MODELING VOLTAGE IN BATTERY CELLS UNDER DISCHARGE

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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 a 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 probabilistic representation of the solution in terms of Brownian motion with drift reflected at the boundaries on both sides of a finite interval. Moving on to nonlinear battery models we consider a discrete time Markov chain with states representing nominal and remaining capacities of the battery. A nonlinear ODE appears in a natural scaling limit, which leads to a wider 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.

1. INTRODUCTION

The subject of this work is mathematical modeling of state-of-charge and voltage level 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 capacity 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 intensity loads and short dutycycles. There are no known methods or techniques providing a "battery-charge indicator" for such systems. A possible approach is progress on the battery life prediction problem. In this direction, our paper intends to cover some of the required modeling groundwork.

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.

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Two recent survey and review works[8, 12] represent the state-of-art of modeling based on the fundamental principles of electrochemistry, and emphasise 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.*[12], 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.*[5], 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. [[15, 3]].

Battery modeling based on a somewhat different mathematical approach in comparison to chemical engineering modeling have appeared in communication engineering for computer science applications, see e.g. Jongerden and Haverkort[6]. 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. 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 [[14]]: *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[11, 13, 6]. Battery models have seen very little exposure in traditional journals and publications typical for applied mathematics; one of a few recent exceptions is [[4]].

Our conceptual approach in this work will be that of communications engineering in the sense that we rely on the notion that a lithium coin cell is a generic device subject to some fundamental principles. Without ignoring or overly simplifying the complex mechanisms of modern batteries our main interest is to capture the essential response of the battery to discharge. Hence we use only a few parameters and basic battery data rather than detailed reaction coefficients and material characteristics valid for a specific type of battery cell chemistry.

Two important aspects of battery behavior that must be covered by the dynamics of a mathematical model are internal resistance and the ability of a cell to recover charge during operation. As for internal resistances along the interior circuit of a battery under load, the basic approach is that of constant voltage drop according to Ohm's law and more general versions often refer to an equivalent circuits approach. Charge recovery, believed to depend on a number of internal mechanisms of which convection, migration, diffusion and charge-transfer are discussed in some detail below, is the main theme of this article.

The mathematical approach of the paper has its roots in linear dynamics starting from the so called kinetic battery model[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 [[6]] and further investigated in [[7]], more general spatial versions of these models are related to a class of second order diffusion equations with Robin type boundary conditions introduced in [[11, 13]].

In Section 2, following preliminaries on capacities, recovery mechanisms and discharge profiles, we introduce the basic 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 again allow us to study the balance of nominal and remaining stored capacity. Section 3 is devoted to the prospects of using alternative nonlinear models for similar purposes as the linear models in Section 2. We begin with a discrete time Markov chain 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. Indeed, with proper choice of nonlinear dynamics for charge recovery due to transfer, diffusion and migration effects, we 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 capacity.** We consider a 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 transfered 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 it holds no more energy. 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 pointwise to the device driven by the battery. As an additional level of generality it is straigtforward 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 $\Lambda'(t) = \lim_{h \to} h^{-1}\Lambda(t + h)$ and the average discharge current [A] is the quantity $\bar{\lambda} = \lim_{t \to \infty} t^{-1}\Lambda(t)$, 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

$$u(t) = \text{nominal capacity [Ah] at time } t, \quad u(0) = N$$

$$\widetilde{u}(t) = u(t)/N = \text{state of charge at time } t, \quad \widetilde{u}(0) = 1$$

$$E(t) = \text{voltage [V] at time } t, \quad E(0) = E_0.$$

While there is no obvious method of observing state-of-charge empirically, voltage is accesible 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 nominal capacity and voltage we recall that the actual load a time t is given by $\Lambda'(t)$ and apply what is known as the equilibrium Nernst equation, to obtain

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

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, for example leading to a charge and voltage relation of the form

$$E(t) = E_0 + K_e \ln(\widetilde{u}(t)) - \Lambda'(t)\Big(r_1(1 - \widetilde{u}(t)) + \frac{r}{1 - c_1(1 - \widetilde{u}(t))}\Big), \quad 0 \le c_1 < 1.$$

2.2. **Recovery mechanisms.** 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. Such effects should exist as long as the theoretical capacity of the cell has not yet been fully consumed, that is as long as $v(t) \ge 0$. 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 $\tau = \tau_{\mathrm{on}} + \tau_{\mathrm{off}}$ and the dutycycle is given by the fraction $q = \tau_{\mathrm{on}}/\tau$. We introduce

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

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 $\Lambda(t) = \delta\tau_{\mathrm{on}} N_t^{(1/\tau)}$, 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 $\delta\tau_{\mathrm{on}}$ which occur interspaced by independent and exponentially distributed waiting times with expected value τ. Again the average discharge current is $\bar{\lambda} = \ell\tau_{\mathrm{on}}/\tau = \delta q$.

