor Networks and similar Internet-of-Things systems. These networks consist of inter-connected low-cost nodes, equipped with basal sensors, computer, radio and a battery, expected to run for many years under very low

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intensity loads and short dutycycles. Within the tight cost restrictions typical of such systems, methods or techniques providing “battery-charge indicators” do not seem to be within reach currently. To make progress in this direction it is essential to address the problem of predicting battery life. Our paper intends to cover some of the required modeling groundwork and discuss analysis of linear, nonlinear and stochastic aspects of modeling battery cells.

Mathematical modeling of batteries has developed over several decades along with the growth of new battery technologies and materials. Yet, there has been relatively little in-depth study of widely available, inexpensive coin cell batteries and on special load characteristics including short load periods. Primarily, lithium and lithium-ion battery models have been developed within electrochemical engineering. Two recent survey and review works [8, 14] represent the state-of-art of modeling based on the fundamental principles of electrochemistry, and emphasize the wide range of scales involved. The temporal and spatial scales of the physics and chemistry of the battery range from macroscopic level all the way down to the atomistic level. The tutorial review by Landstorfer and Jacob [8] provides a framework of non-equilibrium thermodynamics as the foundation for studying the electrode, electrolyte and interface reactions in great detail. The review work by Ramadesigan *et al.* [14], summarizes the literature on such models and, in addition, brings a systems engineering approach applied to Li-ion batteries. This type of model can be said to begin with the pseudo-two-dimensional (P2D) model of Doyle *et al.* [4], which leads to a coupled system of non-linear PDEs. More generally, coupled systems of equations with complex boundary conditions are derived, which connect charge concentrations with transport and kinetics of reactant species. Several approaches have been proposed to simplify the resulting sets of equations and allow for numerical computations, see e.g. [17, 3].

In this work we use the different mathematical approach to battery modeling developed in communication engineering for computer science applications, see e.g. Jongerden and Haverkort [5]. Where chemical engineering modeling typically begins with a detailed scheme of reactions and mechanisms in the various phases and interfaces of the cell, these models view the battery as a generic device subject to some fundamental principles. The main focus of the modeling changes and is now rather the response of the battery to external load. A typical purpose is load scheduling to optimize battery utilization. Important aspects of battery behavior from this point of view are the rate-capacity effect and charge recovery. Quoting [16]: *The former refers to the fact that a lower discharge rate is more efficient than a higher; more charge can be extracted from the battery before reaching a given cut-off value. The latter refers to the fact that an intermittent discharge is more efficient than a continuous one. Because of these effects, different battery loads that use the same total charge do not result in the same device lifetime.* The most basic of these methods use linear ODEs [9, 10] and gradually build complexity by using PDEs and other means [13, 15, 5]. A further direction is stochastic modeling using Markov chain dynamics [1, 2].

The aim of our work is to investigate to what extent these simplified battery models are able to capture important aspects of battery behavior, and to get new insights

by developing the mathematical models further. Of special interest is the essential response of the battery to deterministic or random on-off discharge patterns typical for batteries in wireless sensor networks, and the ability of a cell to recover charge during operation. Charge recovery is believed to depend on a number of internal mechanisms, such as convection, diffusion, migration, and charge-transfer. In the modeling work we put special emphasis on separating the roles of diffusion, which is the motion of electroactive species in the presence of a concentration gradient, and migration, the motion of charged species in an electric field.

Our starting point is the kinetic battery model of Manwell and McGowen [9, 10], which describes the joint evolution of available charge and bound charge over time. Charge recovery in this framework consists in the continuous transition of bound charge to available charge. As observed in [5] and further investigated in [6], more general spatial versions of these models are related to the diffusion model of Rakhmatov and Vrudhula [13, 15], and leads to a class of second order diffusion equations with Robin type boundary conditions. Quoting [12], the linear dynamics of the kinetic battery model is *useful in getting an intuitive idea of how and why the recovery occurs but it needs a number of additions to be useful for the types of batteries used in mobile computing*. Using experimental data from Ni-MH batteries, [12] proposed a modified, non-linear, factor in the flow charge and discussed related stochastic versions of the model. In an effort to compare more systematically linear and nonlinear dynamics in kinetic and stochastic battery models, we study discrete time Markov chains with nonlinear jump probabilities derived from a simplified charge transport scenario. By a scaling approximation we obtain in the limit a deterministic nonlinear ODE, with explicit solutions which, in principle, can be compared to those of the linear approach. The unifying mathematical aspect in our analysis is the representation of remaining and available capacities as time-autonomous systems.

In Section 2, following preliminaries on capacities, internal charge recovery and discharge profiles, we consider the kinetic battery model and discuss a variation. Then we set up an extended version of the spatial kinetic battery model with a finite number of serial compartments, derive the spatially continuous limiting PDE, and give a probabilistic representation of the solution of the PDE in terms of Brownian motion with drift reflected at the boundaries on both sides of a finite interval. The solution represents the capacity storage of a battery and these tools allow us to study the balance of available and remaining stored capacity. Section 3 studies a nonlinear, stochastic Markov chain model and its deterministic ODE approximation. With proper choice of nonlinear dynamics for charge recovery due to transfer, diffusion and migration effects, we then propose a somewhat wider class of nonlinear ODE of potential use for battery modeling. As a consequence, it is possible to study performance measures such as battery life, delivered capacity and gain, and to compare and optimize the performance of batteries.

2. Linear Battery Models

2.1. Nominal, theoretical and available capacity

We consider a primary (non-rechargeable) battery cell consisting of two electrodes, anode and cathode, linked by an electrolyte. The cell contains a certain amount of chemically reactive material which is converted into electrical energy by an oxidation reaction at the anode. Primary lithium batteries have a lithium anode and may have soluble or solid electrolytes and cathodes. The mass of material involved in the battery reaction yields a higher concentration of electrons at the anode, and hence by Faraday's first law the transfer of a proportional quantity of electrical charge. This determines a terminal voltage between the pair of electrodes. By closing a wired circuit between the terminals a current of electrons will start moving through the wire from anode to cathode where they react with a positively charged reactant, manifesting the ability of the battery to drive electric current. The intensity of the current depends on the total resistance along the wire. Inside the battery the movement of charge-carriers forms a corresponding ionic current, which is controlled by a variety of mechanisms, among them migration of ions, diffusion of reactant species, and charge-transfer reaction. Migration is generated by an electric potential gradient (electric field) and convective diffusion by the concentration gradient. Conductivity arises from the combination of migration and diffusion. Charge-transfer reactions take place when migrating ions are transferred from the electrolyte bulk through the anode surface.

It is sometimes helpful to keep track of proper units. The battery has a given voltage E_0 in volts [V] and a theoretical capacity T in ampere hours [Ah], representing the entire storage of chemically reactive material in the cell. We write N [Ah] for the nominal capacity of a fully loaded cell, where $N \leq T$. This is the amount of electric charge which is delivered if the cell is put under constant, high load and drained until a predefined cut-off voltage is reached. Measuring time t in hours [h] we write $\Lambda(t)$ for the consumed capacity [Ah] and $v(t) = T - \Lambda(t)$ for the remaining capacity [Ah], at time t . Here, $\Lambda = (\Lambda(t))_{t \geq 0}$ is an increasing function, typically continuous with the slope representing intensity of the current. It is also plausible to let the discharge function have jumps to be interpreted as spikes of charge units being released point-wise to the device driven by the battery. As an additional level of generality it is straightforward to consider Λ defined on a probability space and subject to a suitable distributional law of a random process. The instantaneous discharge current [A] at t is the derivative $\Lambda'(t) = \lim_{h \rightarrow 0} h^{-1} \Lambda(t + h)$ and the average discharge current [A] is the quantity $\bar{\Lambda} = \lim_{t \rightarrow \infty} t^{-1} \Lambda(t)$, assuming this limit exists.

