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Optimum Charging Profile for Lithium-ion Batteries to Maximize Energy Storage and Utilization

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The optimal profile of charging current for a lithium-ion battery is estimated using dynamic optimization implemented via control vector parameterization (CVP). An efficient reformulated model is used for simulating the system behavior of the Li-ion battery. Dynamic optimization is made possible due to the computationally inexpensive reformulated model. It is found that, if the battery is charged using the optimum profile estimated by dynamic optimization, more energy can be stored as compared with conventional charging of the battery. An attempt has been made to understand the dynamics of Li-ion batteries with competing transport and reaction phenomena at various scales and location inside the battery.

Introduction

Electrochemical power sources such as lithium-ion batteries have had significant improvements in design, modeling, and operating range and are expected to play a vital role in the future in automotive, power storage, military, and space applications. Lithium-ion chemistry has been identified as a preferred candidate for high-power/high-energy secondary batteries. Applications for batteries range from implantable cardiovascular defibrillators (ICDs) operating at 10 μA current to hybrid vehicles requiring pulses of up to 100 A. Problems that persist with lithium-ion batteries include underutilization, capacity fade, and thermal runaway caused by operation outside the safe window [1]. The capability of a battery to store energy reduces with number of cycles due to formation of undesirable side reaction products during the discharging and charging process. To optimally use resources, an important problem is to maximize the stored energy in the battery.

In many applications, the ability to recharge quickly and efficiently is a critical requirement for a storage battery. In a Li-ion battery, during charging, the lithium ions first diffuse out of the lithium-metal oxide in the positive electrode, migrate through the electrolyte, and then diffuse into the carbon matrix in the negative electrode. Various processes occur simultaneously, which reduces the efficiency of the charging process and results in reducing the capacity to store energy in these secondary batteries.

The processes inside the battery are highly nonlinear and interactive in nature, and depend on various processes such as kinetics of the reactions, temperature of the reactions, rate of the diffusion of lithium ions, etc. A valuable objective is to characterize these nonlinearities and to regulate the various micro-scale processes in an optimal way to enhance the energy-storing capacity of the battery. Achieving this objective is challenging due to the meager knowledge on these processes at the microscale level. On the positive side, a significant amount of details on these processes at the continuum level are available [1-7]. The capability to accurately predict the values of internal state variables such as state of charge would also be useful. Predicting the behavior accurately will expect to help in extending the life of the battery and improve the capability to store more energy.

A dynamic optimization framework for the lithium-ion battery is presented. Particularly, for the estimation of the optimum profile of charging current has been carried out for storing maximum energy in the lithium-ion battery during charge. During optimized charging, various processes such as charge transfer, kinetics of the reactions, and rates of diffusion differ compared to un-optimized charging. The paper explores the changing dynamics of the system by using an optimal current profile for charging. Dynamic behaviors are compared for various non measurable internal variables including solid-phase and electrolyte concentrations and potentials under different scenarios of battery charging. Three different types of charging processes are investigated:

- Conventional charging with 1C rate: defined as constant current charging of the battery with current equivalent to 1C rate until the cut-off potential or the time limit,
- Constant current charging with optimized C rate: defined as constant current charging of the battery with an optimized C rate (value of current) until the cut-off potential or the time limit,
- (Dynamically) optimized charging profile: defined as charging with an optimal profile of current estimated using the dynamic optimization technique.

Dynamic Optimization Framework

An optimal control problem formulation is considered:

$$\min_{\substack{\mathbf{z}(t)\\ \mathbf{u}(t)\\ \mathbf{p}}} \Phi \tag{1}$$

such that

$$\frac{d}{dt}\mathbf{z} = \mathbf{f}(\mathbf{z}(t), \mathbf{y}(t), \mathbf{u}(t), \mathbf{p}),\ f(\mathbf{z}(0)) = 0,\ g(\mathbf{z}(1)) = 0, \tag{2}$$

$$\mathbf{g}(\mathbf{z}(t), \mathbf{y}(t), \mathbf{u}(t), \mathbf{p}) = 0, \tag{3}$$

$$\mathbf{u}_L \leq \mathbf{u}(t) \leq \mathbf{u}_U,\ \mathbf{y}_L \leq \mathbf{y}(t) \leq \mathbf{y}_U,\ \mathbf{z}_L \leq \mathbf{z}(t) \leq \mathbf{z}_U \tag{4}$$

In this formulation, $\mathbf{z}(t)$ is the vector of differential state variables, $\mathbf{y}(t)$ is the vector of algebraic variables, $\mathbf{u}(t)$ is the vector of control variables, and $\mathbf{p}$ is the vector of parameters. The objective function Φ is formulated as maximum energy stored in the lithium-ion battery using reformulated model [8]. Numerous methods are available for solving constrained optimization problems. Typical methods for dynamic optimization include (1) the application of variational calculus, (2) Pontryagin's maximum principle, (3) control vector iteration, (4) control vector parameterization, and (5) simultaneous nonlinear programming [9-11]. Control vector parameterization (CVP) is the most commonly use in industrial applications and is used in this paper.