2.4. **Kinetic battery model.** The Kinetic Battery Model, originally introduced for lead acid batteries by Manwell and McGowan[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 charges. Discharge is the consumption of available charge and charge recovery is the flow of matter from the bound well to the available one. The nominal 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,

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

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,

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

A drawback of the dynamics given in (3) appears to be that no matter what the intensity is of the discharge current, the strength of recovery is the same. On the contrary, the charge transfer mechanism mentioned above suggests that actual recovery depends on processes at the electrolyte-electrode interface which would naturally be controlled by the load current. As a simple means of incorporating charge transfer in the kinetic battery model we hence propose replacing k by $\bar\lambda k$ in Eq. (3). In Section 3.5 below we will discuss a related notion of load-invariance. Briefly, load-invariance means that the relation between voltage and consumed capacity is the same regardless of the discharge current, which then only controls the speed at which the battery is emptied.

Since $cv(t) - u(t) = N - u(t) - c\Lambda(t)$, charge recovery could be viewed as a migration effect due to the term $N - u(t)$ together with (negative) drift. To clarify these connections Ref. [[7]] 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

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

where $p + q = 1$ and the parameter $p \geq 0$ controls additional charge recovery due to migration. The linear system (4) is readily solved as

(5) $$u(t) = N - cq\Lambda(t) - (1 - cq) \int_0^t e^{-k_c(t-s)} \, \Lambda(ds).$$

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

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

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 solution of (5) is a stochastic Poisson integral, which may be written

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

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. As far as we know on the other hand, electrochemical modeling detailing reaction kinetics and internal transport mechanisms would rarely focus on topics relevant for engineering battery performance. A significant step towards bridging such gaps 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.** Vrudhula and Rakhmatov[19, 11], introduced the idea of placing a finite number of charge compartments in series along a 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. In Ref. [[11]] the authors consider furthermore a scaling argument for the asymptotic limit of many small compartments, and derive a diffusion equation satisfied by the limiting charge concentration profile. In this section we present further developments of this theory, building on previous work in Ref. [[7]]. Indeed, we analyze the effects of charge recovery in the spatial setting and provide in explicit form the nominal 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 $u(t) = (u_1(t), \ldots, u_m(t))$ 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

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

In greater generality, (6) yield

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

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

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

Then

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

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 $m \to \infty$ 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. [[7]] and we will use a similar method for the general setting.

Let $\ell = (T - N)/N$ and consider the strip $0 \le x \le \ell$ partitioned in m equal intervals of length $\varepsilon = \ell/m$. For $x = j\varepsilon$, $j = 1, \ldots, m$, 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 $x \in \{2/m, \ldots, (\ell-1)/m\}$,

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

where B_ε is the linear drift operator

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

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

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

and

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

Based on the above relations for the system of m compartments one can see that in order to balance all terms in the limit $m \to \infty$, it is natural to introduce two drift parameters μ and $\rho \geq 0$ and replace c by $c_m = (1 + \mu/m)/2$ and p by $p_m = \rho/m$. Then, for large m,

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

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

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

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 $\varepsilon = 1/m \to 0$, is defined on $0 \le x \le \ell$ by

$$du(t,x) = -\Lambda(dt)\delta_0(dx) + 2\kappa\ell^2\frac{\partial^2 u}{\partial x^2}(t,x)\,dt + 4\kappa\ell(\mu - \rho)\frac{\partial u}{\partial x}(t,x)\,dt,$$

$$\ell\frac{\partial u}{\partial x}(t,0+) = -2\mu u(t,0) - 2\rho(N - u(t,0))$$

(7)
$$\ell\frac{\partial u}{\partial x}(t,\ell-) = 2\mu u(t,\ell) + 2\rho(N - u(t,\ell)), \qquad u(0,x) = u_0(x).$$