We are interested in the behavior of the battery cell when exposed to the accumulated discharge process Λ , in particular regarding

$$\begin{aligned} u(t) &= \text{available capacity [Ah] at time } t, & u(0) &= N \\ \tilde{u}(t) &= u(t)/N = \text{state of charge at time } t, & \tilde{u}(0) &= 1 \\ E(t) &= \text{voltage [V] at time } t, & E(0) &= E_0. \end{aligned}$$

While there is no obvious method of observing state-of-charge empirically, voltage is accessible to measurements at least in principle. To describe typical voltage, we imagine that a fully charged battery at time $t = 0$ is connected to a closed circuit at constant discharge current $\delta = \Lambda'(t)|_{t=0}$ [A]. The result is an instant voltage drop from U_0 to a new level at approximate voltage $U_0 - \delta r$, where r is an internal resistance [ohm] of the cell. As long as charge is consumed, the state-of-charge will then begin to decline over time accompanied by a subsequent change of voltage. If after a period of discharge the current is disconnected and the battery temporarily put to rest, then the voltage increases. First, instantly, by the amount δr and then over the course of the off-period at some rate due to recovery effects inside the cell. The resulting voltage versus time curve extended over a longer time span would typically stay nearly constant or exhibit slow decline over most of the active life of the battery followed by a steeper decent until a cut-off level E_{cut} is reached, beyond which the cell is considered to be non-operational. To relate state of charge and voltage we recall that the actual load a time t is given by $\Lambda'(t)$ and apply the equilibrium Nernst equation, [11] Ch. 1, to obtain

$$E(t) = E_0 - \Lambda'(t)r + K_e \ln(\tilde{u}(t)), \quad K_e = \frac{RT_a}{zF}, \quad (1)$$

where R is the ideal gas constant, T_a is absolute temperature, z is the valency of the battery reactant ($z = 1$ for Lithium), F is Faraday's constant, and dimensions are such that K_e is measured in volts. The internal resistance, however, may have a more complex origin arising from a series of resistances in the electrodes and electrolyte. Electrical circuit models use equivalent electrical circuits to capture such current-voltage characteristics. In this direction, [7] consider a hybrid model of kinetic battery and electrical circuit models to facilitate the derivation of voltage in terms of exponential and polynomial functions of state of charge. Building on this approach, [16] fits empirical battery data in order to evaluate battery models for wireless sensor network applications.

2.2. Internal charge recovery

The general principle for charge recovery is that of balancing the discharge rate by a positive drift of the available capacity due to the release and transport of stored charges. Such effects should exist as long as the theoretical capacity of the cell has not yet been fully consumed, that is $v(t) \geq 0$. The first recovery mechanism to take into account is (solid-state) diffusion of charge carriers caused by the build-up of a concentration gradient in the electrolyte during discharge. The drift of the process is convective flow and a diffusion coefficient controls random variations around the main direction of transport. Diffusion transport of charge carriers might be a slow process which persists even if the load is removed and the battery put to rest, and runs until charge concentrations have reached local equilibrium. Another mechanism for gaining capacity due to recovery is migration of charge-carriers caused by the electric field, as an action of a potential gradient. The strength of this effect should increase with the gap $N - u(t)$ between maximal and actual capacity. It appears reasonable to assume

that the effect of migration is ongoing whether the battery is under load or at rest. The final aspect of recovery we wish to include in the modeling scenario is charge transfer, meaning the transfer of charges from electrolyte through an interface to the terminal electrode. A simplified approach for this effect is that of a friction mechanism, such that a fraction of recovered charges are actually effectuated proportional to the applied load current, either instantaneous current or average current over long time.

2.3. Discharge profiles

The battery models we study are introduced in relation to an arbitrary accumulated discharge function Λ . To engage in a more detailed analysis of battery performance we consider three stylized examples of Λ , which represent typical discharge patterns for the intended usage of the battery.

Constant current. The first such pattern is that of draining the battery at a constant current λ which remains the same over the entire battery life until the cell is emptied. Clearly, $\Lambda(t) = \lambda t$ and $\bar{\lambda} = \lambda$.

Deterministic on-off pattern. The second example is relevant for the case when we know in advance both the amount of work the battery is supposed to power and the scheduled timing of loads. For such cases we consider a deterministic pulse-train which consists of a periodic sequence of cycles of equal length. Each cycle begins with an active on-period during which a pulse of constant load is transmitted, followed by an off-period of rest and no load. Specifically we assume that a current δ [A] is drawn continuously during each on-period of length τ_{on} followed by a dormant off-period of length τ_{off} . Hence the cycle duration is $\tau = \tau_{\text{on}} + \tau_{\text{off}}$ and the dutycycle is given by the fraction $q = \tau_{\text{on}}/\tau$. We introduce

$$J_t = \sum_{j=0}^{\infty} 1_{\{j\tau \leq t < (j+1)\tau\}}, \quad t \geq 0,$$

so that $J_t = 1$ if t belongs to an on-period and $J_t = 0$ for t in an off-period. Then the consumed capacity is

$$\Lambda(t) = \delta \int_0^t J_s ds, \quad t \geq 0,$$

and $(\Lambda(t))$ is a piecewise continuous function with non-decreasing rate $\Lambda(dt) = \delta J_t dt$. The average discharge rate equals $\bar{\lambda} = \delta q$.

Random discharge pattern. Our third stylized example of discharge mechanisms represents the case where no information except average load is available in advance of battery operation. In this situation we consider completely random discharge with the load to be drawn from the battery per time unit scattered independently and uniformly random in the sense of the Poisson process. Here we take $\Lambda(t) = \delta \tau_{\text{on}} N_t^{(1/\tau)}$, where $(N_t^{(\lambda)})_{t \geq 0}$ denotes a standard Poisson process on the half line with constant intensity $\lambda > 0$. This amounts to saying that the battery is drained from energy in small jumps of charge $\delta \tau_{\text{on}}$ which occur interspaced by independent and exponentially distributed waiting times with expected value τ . Again the average discharge current is $\bar{\lambda} = \ell \tau_{\text{on}}/\tau = \delta q$.

2.4. Kinetic battery model

The Kinetic Battery Model, originally introduced for lead acid batteries in [9, 10], takes the view that remaining capacity of the battery is split in two wells, or compartments, one representing available charge and the other bound charge. Discharge is the consumption of available charge and charge recovery is the flow of matter from the bound well to the available one. The available capacity $u(t)$ in this model is precisely the amount of charge in the available well as function of time. Hence we call $y(t) = v(t) - u(t)$, the bound charge and decompose remaining capacity as $v(t) = u(t) + y(t)$, $u(0) = N$, $y(0) = T - N$. With the use of the fraction $c = N/T$, $0 < c < 1$, the two wells are assigned a measure of height given by $u(t)/c$ and $y(t)/(1-c)$. The principle of the kinetic battery model is that bound charge becomes available at a rate which is proportional to the height difference $y(t)/(1-c) - u(t)/c$. Once available, no charges return to the bound state. Thus,

$$\begin{cases} du(t) &= -\Lambda(dt) + k\left(\frac{y(t)}{1-c} - \frac{u(t)}{c}\right) dt, & u(0) = N \\ dy(t) &= -k\left(\frac{y(t)}{1-c} - \frac{u(t)}{c}\right) dt, & y(0) = T - N, \end{cases} \quad (2)$$

where $k > 0$ is a reaction parameter. By assumption, $v(t) = u(t) + y(t) = T - \Lambda(t)$, $t \geq 0$. It is convenient therefore to consider the pair $(v(t), u(t))$. With $k_c = k/c(1-c)$ as an alternative parameter,

$$du(t) = -\Lambda(dt) + k_c(cv(t) - u(t)) dt, \quad u(0) = N. \quad (3)$$

In (3), charge recovery as represented by the factor $cv(t) - u(t) = N - u(t) - c\Lambda(t)$ may be seen as the combination of a migration effect due to the term $N - u(t)$ together with (negative) drift $-c\Lambda(t)$. To clarify these connections, Ref. [6] studied a reweighted version of the model. In this paper we wish to develop these ideas further and hence consider the closely related reweighted model

$$du(t) = -\Lambda(dt) + k_c(cv(t) - u(t) + p(N - u(t))) dt, \quad u(0) = N, \quad (4)$$

where the parameter p controls charge recovery due to migration. The case $p \geq 0$ reflects migration of additional charge from the bound well adding to the internal charge recovery. The case $p \leq 0$ represents loss of recovery due to migration. The linear system (4) is readily solved as

$$u(t) = N - c\Lambda(t) - (1-c) \int_0^t e^{-k_c(1+p)(t-s)} \Lambda(ds). \quad (5)$$

For later reference we note that the relevant version of (2) for this extended case is

$$\begin{cases} du(t) &= -\Lambda(dt) + k_c(cy(t) - (1-c)u(t) + p(N - u(t))) dt, \\ dy(t) &= -k_c(cy(t) - (1-c)u(t) + p(N - u(t))) dt. \end{cases} \quad (6)$$

We emphasize that the discharge profile $\Lambda(t)$ is arbitrary for this version of the kinetic battery model. For example, with the random discharge pattern discussed in section

2.3 the integral in (5) is a stochastic Poisson integral and the corresponding solution is a random process $U(t)$, which may be written

$$U(t) = N - \delta\tau_{\text{on}} \sum_{s_i \leq t} (c + (1 - c)e^{-k_c(1+p)(t-s_i)}),$$

where the sum extends over all jumps s_i in $[0, t]$ of a Poisson process with intensity $1/\tau$.