The reformulated model used in this work is derived from the first-principles porous electrode-based electrochemical engineering model. We have worked extensively in model reformulation and have published the details on the reformulation of the lithium-ion battery model [8]. Dynamic optimization solves the system several times and then estimates the optimum for the given objective function. A Fortran implementation of the reformulated model takes only 15-50 ms to predict a discharge curve whereas the original model can take up to a few seconds to minutes depending on the solver, environment, and the computer. Also, the memory requirement is far less compared for the reformulated model compared to finite-difference models. The dynamic optimization requires many individual simulation runs, so a computationally expensive model would result in very long time to obtain optimization results. Due to the longer simulation times, dynamic optimization of batteries using first-principles-based models has not been attempted or reported in the literature to our knowledge. Obviously, this situation is not ideal for emerging applications like hybrid power systems or for on-line control, optimization, and monitoring of batteries and other electrochemical power sources. Though this paper provides results for a single cell/battery, current work involves optimizing charging profile for cells in series/parallel in a battery pack in which different cells might have different SOCs that are not directly measurable.

Simulation Results and Discussion

To illustrate the computational efficiency of the approach, this paper performs all implementations in Matlab, which is much slower than Fortran for carrying out optimizations. The reformulated model was solved using our own robust DAE solver, which is somewhat less efficient than some existing DAE solvers (e.g., DASSL/DASPK/Jacobian [12-13]). The optimization was carried out using Matlab's optimization toolbox on a 3 GHz Intel Core 2 Duo CPU with 3.25 GB of RAM. The reformulated model is solved for one hour of operation with 4.05 V cut off voltage as the constraint on the model solution. It is assumed in the battery literature [14] that, the battery will be safe if operated below 4.05 V. The system was solved for three different operating scenarios of charging *viz.*: (1) 1C rate charging; (2) constant current charging with optimized C rate and (3) (dynamically) optimized charging profile estimated using dynamic optimization procedure.

Fig. 1 illustrates the current time profile used under three different types of charging. The charging at 1C rate corresponds to a current of 30 A/m^2 and the optimized C rate gives a current of 17.207 A/m^2 to the battery. When charging with the dynamically optimized current profile, the optimum current profile decreases with time similar to that of a first-order process with negative gain. The optimal profile initially supplies more current and then decreases the current slowly over the time of charging. The stored energy is higher in dynamically optimized charging as compared with other two types of charging at a constant rate.

Fig. 2 shows the voltage time profile for the lithium-ion battery during three different scenarios of charging. All three types of charging have initial rapid increases in the voltage and end operations at the same voltage, with widely different profiles at intermediate times. The dynamically optimization results in much faster charging rate than the other two types of charging (Fig. 3). The rate of conventional charging using the 1C rate is higher than the constant current charging with optimized C rate charging and hence, cut off potential is quickly reached. The rate of the dynamically optimum charging is nearly linear after the dimensionless time is equal to 25.

Fig. 3 shows the amount of the time profiles are very different for the energy stored in the lithium-ion battery during the three different charging scenarios. Unlike the constant charging scenario, the dynamically optimized charging scenario increases nonlinearly with time. The final energy stored using the dynamically optimized profile is higher. Although the rate of energy storage for conventional constant charging is higher than the constant current charging with optimized C rate, the amount of energy stored in the latter case is much more than the conventional charging at 1C rate. This happens due to the cut-off potential being encountered early in the conventional charging as compared to the conventional charging with optimized C rate (Fig. 2). The dynamically optimized charging protocol yields (29.38%) better storage compared to constant charging at the optimized C rate.

Fig. 4 shows the time profile for the electrolyte concentration at the cathode/current collector interface for the three different charging scenarios. This electrolyte concentration has a higher peak value during dynamically optimized charging followed by the conventional charging at 1C rate and then conventional charging with optimized C rate. This is due to the higher initial supply of current during dynamically optimized charging as compared to the other two types of charging (Fig. 1). For the chosen chemistry, mass transfer limitations in the electrolyte occur at higher currents. This protocol indicates that, to increase the energy density, store more energy at shorter time albeit causing mass transfer limitations in the electrolyte and let the concentration equilibrate at longer times to ensure longer operability of the battery (70 dimensionless times). In the latter part of charging, the electrolyte concentration at the positive electrode decreases during dynamically optimized charging, whereas it almost remains constant during conventional charging with optimized C rate. During dynamically optimized charging, the electrolyte concentration decreases over time and the lithium-ion transfer process slows down while more lithium ions are packed into the carbon matrix in the negative electrode.