Here, $u(t,0)_{t\ge0}$ is the available charge of the battery and $\{u(t,x), 0 < x < \ell\}_{t\ge0}$ 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 $(\xi_t)_{t\ge0}$ denote Brownian motion with variance parameter $4\kappa\ell^2$ and constant drift $-4\kappa\ell\delta$. Here, the parameter δ in the drift of the Brownian motion corresponds to $\delta = \mu - \rho$ in (7). It turns out that we may relax the assumption that ρ is nonnegative and from now on consider ρ and μ real parameters. Another restriction will be stated below. We assume that (ξ_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 (ξ_t) so that $P(\xi_t \in dx|\xi_0 = y) = p_\ell(t,y,x)\,dx$. We will use a spectral type representation for $p_{\ell,\delta}(t,y,x)$ known to be

(8)
$$p_{\ell,\delta}(t,y,x) = \frac{2\delta}{\ell}\frac{e^{-2\delta x/\ell}}{1 - e^{-2\delta}} + \frac{2e^{-\delta(x-y)/\ell}}{\ell} \times$$

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

The above expression is derived in Ref. [[16]] and discussed and compared with an alternative representations in Ref. [[18]]. In particular, for the symmetric case, letting $\delta \to 0$,

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

Asymptotically, as t tends to infinity,

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

for any y, $0 \le y \le \ell$.

Theorem 1. *Suppose that the spatial kinetic battery model with reaction parameter $\kappa > 0$, migration parameter ρ, and diffusion parameter $\mu \ne \rho$, is defined on an interval $\ell = (T - N)/N > 0$ where N is the nominal capacity and T the theoretical*

capacity. A given nonnegative function $(u_0(y))$, $0 \le y \le \ell$, 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 $0 \le x \le \ell$, where u_∞ is defined in (12). Then the bound charge profile $\{u(t,x), 0 \le x \le \ell, t \ge 0\}$ of the battery, defined as the solution of the PDE (7), is given by

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

where $M = \rho N/(\rho - \mu)$, $\delta = \mu - \rho \ne 0$, and $p_{\ell,\delta}(t,y,x)$ is defined in (8). Restricting to the special case of constant initial charge $u_0 \equiv N$, the solution is

$$u(t,x) = M + (N\mu/\delta - \Lambda(t)/\ell)\frac{2\delta\,e^{-2\delta x/\ell}}{1 - e^{-2\delta}}$$

$$+ 4\mu N e^{-\delta x/\ell} \sum_{n=1}^\infty (\cos(\frac{n\pi x}{\ell}) - \frac{\delta}{n\pi}\sin(\frac{n\pi x}{\ell}))\frac{((-1)^n e^\delta - 1)n^2\pi^2}{(\delta^2 + n^2\pi^2)^2}e^{-2\kappa(\delta^2+n^2\pi^2)t}$$

$$- \frac{2e^{-\delta x/\ell}}{\ell}\sum_{n=1}^\infty(\cos(\frac{n\pi x}{\ell}) - \frac{\delta}{n\pi}\sin(\frac{n\pi x}{\ell}))\frac{n^2\pi^2}{\delta^2+n^2\pi^2}\int_0^t e^{-2\kappa(\delta^2+n^2\pi^2)(t-s)}\,\Lambda(ds).$$

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

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

$$\ell\frac{\partial u}{\partial x}(t,0+) = -2\mu u(t,0), \quad \ell\frac{\partial u}{\partial x}(t,\ell-) = 2\mu u(t,\ell), \quad u(0,x) = u_0(x),$$

has been studied in Ref. [[7]]. The solution is given by

$$(10) \qquad u(t,x) = \int_0^\ell u_0(y)p_{\ell,\mu}(t,y,x)\,dy - \int_0^t p_{\ell,\mu}(t-s,0,x)\,\Lambda(ds).$$

To handle the case of a nonzero migration effect, $\rho > 0$, in (7) we first observe that the non-homogenous term in (10) which involves $\Lambda(dt)$ will remain the same. Hence it suffices to discuss the solution of 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 $\rho \ge 0$, such that $\delta = \mu - \rho \ne 0$, the solution is given by

$$(11) \qquad u(t,x) = \frac{\rho N}{\rho - \mu} + \int_0^\ell \left(u_0(y) - \frac{\rho N}{\rho - \mu}\right)p_{\ell,\mu-\rho}(t,y,x)\,dy.$$

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 (11). Moreover,

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

which shows that boundary condition at $x = 0$ is satisfied for $M = \rho N/(\rho - \mu)$. Similarly for the boundary condition at $x = \ell$. $\qquad\square$