Of course, the kinetic battery model could only give a crude indication of the processes behind real battery behavior. In contrast, the diffusion battery model of Rakhmatov and Vrudhula introduced in [21] is an approach closer to electrochemical modeling, detailing reaction kinetics and internal transport mechanisms. Both types of models are relevant for engineering battery performance. A significant step towards unifying these approaches is the extension to spatial versions of the kinetic battery model, where charges move inside of a reservoir of bound charge according to the same local dynamics as the simplest case above.

2.5. Spatial kinetic battery model

The diffusion battery model [21, 13], views battery operation as the diffusion of ions between two electrodes separated by an electrolyte consisting of a linear region $[0, \ell]$ of the one-dimensional line. Initially, the electroactive species are uniformly distributed over space. Over time, the concentration $C(t, x)$ of electroactive species at time $t \geq 0$ and distance x from the electrode at $x = 0$ develop following Fick's laws of diffusion with suitable boundary conditions at both electrode endpoints $x = 0$ and $x = \ell$. In [5], comparing kinetic and diffusion battery models, Jongerden and Haverkort introduced the idea of placing a finite number of charge compartments in series along the spatial range and letting charges move between adjacent components according to Eq. (2). Discharge occurs at the anode which is located in one end point of the spatial interval. Starting from a state of fully charged compartments a spatial charge profile develops over time and determines the pace at which the battery is drained. This system is shown to match the diffusion model when the diffusion equations for $C(t, x)$ are discretized over an equally sized partition of $[0, \ell]$. In this sense the diffusion model is a continuous version of the kinetic battery model. In this section we present further developments of this theory, building on previous work in Ref. [6]. Indeed, we analyze the effects of charge recovery in the spatial setting and provide in explicit form the available charge and other performance measures in terms of basic parameters of diffusion and migration.

We begin by considering a battery cell consisting of m adjacent fluid compartments and a function $u(t) = (u_1(t), \dots, u_m(t))$ which gives the charge content in each component over time. Here u_1 is the available charge, u_2 is a bound well charge for u_1 and so on until u_m , which is a bound well charge for u_{m-1} . By letting Eqn. (2) act pairwise

on adjacent compartments, we obtain the coupled system of linear equations

$$\begin{cases} du_1(t) = -\Lambda(dt) + k_c(cu_2(t) - (1-c)u_1(t)) dt \\ du_2(t) = -k_c(cu_2(t) - (1-c)u_1(t)) dt + k_c(cu_3(t) - (1-c)u_2(t)) dt \\ \vdots \\ du_{m-1}(t) = -k_c(cu_{m-1}(t) - (1-c)u_{m-2}(t)) dt \\ \quad + k_c(cu_m(t) - (1-c)u_{m-1}(t)) dt \\ du_m(t) = -k_c(cu_m(t) - (1-c)u_{m-1}(t)) dt. \end{cases}$$

In greater generality, the reweighted version (6) yields

$$\begin{cases} du_1(t) = -\Lambda(dt) + k_c(cu_2(t) - (1-c)u_1(t)) dt + k_cp(N - u_1(t)) dt \\ du_2(t) = -k_c(cu_2(t) - (1-c)u_1(t)) dt + k_c(cu_3(t) - (1-c)u_2(t)) dt \\ \quad - k_cp(u_2(t) - u_1(t)) dt \\ \vdots \\ du_{m-1}(t) = -k_c(cu_{m-1}(t) - (1-c)u_{m-2}(t)) dt \\ \quad + k_c(cu_m(t) - (1-c)u_{m-1}(t)) dt - k_cp(u_{m-1}(t) - u_{m-2}(t)) dt \\ du_m(t) = -k_c(cu_m(t) - (1-c)u_{m-1}(t)) dt - k_cp(N - u_{m-1}(t)) dt. \end{cases}$$

To see more clearly the structure in this system of equations, we introduce the parameter $\mu_c = 2c - 1$ and employ the notations

$$\nabla u_k(t) = u_{k+1}(t) - u_k(t), \quad \Delta u_k(t) = u_{k-1}(t) - 2u_k(t) + u_{k+1}(t).$$

Then

$$\begin{cases} du_1(t) = -\Lambda(dt) + k_c\left(\frac{1}{2}\nabla u_1(t) + \mu_c(u_1(t) + u_2(t))/2 + p(N - u_1(t))\right) dt \\ du_2(t) = k_c\left(\frac{1}{2}\Delta u_2(t) + \mu_c(\nabla u_2(t) + \nabla u_1(t))/2 - p\nabla u_1(t)\right) dt \\ \vdots \\ du_{m-1}(t) = k_c\left(\frac{1}{2}\Delta u_{m-1}(t) + \mu_c(\nabla u_{m-1}(t) + \nabla u_{m-2}(t))/2 - p\nabla u_{m-2}(t)\right) dt \\ du_m(t) = -k_c\left(\frac{1}{2}\nabla u_{m-1}(t) + \mu_c(u_{m-1}(t) + u_m(t))/2 + p(N - u_{m-1}(t))\right) dt. \end{cases}$$

Here, the parameter p controls drift originating from the terms proportional to $N - u(t)$ in (6). In particular, the nominal capacity N remains as a parameter in the boundary equations for u_1 and u_m .

2.6. Limiting PDE, continuous space

Our next goal is to identify a limiting partial differential equation for the charge concentration profile $u(t)$ in the limit $m \rightarrow \infty$ as the size of the charge compartments tends to zero and the number of wells goes to infinity. The case $p = 0$ is studied in Ref. [6] and we will use a similar method for the general setting.

Let $\ell = (T - N)/N$ and consider the strip $0 \leq x \leq \ell$ partitioned in m equal intervals of length $\varepsilon = \ell/m$. For $x = j\varepsilon$, $j = 1, \dots, m$, we define $u_\varepsilon(t, x) = u_j(t)$ and note that

$$\nabla u_\varepsilon(t, x) = u_\varepsilon(t, x + \varepsilon) - u_\varepsilon(t, x)$$

and

$$\Delta u_\varepsilon(t, x) = u_\varepsilon(t, x - \varepsilon) - 2u_\varepsilon(t, x) + u_\varepsilon(t, x + \varepsilon).$$

To match spatial and temporal scaling we introduce the scaled parameters $\kappa = k/m^2$, $\kappa_c = \kappa/c(1 - c)$. The relations derived above for u_j , $2 \leq j \leq m - 2$ imply, for $x \in \{2/m, \dots, (\ell - 1)/m\}$,

$$du_\varepsilon(t, x) = \kappa_c \left(\ell^2 \frac{1}{2} \frac{\Delta u_\varepsilon(t, x)}{\varepsilon^2} + \ell B_\varepsilon u_\varepsilon(t, x) \right) dt$$

where B_ε is the linear drift operator

$$B_\varepsilon u_\varepsilon(t, x) = m\mu_c \frac{\nabla u_\varepsilon(t, x) + \nabla u_\varepsilon(t, x - \varepsilon)}{2\varepsilon} - mp \frac{\nabla u_\varepsilon(t, x - \varepsilon)}{\varepsilon}.$$

The additional relations for u_1 and u_m correspond to boundary equations for u_ε , which attain the form

$$\frac{du_\varepsilon(t, \varepsilon)}{m} = -\frac{\Lambda(dt)}{m} + \frac{\kappa_c}{2} \left\{ \ell \frac{\nabla u_\varepsilon(t, \varepsilon)}{\varepsilon} + m\mu_c(u_\varepsilon(t, \varepsilon) + u_\varepsilon(t, 2\varepsilon)) + 2mp(N - u_\varepsilon(t, \varepsilon)) \right\} dt$$

and

$$\frac{du_\varepsilon(t, \ell)}{m} = -\frac{\kappa_c}{2} \left\{ \ell \frac{\nabla u_\varepsilon(t, \ell - \varepsilon)}{\varepsilon} + m\mu_c(u_\varepsilon(t, \ell - \varepsilon) + u_\varepsilon(t, \ell)) + 2mp(N - u_\varepsilon(t, \ell - \varepsilon)) \right\} dt$$

Based on the above relations for the system of m compartments one can see that in order to balance all terms in the limit $m \rightarrow \infty$, it is natural to introduce two drift parameters μ and ρ , both of arbitrary sign, and replace c by $c_m = (1 + \mu/m)/2$ and p by $p_m = \rho/m$. Then, for large m ,

$$c_m \sim 1/2, \quad \kappa_{c_m} \sim 4\kappa, \quad m\mu_{c_m} \sim \mu, \quad mp_m \sim \rho,$$

where $\kappa > 0$ is a reaction parameter, μ a diffusion parameter and ρ a migration parameter. This gives the approximate system

$$du_\varepsilon(t, x) = -\Lambda(dt)\delta_\varepsilon(dx) + 2\kappa\ell^2 \frac{\Delta u_\varepsilon(t, x)}{\varepsilon^2} dt + 4\kappa\ell(\mu - \rho) \frac{\nabla u_\varepsilon(t, x)}{\varepsilon} dt$$

with Robin type boundary conditions

$$\ell \frac{\nabla u_\varepsilon(t, \varepsilon)}{\varepsilon} + 2\mu u_\varepsilon(t, \varepsilon) + 2\rho(N - u_\varepsilon(t, \varepsilon)) = 0$$

and

$$\ell \frac{\nabla u_\varepsilon(t, \ell - \varepsilon)}{\varepsilon} + 2\mu u_\varepsilon(t, \ell) + 2\rho(N - u_\varepsilon(t, \ell)) = 0.$$

We conclude that the relevant limiting equation in the limit $\varepsilon = 1/m \rightarrow 0$, is defined on $0 \leq x \leq \ell$ by

$$\begin{aligned} du(t, x) &= -\Lambda(dt)\delta_0(dx) + 2\kappa\ell^2 \frac{\partial^2 u}{\partial x^2}(t, x) dt + 4\kappa\ell(\mu - \rho) \frac{\partial u}{\partial x}(t, x) dt, \\ \ell \frac{\partial u}{\partial x}(t, 0+) &= -2\mu u(t, 0) - 2\rho(N - u(t, 0)) \\ \ell \frac{\partial u}{\partial x}(t, \ell-) &= 2\mu u(t, \ell) + 2\rho(N - u(t, \ell)), \quad u(0, x) = u_0(x). \end{aligned} \quad (7)$$

Here, $u(t, 0)_{t \geq 0}$ is the charge density at the boundary of the battery and $\{u(t, x), 0 < x < \ell\}_{t \geq 0}$ is the fluid level of a reservoir of bound charge such that $\int_{(0, \ell)} u(t, x) dx$ is what remains in the reservoir at time t .

2.7. Probabilistic solution

To state a probabilistic representation of the solution to (7), let $(B_t)_{t \geq 0}$ denote Brownian motion with variance parameter $4\kappa\ell^2$ and constant drift $-4\kappa\ell\delta$. The parameter δ in the drift of the Brownian motion corresponds to $\delta = \mu - \rho$ in (7). We assume that (B_t) is confined to the interval $(0, \ell)$ and subject to reflecting boundaries at both end points 0 and ℓ . Let $p_{\ell, \delta}(t, y, x)$ be the transition density of (B_t) so that $P(B_t \in dx | \xi_0 = y) = p_{\ell, \delta}(t, y, x) dx$. We will use a spectral type representation for $p_{\ell, \delta}(t, y, x)$ known to be

$$\begin{aligned} p_{\ell, \delta}(t, y, x) &= \frac{2\delta}{\ell} \frac{e^{-2\delta x/\ell}}{1 - e^{-2\delta}} + \frac{2e^{-\delta(x-y)/\ell}}{\ell} \times \\ &\sum_{n=1}^{\infty} \left(\cos\left(\frac{n\pi x}{\ell}\right) - \frac{\delta}{n\pi} \sin\left(\frac{n\pi x}{\ell}\right) \right) \left(\cos\left(\frac{n\pi y}{\ell}\right) - \frac{\delta}{n\pi} \sin\left(\frac{n\pi y}{\ell}\right) \right) \frac{e^{-2\kappa(\delta^2 + n^2\pi^2)t}}{1 + (\delta/n\pi)^2}. \end{aligned} \quad (8)$$

The above expression is derived in Ref. [18] and discussed and compared with an alternative representations in Ref. [20]. In particular, for the symmetric case, letting $\delta \rightarrow 0$,

$$p_{\ell, 0}(t, y, x) = \frac{1}{\ell} + \frac{2}{\ell} \sum_{n=1}^{\infty} \cos(n\pi x/\ell) \cos(n\pi y/\ell) e^{-2\kappa n^2 \pi^2 t}.$$

Asymptotically, for $0 \leq y \leq \ell$ as t tends to infinity,

$$\lim_{t \rightarrow \infty} p_{\ell, \delta}(t, y, x) = \frac{2\delta}{\ell} \frac{e^{-2\delta x/\ell}}{1 - e^{-2\delta}}, \quad \lim_{t \rightarrow \infty} p_{\ell, 0}(t, y, x) = \frac{1}{\ell}, \quad 0 \leq x \leq \ell. \quad (9)$$

Theorem 1. Suppose that the spatial kinetic battery model with reaction parameter $\kappa > 0$, migration parameter ρ , and diffusion parameter μ is defined on an interval $\ell = (T - N)/N > 0$ where N is the nominal capacity and T the theoretical capacity. Let $\delta = \mu - \rho$. A given nonnegative function $\{u_0(y), 0 \leq y \leq \ell\}$, is the initial charge profile of the battery and $\Lambda(dt)$ is a given discharge pattern. We restrict to the range of parameters where the battery model is physically realized, by assuming that ρ, μ, N, ℓ ,

and u_0 are such that $u_\infty(x) > 0$ for $0 \leq x \leq \ell$, where u_∞ is defined in (13). Then the bound charge profile $\{u(t, x), 0 \leq x \leq \ell, t \geq 0\}$ of the battery, defined as the solution of the PDE (7), is given for the case $\delta \neq 0$ by

$$u(t, x) = \int_0^\ell u_0(y) p_{\ell, \delta}(t, y, x) dy - \int_0^t p_{\ell, \delta}(t-s, 0, x) \Lambda(ds) + \frac{\rho N}{\delta} \int_0^\ell (p_{\ell, \delta}(t, y, x) - \frac{1}{\ell}) dy,$$

and for the case $\delta = 0$ by

$$\begin{aligned} u(t, x) = & \int_0^\ell u_0(y) p_{\ell, 0}(t, y, x) dy - \int_0^t p_{\ell, 0}(t-s, 0, x) \Lambda(ds) \\ & + \rho N \left(1 - \frac{2x}{\ell}\right) + 4\rho \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{\ell}\right) \frac{((-1)^n - 1)}{n^2 \pi^2} e^{-2\kappa(n^2 \pi^2)t} \end{aligned} \quad (10)$$

where $p_{\ell, \delta}(t, y, x)$ is defined in (8).

Proof. The special case of diffusion but no migration, which is the PDE (7) with $\rho = 0$, that is

$$\begin{aligned} du(t, x) = & -\Lambda(dt) \delta_0(dx) + 2\kappa \ell^2 \frac{\partial^2 u}{\partial x^2}(t, x) dt + 4\kappa \ell \mu \frac{\partial u}{\partial x}(t, x) dt, \quad 0 \leq x \leq \ell \\ \ell \frac{\partial u}{\partial x}(t, 0+) = & -2\mu u(t, 0), \quad \ell \frac{\partial u}{\partial x}(t, \ell-) = 2\mu u(t, \ell), \quad u(0, x) = u_0(x), \end{aligned}$$

has been studied in Ref. [6]. The solution is given by

$$u(t, x) = \int_0^\ell u_0(y) p_{\ell, \mu}(t, y, x) dy - \int_0^t p_{\ell, \mu}(t-s, 0, x) \Lambda(ds). \quad (11)$$

To handle the case of a nonzero migration effect, $\rho \neq 0$, in (7) we first observe that the non-homogeneous term in (11) which involves $\Lambda(dt)$ remains the same. Hence it suffices to discuss the solution of (7) for the homogeneous case $\Lambda(dt) \equiv 0$, which represents a battery at rest without discharge current. We claim that for any drift parameters μ and ρ , such that $\delta = \mu - \rho \neq 0$, the solution is given by

$$\begin{aligned} u(t, x) = & \frac{\rho N}{\rho - \mu} + \int_0^\ell \left(u_0(y) - \frac{\rho N}{\rho - \mu}\right) p_{\ell, \mu - \rho}(t, y, x) dy \\ = & \int_0^\ell u_0(y) p_{\ell, \delta}(t, y, x) dy + \frac{\rho N}{\delta} \int_0^\ell (p_{\ell, \delta}(t, y, x) - \frac{1}{\ell}) dy. \end{aligned} \quad (12)$$