Asymptotic charge profile. For a battery at rest, so that $\Lambda(t) \equiv 0$, we have by (9) and (11) that $u_\infty(x) = \lim_{t\to\infty} u(t,x)$ is given by

$$(12) \qquad u_\infty(x) = \frac{\rho N}{\rho - \mu} + \frac{2(\mu - \rho)}{\ell}\frac{e^{-2(\mu-\rho)x/\ell}}{1 - e^{-2(\mu-\rho)}}\left(\int_0^\ell u_0(y)\,dy - \frac{\rho N\ell}{\rho - \mu}\right).$$

In particular, for $u_0(y) = N$,

$$u_\infty(x) = N\left(\frac{\rho}{\rho - \mu} + \frac{2\mu e^{-2(\mu-\rho)x/\ell}}{1 - e^{-2(\mu-\rho)}}\right), \quad 0 \le x \le \ell.$$

Of course, $\rho = 0$ yields the truncated exponential function

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

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

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

$$du(t,x) = -\Lambda(dt)\delta_0(dx) + 2\kappa\ell^2\frac{\partial^2 u}{\partial x^2}(t,x)\,dt - 4\kappa\ell\rho\frac{\partial u}{\partial x}(t,x)\,dt, \quad 0 \le x \le \ell$$

$$\ell\frac{\partial u}{\partial x}(t,0+) = -2\rho(N - u(t,0))$$

$$(13) \qquad \ell\frac{\partial u}{\partial x}(t,\ell-) = 2\rho(N - u(t,\ell)), \qquad u(0,x) = N.$$

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. **Modeling voltage.** Based on the results obtained so far we are now in position
to study the change of voltage as function of time. The results in this subsection
applies to the case of constant current $\Lambda(t) = \lambda t$. For simplicity we also assume
constant initial capacity $u_0 = N$. Then the nominal capacity predicted by the
spatial kinetic battery model according to Theorem 2.1 is

$$u(t,0) = M + \frac{2N\mu - 2\delta\lambda t/\ell}{1 - e^{-2\delta}} + 4\mu N \sum_{n=1}^{\infty} \frac{((-1)^n e^\delta - 1)n^2\pi^2}{(\delta^2 + n^2\pi^2)^2} e^{-2\kappa(\delta^2 + n^2\pi^2)t}$$

$$(14) \qquad\qquad -\frac{\lambda}{\kappa\ell} \sum_{n=1}^{\infty} \frac{n^2\pi^2}{(\delta^2 + n^2\pi^2)^2}(1 - e^{-2\kappa(\delta^2 + n^2\pi^2)t}).$$

The corresponding state of charge is $\widetilde{u}(t,0) = u(t,0)/N$ and the voltage $E(t)$ as
a function of time is obtained from Eqn. (1) or a similar, more realistic, relation
between charge and voltage as discussed in Section 2.1.

It is sometimes desirable to consider voltage as a function not of time but 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

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

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

$$u = N - cq(T - v) - \gamma_c(1 - cq)(1 - e^{-(T-v)/\gamma_c}), \quad \gamma_c = \lambda/k_c > 0,$$

is an autonomous system, and we may express the resulting voltage $E = E(u)$ as
a function of v. In the same spirit we now 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

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

To explain further our approach to this problem it is convenient to first look at the
simpler case of migration but no diffusion, that is $\rho > 0$ and $\mu = 0$. Then

$$u(t,0) = N - \frac{\lambda t\omega_\rho}{\ell} - \frac{\lambda}{\kappa\ell} \sum_{n=1}^{\infty} \frac{n^2\pi^2(1 - e^{-2\kappa(\rho^2 + n^2\pi^2)t})}{(\rho^2 + n^2\pi^2)^2}, \quad \omega_\rho = \frac{2\rho}{e^{2\rho} - 1}.$$