Indeed, it is straightforward to verify that for any constant M the function

$$g(t, x) = M + \int_0^\ell (u_0(y) - M) p_{\ell, \delta}(t, y, x) dy$$

satisfies the target equation. Moreover,

$$\begin{aligned} \ell \frac{\partial g}{\partial x}(t, x)|_{x=0} = & 2\delta(M - g(t, 0)) \\ = & -2\mu g(t, 0) - 2\rho((\rho - \mu)M/\rho - g(t, 0)), \end{aligned}$$

which shows that boundary condition at $x = 0$ is satisfied for $M = \rho N / (\rho - \mu)$. Similarly for the boundary condition at $x = \ell$. Finally, to cover the case $\delta = 0$ one shows that

$$\lim_{\delta \rightarrow 0} \frac{\rho N}{\delta} \int_0^\ell (p_{\ell, \delta}(t, y, x) - \frac{1}{\ell}) dy$$

equals the sum of the two last terms in (10). \square

Constant initial charge. Restricting to the special case of constant initial charge $u_0 \equiv N$, the solution for $\delta \neq 0$ is

$$\begin{aligned} u(t, x) = & \left(\frac{\mu N}{\delta} - \frac{1}{\ell} \Lambda(t) \right) \frac{2\delta e^{-2\delta x/\ell}}{1 - e^{-2\delta}} - \frac{\rho N}{\delta} \\ & + 4\mu N e^{-\delta x/\ell} \sum_{n=1}^{\infty} \left(\cos\left(\frac{n\pi x}{\ell}\right) - \frac{\delta}{n\pi} \sin\left(\frac{n\pi x}{\ell}\right) \right) \frac{((-1)^n e^\delta - 1) n^2 \pi^2}{(\delta^2 + n^2 \pi^2)^2} e^{-2\kappa(\delta^2 + n^2 \pi^2)t} \\ & - \frac{2e^{-\delta x/\ell}}{\ell} \sum_{n=1}^{\infty} \left(\cos\left(\frac{n\pi x}{\ell}\right) - \frac{\delta}{n\pi} \sin\left(\frac{n\pi x}{\ell}\right) \right) \frac{n^2 \pi^2}{\delta^2 + n^2 \pi^2} \int_0^t e^{-2\kappa(\delta^2 + n^2 \pi^2)(t-s)} \Lambda(ds) \end{aligned}$$

and for $\delta = 0$,

$$\begin{aligned} u(t, x) = & N \left(1 + \rho - \frac{2\rho x}{\ell} \right) - \frac{1}{\ell} \Lambda(t) + 4\mu N \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{\ell}\right) \frac{((-1)^n - 1)}{n^2 \pi^2} e^{-2\kappa n^2 \pi^2 t} \\ & - \frac{2}{\ell} \sum_{n=1}^{\infty} \cos\left(\frac{n\pi x}{\ell}\right) \int_0^t e^{-2\kappa n^2 \pi^2 (t-s)} \Lambda(ds) \end{aligned}$$

Asymptotic charge profile. For a battery at rest, so that $\Lambda(t) \equiv 0$, we have by (9) and (12) that $u_\infty(x) = \lim_{t \rightarrow \infty} u(t, x)$ is given by

$$u_\infty(x) = \frac{1}{\ell} \int_0^\ell u_0(y) dy \frac{2\delta e^{-2\delta x/\ell}}{1 - e^{-2\delta}} + \frac{\rho N}{\delta} \left(\frac{2\delta e^{-2\delta x/\ell}}{1 - e^{-2\delta}} - 1 \right), \quad 0 \leq x \leq \ell. \quad (13)$$

In particular, for $u_0(y) = N$, $\rho = 0$ yields the truncated exponential function

$$u_\infty(x) = N \frac{2\mu e^{-2\mu x/\ell}}{1 - e^{-2\mu}}, \quad 0 \leq x \leq \ell,$$

and $\mu = 0$ the trivial asymptotic solution $u_\infty(x) = N$, $0 \leq x \leq \ell$.

Non-homogeneous case, migration but no diffusion. The system (7) for the case $\mu = 0$ and arbitrary ρ , where we also restrict to the initial condition $u_0(x) = N$, $0 \leq x \leq \ell$, takes the form

$$\begin{aligned} du(t, x) = & -\Lambda(dt) \delta_0(dx) + 2\kappa \ell^2 \frac{\partial^2 u}{\partial x^2}(t, x) dt - 4\kappa \ell \rho \frac{\partial u}{\partial x}(t, x) dt, \quad 0 \leq x \leq \ell \\ \ell \frac{\partial u}{\partial x}(t, 0+) = & -2\rho(N - u(t, 0)) \\ \ell \frac{\partial u}{\partial x}(t, \ell-) = & 2\rho(N - u(t, \ell)), \quad u(0, x) = N. \end{aligned} \quad (14)$$

The solution is

$$u(t, x) = N - \int_0^t p_{\ell, -\rho}(t - s, 0, x) \Lambda(ds).$$

Varying the discharge profile. Of course, the result in Theorem 1 for the capacity reservoir $u(t, x)$ will be obtained in a more or less explicit form depending on which discharge profile Λ applies. But, in principle, the results of Theorem 1 allow comparison of the capacity dynamics under the discharge patterns discussed in Section 2.3, and others. For example, a family of deterministic on-off patterns with given parameters may be compared to the reference case of constant current discharge. If the discharge pattern is Poisson or otherwise random then the response in capacity and voltage drop will be random as well. The next subsection is concerned with the case of constant discharge.

2.8. Autonomous system

The results in this subsection applies to the case of constant current $\Lambda(t) = \lambda t$. For simplicity we assume constant initial capacity $u_0 = N$. Then the available capacity predicted by the spatial kinetic battery model according to Theorem 2.1 is

$$\begin{aligned} u(t, 0) = & \frac{\mu N}{\delta} \omega_\delta - \frac{\rho N}{\delta} + 4\mu N \sum_{n=1}^{\infty} \frac{((-1)^n e^\delta - 1) n^2 \pi^2}{(\delta^2 + n^2 \pi^2)^2} e^{-2\kappa(\delta^2 + n^2 \pi^2)t} \\ & - \omega_\delta \frac{\lambda t}{\ell} - \frac{\lambda}{\kappa \ell} \sum_{n=1}^{\infty} \frac{n^2 \pi^2}{(\delta^2 + n^2 \pi^2)^2} (1 - e^{-2\kappa(\delta^2 + n^2 \pi^2)t}), \quad \omega_\delta = \frac{2\delta}{1 - e^{-2\delta}}, \end{aligned} \quad (15)$$

and the corresponding state of charge is $\tilde{u}(t, 0) = u(t, 0)/N$. It is illustrative to consider the available capacity as a function of the remaining capacity stored in the battery. This point of view is explicit in the simple kinetic battery model under constant current, namely if we consider $(v(t), u(t))$ with $v(t) = T - \lambda t$ and

$$u(t) = N - c\lambda t - \lambda(1 - c)(1 - e^{-k_c(1+p)t})/k_c, \quad c = N/T,$$

which is the solution of (5) for the case $\Lambda(t) = \lambda t$. Then (v, u) with $u = u(v)$ given by

$$u = cv - \gamma_{c,p}(1 - c)(1 - e^{-(T-v)/\gamma_{c,p}}), \quad \gamma_{c,p} = \frac{\lambda}{k_c(1 + p)},$$

is an autonomous system, and we may express functionals of u , such as voltage $E = E(u)$, in terms of v . In the same spirit we seek to express $u(t, 0)$ for the spatial kinetic battery model as a function of remaining capacity. In our model the relevant remaining capacity function is what is stored in the entire reservoir of size ℓ at time t , namely

$$v(t) = u(t, 0) + \int_0^\ell u(t, x) dx = u(t, 0) + N\ell - \lambda t.$$

By replacing λt in (15) with $u(t, 0) - v(t) + N\ell$,

$$\begin{aligned}
u(t, 0) = & (v(t) - u(t, 0)) \frac{\omega_\delta}{\ell} + \frac{\rho N}{\delta} (\omega_\delta - 1) \\
& + 4\mu N \sum_{n=1}^{\infty} \frac{((-1)^n e^\delta - 1) n^2 \pi^2}{(\delta^2 + n^2 \pi^2)^2} e^{-2\kappa(\delta^2 + n^2 \pi^2)(u(t, 0) - v(t) + N\ell)/\lambda} \\
& - \frac{\lambda}{\kappa \ell} \sum_{n=1}^{\infty} \frac{n^2 \pi^2}{(\delta^2 + n^2 \pi^2)^2} (1 - e^{-2\kappa(\delta^2 + n^2 \pi^2)(u(t, 0) - v(t) + N\ell)/\lambda}), \tag{16}
\end{aligned}$$

which is an autonomous system for the pair $(v, u) = (v(t), u(t, 0))$. Figure 1 indicates the typical shape of solution curves (v, u) for fixed, but arbitrary, parameter values $T = 1000$, $N = 100$, $\ell = (T - N)/N = 9$, $\lambda = 1000$, and $\kappa = 0.5$, and for varying ρ and μ . The diagonal line from $(0, 0)$ to (T, N) in the (v, u) phaseplane represents an idealized situation where all theretical capacity of the battery is consumed at a steady pace. The additional straight line from $(T - N, 0)$ to (T, N) represents a battery which is drained at rate λ without any recovery of bound charge at all.