Here the relation to remaining capacity is $\lambda t = u(t,0) - v(t) + N\ell$, and hence

$$u = (v - u)\frac{\omega_\rho}{\ell} + N(1 - \omega_\rho) - \frac{\lambda}{\kappa\ell} \sum_{n=1}^{\infty} \frac{n^2\pi^2(1 - e^{-2\kappa(\rho^2 + n^2\pi^2)(u - v + N\ell)/\lambda})}{(\rho^2 + n^2\pi^2)^2},$$

which is an autonomous system for $(v, u) = (v(t), u(t, 0))$. Figure 1 indicates the typical shape of solution curves (v, u) for a few arbitrary parameter values, in particular $\ell = (T - N)/N = 9$.
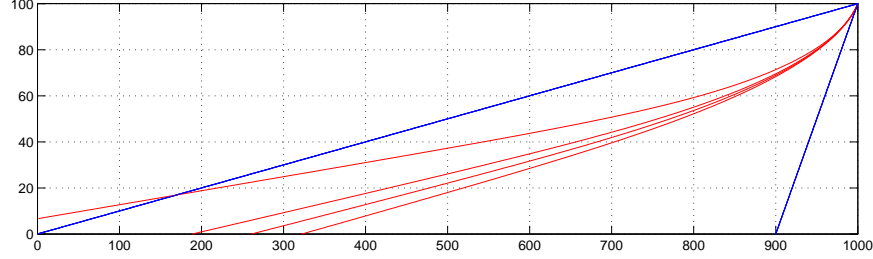

FIGURE 1. $T = 1000$, $N = 100$, $\lambda = 1000$, $\kappa = 0.5$, $\mu = 0$, $\rho = 0$, 0.1, 0.2, 0.5;

In greater generality, by replacing λt in (14) with $u(t, 0) - v(t) + N\ell$,

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

which is again an autonomous systems for nominal versus remaining capacity. As an illustration Figure 2 shows solution traces (v, u) for fixed values of T. N, λ and κ, and with four different combinations of μ and ρ which all give approximately the same utilization of the total available battery capacity.
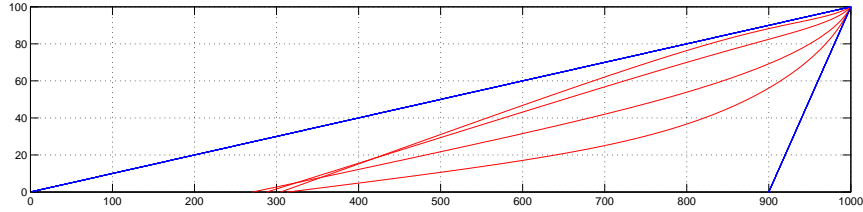

FIGURE 2. $T = 1000$, $N = 100$, $\lambda = 1000$, $\kappa = 0.5$, various combinations of μ and ρ

3. Nonlinear Battery Models

In this section we will introduce an approach to nonlinear battery modeling which begins with a discrete time Markov chain model moving on a set of bivariate states representing nominal 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. As a next step we investigate the scaled capacities as the number of slots per time unit tends to infinity and the discharge process converges to that of a constant rate. In the limit we obtain deterministic capacity funtions 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

$$V_n = \text{remaining capacity [Ah] in time slot } n$$

$$X_n = \text{nominal capacity [Ah] in time slot } n.$$

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 $V_n = T - \Lambda_n$ 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 $\beta > 0$

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

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

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

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

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

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 $(v, x) \to (v - \delta, x - \delta)$ and if $Z_{n+1} = 0$ then

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

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

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

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 wiew $V^{(m)}(t)$ 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 $1/\sqrt{m}$. Moroever, by considering the differential change of $X^{(m)}(t)$ over a time interval $(t, t+h)$ where $h = 1/m$,

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

and

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

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

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

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

$$(15) \qquad \begin{aligned} x_t' &= -\delta q + (1-q)\delta(1 - e^{-\beta v_t})(1 - e^{-\alpha q(N - x_t)}), & x_0 &= N, \\ v_t' &= -\delta q, & v_0 &= T. \end{aligned}$$

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

$$(16) \quad x_t = N - \frac{1}{\alpha q} \ln\left(1 - \alpha q \int_0^{T - v_t} \exp\left\{ -\alpha s + (1-q)\alpha e^{-\beta v_t}(1 - e^{-\beta s})/\beta \right\} ds\right).$$

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 nominal capacity, and hence the voltage, 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 $m \to \infty$ 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

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

we can solve for X_t and obtain

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

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

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

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 (15), in the limit $m\to\infty$ of the scaled Markov chain $(V^{(m)}(t), X^{(m)}(t))_{t\geq 0}$ with constant discharge rate λ. Now we introduce the quantities