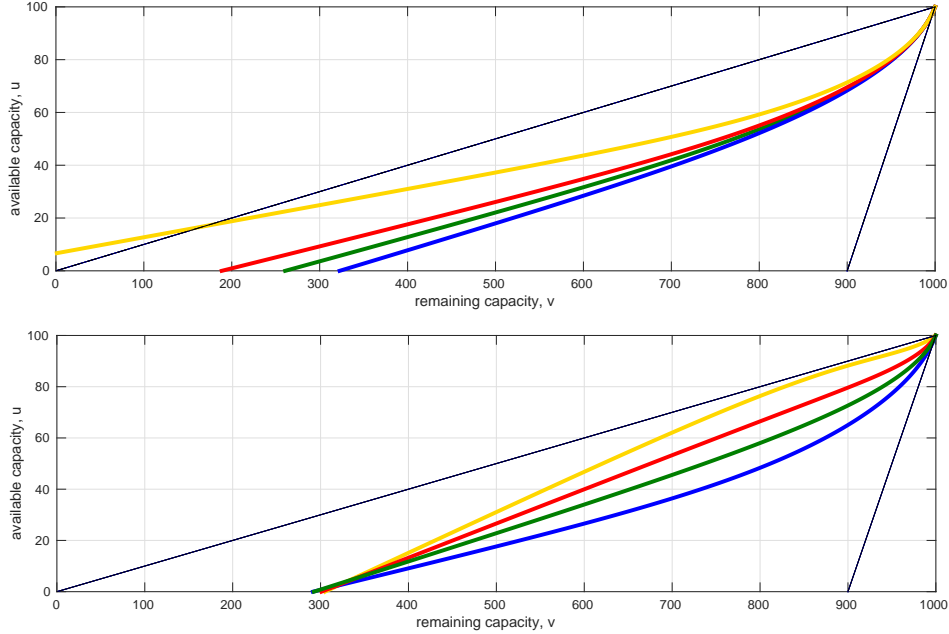


Figure 1: Solution curves of (16) for $T = 1000$, $N = 100$, $\lambda = 1000$, $\kappa = 0.5$. In the upper panel, the diffusion parameter is $\mu = 0$ and the migration parameter varies from $\rho = 0$ (blue curve), $\rho = 0.1$ (green curve), $\rho = 0.2$ (red curve), $\rho = 0.5$ (yellow curve). The lower panel shows four different combinations of μ and ρ which all give approximately the same utilization of the total available battery capacity, namely $\rho = 0.1$, $\mu = -0.1$ (blue curve), $\rho = 0$, $\mu = 0.1$ (green curve), $\rho = -0.1$, $\mu = 0.25$ (red curve), and $\rho = -0.2$, $\mu = 0.4$ (yellow curve).

3. Nonlinear Battery Models

In this section we introduce an approach to nonlinear battery modeling using a discrete time Markov chain on a set of bivariate states representing available and remaining capacities. The chain has nonlinear jump probabilities which we arrive at by analyzing a simplified transport system of charges under diffusion and migration. Then we investigate the scaled capacities as the number of slots per time unit tends to infinity and the discharge process converges to that of constant rate. In the limit we obtain deterministic capacity functions identified as the solution of a nonlinear ordinary differential equation. Informed by these findings we then consider a class of nonlinear ODEs which can be solved explicitly. The solutions arising in this manner potentially reflect the nonlinear dynamics of capacity under discharge of the battery. In addition we indicate two further directions of probabilistic modeling. One is to study the deviation of the Markov chain from its deterministic limit and describe the scaled fluctuations in terms of a diffusion process. Finally we consider the deterministic limit process modified to operate under random discharge, and compare this situation with the previous cases.

3.1. Markov chain model in slotted time

We consider a discrete time Markov chain $(V_n, X_n)_{n \geq 0}$ defined on the state space $E = [0, T] \times [0, N]$, modeling

$$\begin{aligned} V_n &= \text{remaining capacity [Ah] in time slot } n \\ X_n &= \text{available capacity [Ah] in time slot } n. \end{aligned}$$

We assume that N and T are integer multiples of δ and that all jumps are of size δ . All jumps in the first coordinate are downwards. Jumps in the second are allowed to be both up and down as long as $X_n \leq N$. The battery is discharged randomly at constant current δ with probability q per slot. Letting

$$Z_n = \text{number of load units discharged in slot } n, \quad n \geq 1.$$

where $\{Z_i\}$ is a sequence of i.i.d random variables with $P(Z_i = 1) = 1 - P(Z_i = 0) = q$, it follows that $\Lambda_n = \delta \sum_{i=1}^n Z_i$ is the accumulated discharge at slot n and $V_n = T - \Lambda_n$ is the remaining charge in the battery after n slots. The expected discharge rate is $\bar{\lambda} = E(\Lambda_n)/n = \delta q$. Given the sequence $(V_n)_{n \geq 0}$ as input we model $(X_n)_{n \geq 0}$ as a Markov chain modulated by (V_n) . All jumps down of (X_n) are inherited from the discharge profile and follow those of (V_n) . Jumps up will occur according to a Markovian dynamics chosen so as to reflect the recovery properties of the battery. In slot $n + 1$ the transition probabilities depend on the current state X_n and the current discharge information stored in V_n .

Transport system.

In an attempt to model charge recovery the battery cell is thought to consist of a randomly structured, electroactive material which allows transport of charge carrying

species through the electrolyte by liquid or solid state diffusion. Internal charge recovery relies on access to transportation channels of enough connectivity to allow the material to pass from one node to the other. Also, these channels must be “activated” by a sufficient amount of previous discharge events. To try to describe such a system, we introduce

K_n = available concentration of charge in slot n

L_n = number of charge-carrying migration channels in slot n

M_n = number of channels in slot n activated by electrons at the cathode.

Conditional on (V_n, X_n) , the updates K_{n+1} and L_{n+1} are assumed to have Poisson distributions, such that for given nonnegative parameters $\alpha > 0$ and $\beta > 0$

$$K_{n+1} \in \text{Po}(V_n, \beta), \quad L_{n+1} \in \text{Po}(\alpha(N - X_n)),$$

and M_{n+1} is binomially sampled from L_{n+1} , so that

$$M_{n+1} \in \text{Bin}(L_{n+1}, q) \stackrel{d}{=} \text{Bin}(N - X_n, q\alpha) \stackrel{d}{\sim} \text{Po}(q\alpha(N - X_n)).$$

In case there is no discharge in slot n , that is $Z_n = 0$, then the battery cell is able to recover one unit of charge if both $K_n \geq 1$ and $M_n \geq 1$. Hence

$$\begin{aligned} V_{n+1} &= V_n - \delta Z_{n+1} \\ X_{n+1} &= X_n - \delta Z_{n+1} + \delta(1 - Z_{n+1})\mathbf{1}_{\{K_{n+1} \geq 1, M_{n+1} \geq 1\}} \end{aligned}$$

The dynamics specified by this recursive relation is that, given $(V_n, X_n) = (v, x)$, if $Z_{n+1} = 1$ then the transition in slot $n + 1$ is $(v, x) \rightarrow (v - \delta, x - \delta)$ and if $Z_{n+1} = 0$ then

$$(v, x) \rightarrow \begin{cases} (v, x + \delta) & \text{with probability } (1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)}) \\ (v, x) & \text{---} \quad 1 - (1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)}). \end{cases}$$