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

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

$$d\nu_m(t) = \sigma\,dW_1(t)$$
$$d\xi_m(t) = \sqrt{m}(f(V^{(m)}(t), X^{(m)}(t)) - f(v_t, x_t))\,dt$$
$$+ \sqrt{\lambda\delta + \delta f(V^{(m)}(t), X^{(m)}(t))}\,dW_2(t),$$

where $\nu(0) = \xi(0) = 0$. It follows by a Taylor expansion of $f(v, x)$ that

$$d\xi_m(t) = f'_v(v_t, x_t)\nu_m(t)\,dt + f'_x(v_t, x_t)\xi_m(t)\,dt$$
$$+ \sqrt{\lambda\delta + \delta f(V^{(m)}(t), X^{(m)}(t))}\,dW_2(t).$$

In the scaling limit $m\to\infty$ we therefore expect that the fluctuation process $\xi_m(t)$ converges to a diffusion process $\xi(t)$, such that

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

This stochastic differential equation for $\xi(t)$ can be seen as a generalized Ornstein Uhlenbeck process

$$d\xi(t) = a_t W_1(t)\,dt + b_t\,\xi(t)\,dt + c_t\,dW_2(t),$$

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

3.5. **A general class of nonlinear ODE battery capacity models.** To derive the capacity dynamics in (16) 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 $t \geq 0$.

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 $F : [0, \infty) \to [0, 1]$ and $G : [0, \infty) \to [0, 1]$ be non-decreasing functions with $F(0) = 0$, $G(0) = 0$, and consider equations of the generic shape

$$(17) \qquad dx_t = -\Lambda(dt) + \lambda F(N - x_t)G(v_t)\,dt, \quad t \leq t_0, \quad x_0 = N,$$

where t_0 is battery life defined as the maximal time t for which $x_t \geq 0$. For now, however, we keep the setting of (16) and put $F(u) = 1 - e^{-au}$, where a is a positive constant which should measure the strength of migration of charges due to the existing electric field in the battery.

Constant discharge recovery mechanism. Suppose the battery is discharged continuously at constant current $\lambda > 0$ with discharge profile $\Lambda(t) = \lambda t$. We consider the special case of (17) given by the ODE

$$(18) \qquad x'_t = -\lambda + \lambda(1 - e^{-a(N-x_t)})G(v_t), \quad X_0 = N.$$

Because of the separation of variables we may write

$$h_t(e^{a(N-x_t)} - 1) = \lambda a \int_0^t h_s\,ds$$

where

$$\ln(h_t/h_0) = -\lambda a \int_0^t (1 - G(v_s))\,ds,$$

and hence

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

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 nominal capacity $x = x(v)$ can be viewed as a function of remaining capacity only. Moreover, the capacity dynamnics 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 lifes, 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 dynmamics. Via state-of-charge $\widetilde{x} = x/N$ 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. In principle, experimental data can be tested and parameters estimated. To give an indication of this type of work, Figure 3.5 shows the result of repeated independent simulations based on (18) with G an exponential function, under random Poisson discharge and parameters chosen arbitrarily such that the ouput appears to mimic that of a real battery. The upper panel shows the phaseplane traces of the resulting solutions (v, u). The lower panel shows the resulting decline of the state-of-charge $\widetilde{x}_t$ as a function of time (lower panel). The state-of-charge for constant discharge with the same average load is superimposed (red curve).

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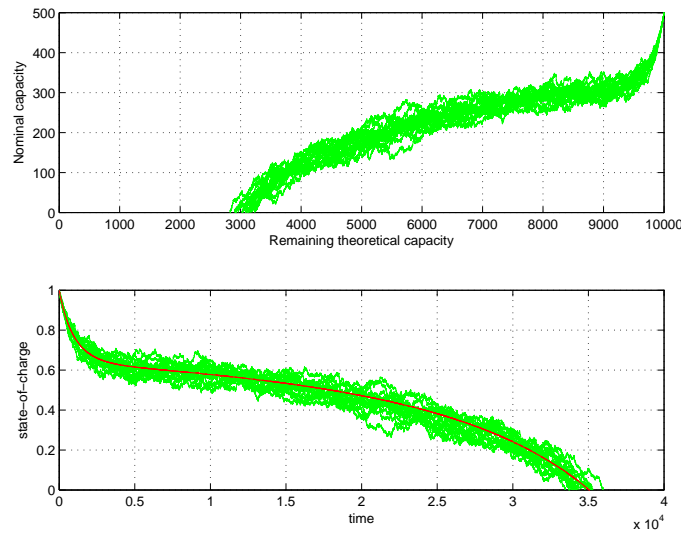
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