Together these relations define a bivariate Markov chain model $(V_n, X_n)_{n \geq 0}$ with dynamics specified by

$$(v, x) \rightarrow \begin{cases} (v - \delta, x - \delta) & \text{with prob. } q \\ (v, x + \delta) & \text{---} \quad (1 - q)(1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)}) \\ (v, x) & \text{---} \quad (1 - q)(1 - (1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)})) \end{cases}$$

and, typically, initial condition $(V_0, X_0) = (T, N)$. We obtain a drift function and a variance function for the Markov chain from

$$E(X_{n+1} - X_n | (V_n, X_n)) = -q\delta + (1 - q)\delta(1 - e^{-\beta V_n})(1 - e^{-\alpha q(N - X_n)})$$

and

$$E((X_{n+1} - X_n)^2 | (V_n, X_n)) = q\delta^2 + (1 - q)\delta^2(1 - e^{-\beta V_n})(1 - e^{-\alpha q(N - X_n)})$$

3.2. Continuous time approximation

The drift function $m(v, x) = E(X_{n+1} - X_n | V_n = v, X_n = x)$ suggests a relevant, approximating ODE for the Markov chain. To formalize this limit procedure it is convenient to introduce a scaling parameter $m \geq 1$. At scaling level m the number of slots per unit time is m and the discharge current jump size is δ/m rather than δ . Consider

$$X_n^m = \text{nominal capacity in slot } n \text{ at scaling level } m$$

and define for continuous time $t \geq 0$,

$$X^{(m)}(t) = X_{[mt]}^m.$$

Similarly, let Λ_n^m be the scaled discharge process with δ replaced by δ/m and put

$$\Lambda^{(m)}(t) = \Lambda_{[mt]}^m, \quad V^{(m)}(t) = T - \Lambda^{(m)}(t).$$

Then

$$\Lambda^{(m)}(t) = \frac{\delta}{m} \sum_{k=1}^{[mt]} Z_i = \frac{q\delta[mt]}{m} + \sqrt{\frac{q(1-q)\delta^2}{m}} \frac{1}{\sqrt{m}} \sum_{k=1}^{[mt]} \frac{Z_i - q}{\sqrt{q(1-q)}}.$$

By the functional central limit theorem we may introduce a Wiener process $W_1(t)$ and for large m view $V^{(m)}(t)$ as an approximation of the continuous time remaining capacity function $V_t = T - \lambda t$, in the sense

$$dV^{(m)}(t) = -\lambda dt + \frac{\sigma}{\sqrt{m}} dW_1(t), \quad V^{(m)}(0) = T,$$

where $\sigma^2 = q(1-q)\delta^2$ and the approximation error is of the order $1/\sqrt{m}$. Moreover, by considering the differential change of $X^{(m)}(t)$ over a time interval $(t, t+h)$ where $h = 1/m$,

$$\begin{aligned} E(X^{(m)}(t+h) - X^{(m)}(t) | (V^{(m)}(t), X^{(m)}(t)) = (v, x)) \\ = h(-\lambda + (1-q)\delta(1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)})) \end{aligned}$$

and

$$\begin{aligned} E((X^{(m)}(t+h) - X^{(m)}(t))^2 | (V^{(m)}(t), X^{(m)}(t)) = (v, x)) \\ = h \frac{1}{m} (\lambda\delta + (1-q)\delta^2(1 - e^{-\beta v})(1 - e^{-\alpha q(N-x)})). \end{aligned}$$

As above we obtain a deterministic limit equation for large m by applying a diffusion approximation with the diffusion term of magnitude $1/\sqrt{m}$. To simplify notation we put

$$f(v, x) = \delta(1-q)(1 - e^{-\beta v})(1 - e^{-\alpha q(1-x)}).$$

Then

$$dX^{(m)}(t) = -\lambda dt + f(V^{(m)}(t), X^{(m)}(t)) dt + \sqrt{\frac{\lambda\delta}{m} + \frac{\delta}{m} f(V^{(m)}(t), X^{(m)}(t))} dW_2(t),$$

where W_2 is another Wiener process. Since $V^{(m)}$ and $X^{(m)}$ have simultaneous jumps, W_1 and W_2 are dependent with a non-zero covariance.

3.3. Deterministic approximation of the Markov chain model

As $m \rightarrow \infty$, the stochastic differential equations for $V^{(m)}$ and $X^{(m)}$ simplify and become the ordinary differential equation

$$\begin{aligned} x'_t &= -\delta q + (1-q)\delta(1 - e^{-\beta v_t})(1 - e^{-\alpha q(N-x_t)}), & x_0 &= N, \\ v'_t &= -\delta q, & v_0 &= T. \end{aligned} \quad (17)$$

Recalling $\lambda = \delta q$, the solution is $v_t = T - \lambda t$ and

$$x_t = N - \frac{1}{\alpha q} \ln \left(1 - \alpha q \int_0^t \frac{h(s)}{h(t)} \lambda ds \right),$$

where

$$h(t)/h(0) = \exp \left\{ \lambda \alpha t - (1-q)\alpha e^{-\beta T} (e^{\lambda \beta t} - 1)/\beta \right\}.$$

Hence

$$\alpha q \int_0^t \frac{h(s)}{h(t)} \lambda ds = \alpha q \int_0^{\lambda t} \exp \left\{ -\alpha s + (1-q)\alpha e^{\lambda \beta t - \beta T} (1 - e^{-\beta s})/\beta \right\} ds$$

and so

$$x_t = N - \frac{1}{\alpha q} \ln \left(1 - \alpha q \int_0^{T-v_t} \exp \left\{ -\alpha s + (1-q)\alpha e^{-\beta v_t} (1 - e^{-\beta s})/\beta \right\} ds \right). \quad (18)$$

Thus, in analogy with the results obtained for the kinetic battery models in the previous section, it follows that $(v, x) = (v(t), x(t))$ is an autonomous system from which we can read off the available capacity as a function of remaining capacity.

On-off discharge pattern

In the Markov chain model of section 3.1, we considered random discharge at current δ with probability q per slot, which converged by the law of large numbers to a constant discharge pattern $\Lambda(t) = \lambda t$, $\lambda = \delta q$, under the approximation scheme of section 3.3. An alternative would be to run the Markov chain (V_n, X_n) relative to a given discharge sequence (Z_n) , such that in the scaling limit emerges an on-off discharge pattern as discussed in section 2.3. We recall that (J_t) is the piecewise constant indicator function which is one during periods when the battery is under load and zero otherwise and that $V_t = T - \delta \int_0^t J_u du$ is the remaining capacity at time t . As the degree of resolution increases by taking $m \rightarrow \infty$ we then expect the process of nominal capacity, $(X^{(m)})_{t \geq 0}$, to converge to a deterministic limiting function $(X_t)_{t \geq 0}$, which solves the ordinary differential equation

$$dX_t = -\delta J_t dt + \delta(1 - J_t)(1 - e^{\alpha q(N-X_t)})(1 - e^{-\beta V_t}) dt.$$

Then

$$e^{\alpha q(N-X_t)} dX_t = \delta(e^{\alpha q(N-X_t)} - 1)\{-J_t + (1 - J_t)(1 - e^{-\beta V_t})\} dt - \delta J_t dt$$

and so, by introducing a generating factor H_t defined by

$$\frac{d}{dt} \ln H_t = \alpha q \delta (-J_t + (1 - J_t)(1 - e^{-\beta V_t})),$$

hence

$$H_t = H_0 \exp \left\{ \alpha q \delta \int_0^t (-J_u + (1 - J_u)(1 - e^{-\beta V_u})) du \right\},$$

we can solve for X_t and obtain

$$X_t = N - \frac{1}{\alpha q} \ln \left(1 + \frac{\alpha q \delta}{H_t} \int_0^t J_s H_s ds \right)$$

With $\lambda = q\delta$ this may be written

$$X_t = N - \frac{1}{\alpha q} \ln \left(1 + \lambda \alpha \int_0^t J_s e^{\lambda \alpha \int_s^t (J_u - (1 - J_u)(1 - e^{-\beta V_u})) du} ds \right),$$

which is a closed form solution for capacity in terms of the given discharge profile, coded by (J_t) and (V_t) with parameters δ and q , and the additional battery parameters α and β .

3.4. Deviation from deterministic behavior

We have found a deterministic function (v_t, x_t) which satisfies the ordinary differential equation (17), in the limit $m \rightarrow \infty$ of the scaled Markov chain $(V^{(m)}(t), X^{(m)}(t))_{t \geq 0}$ with constant discharge rate λ . Now we introduce the random quantities

$$\mathcal{V}_m(t) = \sqrt{m}(V^{(m)}(t) - v_t), \quad \mathcal{X}_m(t) = \sqrt{m}(X^{(m)}(t) - x_t)$$

in order to study the fluctuations of the scaled Markov chain around its deterministic limit (v_t, x_t) . With W_1 and W_2 as in section 3.2 we obtain for large m ,

$$\begin{aligned} d\mathcal{V}_m(t) &= \sigma dW_1(t) \\ d\mathcal{X}_m(t) &= \sqrt{m}(f(V^{(m)}(t), X^{(m)}(t)) - f(v_t, x_t)) dt \\ &\quad + \sqrt{\lambda \delta + \delta f(V^{(m)}(t), X^{(m)}(t))} dW_2(t), \end{aligned}$$

where $\mathcal{V}_m(0) = \mathcal{X}_m(0) = 0$. It follows by a Taylor expansion of $f(v, x)$ that

$$\sqrt{m}(f(V^{(m)}(t), X^{(m)}(t)) - f(v_t, x_t)) \approx f'_v(v_t, x_t) \mathcal{V}_m(t) dt + f'_x(v_t, x_t) \mathcal{X}_m(t)$$

In the scaling limit $m \rightarrow \infty$ we therefore expect that the fluctuation process $\mathcal{X}_m(t)$ converges to a diffusion process $\mathcal{X}(t)$, such that

$$d\mathcal{X}(t) = f'_v(v_t, x_t) \sigma W_1(t) dt + f'_x(v_t, x_t) \mathcal{X}(t) dt + \sqrt{\lambda \delta + \delta f(v_t, x_t)} dW_2(t).$$

This stochastic differential equation for $\mathcal{X}(t)$ can be seen as a generalized Ornstein Uhlenbeck process

$$d\mathcal{X}(t) = a_t W_1(t) dt + b_t \mathcal{X}(t) dt + c_t dW_2(t),$$

with time-inhomogeneous drift and variance coefficients b_t and c_t , which is also modulated by an additional, random, drift $a_t W_1(t)$.

3.5. Other versions of nonlinear ODE battery capacity models

To derive the capacity dynamics in (18) we were guided by a Markov chain argument based on a simplified view of charge transport inside the battery cell. In this final section we mention a more general class of deterministic non-linear recovery models for the dynamics of nominal capacity and state of charge. Again we write x_t for nominal capacity and v_t for the remaining capacity in the cell as functions of time $t \geq 0$. Here $v_t = T - \Lambda(t)$ and $\Lambda(t)$ is the discharge process with average discharge current $\bar{\lambda} = \lambda$.

The general principle for charge recovery is that of balancing the discharge rate in x_t by a positive drift of the nominal capacity due to the release and transport of stored charges. It is reasonable that such effects are proportional to the applied average load $\bar{\lambda}$ and exist as long as the theoretical capacity of the cell has not yet been fully consumed, that is $v_t \geq 0$. Furthermore, the gain in capacity due to recovery depends on the migration of charge-carriers, and the strength of this effect should increase with the gap $N - x_t$ between maximal and actual capacity. Hence, to capture charge recovery in the framework of one-dimensional differential equations, we may let $F : [0, \infty) \rightarrow [0, 1]$ and $G : [0, \infty) \rightarrow [0, 1]$ be non-decreasing functions with $F(0) = 0$, $G(0) = 0$, and consider equations of the generic shape

$$dx_t = -\Lambda(dt) + \lambda F(N - x_t)G(v_t) dt, \quad t \leq t_0, \quad x_0 = N, \quad (19)$$

where t_0 is battery life defined as the maximal time t for which $x_t \geq 0$.

The special case of (19) where $F(u) = 1 - e^{-au}$ and a is a positive constant which measures the strength of migration of charges due to the existing electric field in the battery, is given by

$$dx_t = -\Lambda(dt) + \lambda(1 - e^{-a(N-x_t)})G(v_t) dt, \quad X_0 = N. \quad (20)$$

Because of the separation of variables we may write

$$dh_t(e^{a(N-x_t)} - 1) = a \int_0^t h_s \Lambda(ds), \quad \ln(h_t/h_0) = -a\Lambda(t) + \lambda a \int_0^t G(v_s) ds.$$

For example, taking the simplest case $\Lambda(t) = \lambda t$,

$$x_t = N - \frac{1}{a} \ln \left(1 + \lambda a \int_0^t e^{\lambda a \int_s^t (1-G(v_u)) du} ds \right).$$

Equivalently,

$$x_t = N - \frac{1}{a} \ln \left(1 + a \int_0^{T-v_t} \exp \left\{ a \int_{v_t}^{v_t+s} (1-G(u)) du \right\} ds \right).$$

It is immediate in this model that the pair (v_t, x_t) is autonomous so that available capacity $x = x(v)$ can be viewed as a function of remaining capacity only. Moreover, the capacity dynamics is load-invariant in the sense that the curve $(v, x(v))$ does not depend on λ . In other words, batteries drained using different choices of λ will exhibit different battery life, longer the smaller intensity of the current, but the used capacity $T - v$ at end of life will be the same in each case.

Performance measures

In the framework of the nonlinear ODE approach we have obtained, just as for the linear models studied previously, a phase plane relation $(v, x) = (v_t, x_t)$ for the capacity dynamics. Via state-of-charge $\tilde{x} = x/N$ we may proceed as before to modeling the corresponding voltage. Without going into details this will give us some capacity threshold x_0 below which the battery is no more functioning. Then the unused capacity that remains in the battery at the end of its life time is the unique solution v_0 of $x(v) = x_0$. Thus, the delivered capacity is $D = T - v_0$ and the gained capacity is $G = D - N$. Our model allows for some qualitative conclusions about these quantities as well as numerical studies of special cases. Various discharge processes Λ can be compared against experimental data and relevant parameters estimated. To give an indication of this type of work, Figure 2 shows the result of repeated independent simulations based on (20) with $G(v) = 1 - e^{-\beta v}$ and Λ a random Poisson discharge process as described in Section 2.3. The parameters used for these particular simulations are chosen arbitrarily such that the output appears to mimic that of a real battery. The upper panel shows the phase plane traces of the resulting solutions (v, x) . The lower panel shows the corresponding random paths of the state-of-charge \tilde{x}_t as function of time. Also in the lower panel we have superimposed (solid red curve) the state-of-charge for the case of constant discharge with the same average load, now given by the explicit solution of equation (20) with $\Lambda(t) = \lambda t$.

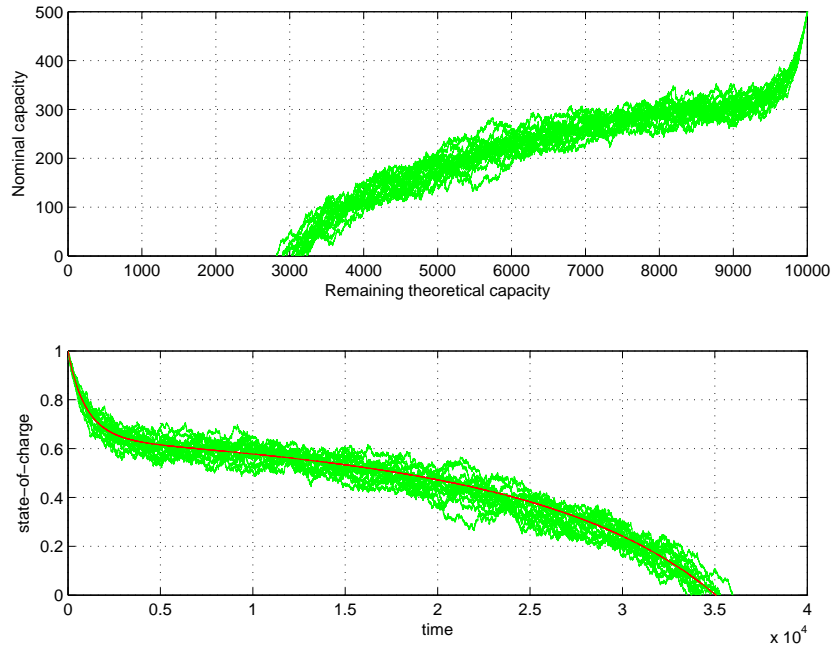


Figure 2: Upper panel: Phase plane solutions (v, x) of (20) with G exponential and Λ simulated Poisson processes. Lower panel: Corresponding simulated paths of state-of-charge \tilde{x}_t as functions of time. The superimposed smooth curve is the deterministic solution for constant discharge of the same average rate.

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