The solid-phase surface concentration at the current collector interfaces for the positive and negative electrodes at each time is different by as much as 50% for the three charging scenarios (see Fig. 5). Each time profile for a solid-phase surface concentration varies monotonically, regardless of the electrode or the charging scenario. The spatially averaged concentration in the anode and cathode $\int c_{s,ave}dx$ also vary monotonically with time (see Fig. 6). We see that % change is more in the anode than the cathode as this battery was inherently limited by diffusion in the anode and the optimum profile helps in overcoming this limitation. However, still the value obtained is far off from the theoretical maximum suggesting that one hour (70 dimensionless times) operation will always mean compromise for charging; however, it can be significantly improved. The theoretical maximum is estimated by charging the Li-ion battery at a very low rate (approx. C/100) without time limitation to the same cut off potential.

Conclusion

The method in which a lithium-ion battery is charged can significantly alter the efficiency, safety, and lifetime of the battery. Various phenomena take place at the electrode/electrolyte level during charging. A continuum reformulated model for the lithium-ion battery is used in this paper to perform dynamic optimization to store the maximum energy in the given battery during charging. The analysis shows a 100% improvement for dynamically optimized charging over the conventional charging at 1C rate and 29.38% improvement with constant current charging at optimized C rate. Time profiles for internal variables were used to explain some of the physics associated with charging for maximum energy storage. Dynamic analysis of all possible intrinsic variables along with optimization for storing the maximum energy in a lithium-ion battery pack is currently being investigated in our group. In addition, optimal profiles for different specific objectives (reduced capacity fade, reduced SEI layer growth, enhanced life, uniform current distribution, ideal temperature behavior with temperature constraints) are being studied.

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Figures

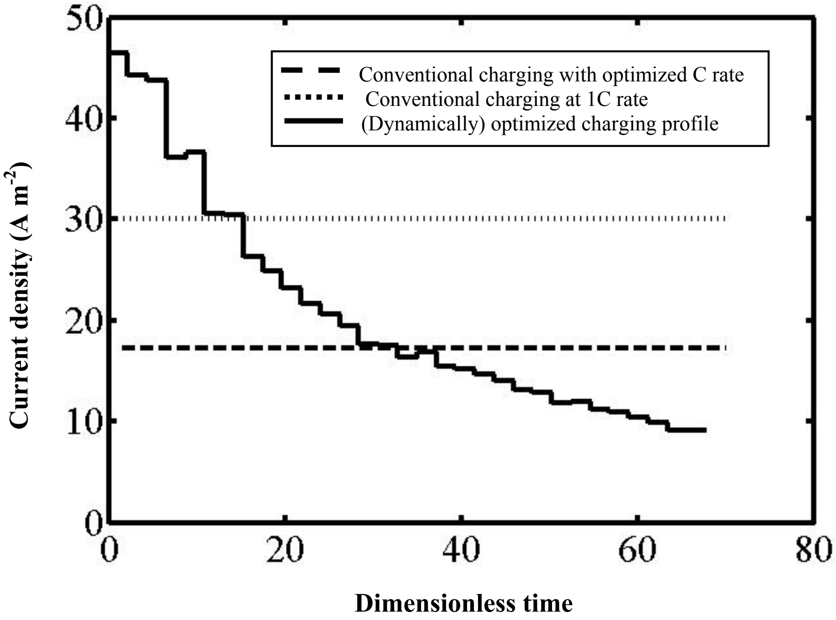

Figure 1: Comparison of current used for charging of lithium ion battery for three different types of charging protocol.

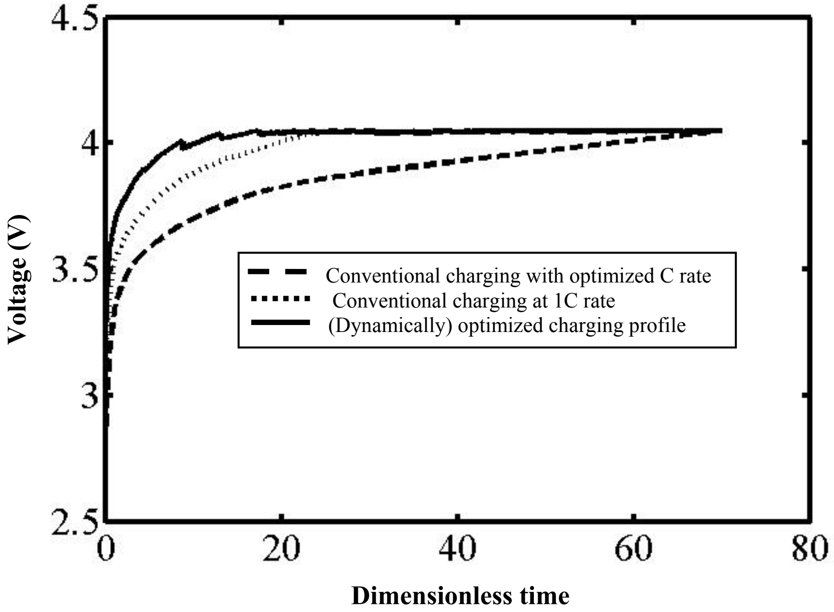

Figure 2: Comparison of voltage of lithium ion battery for three different types of charging protocol.

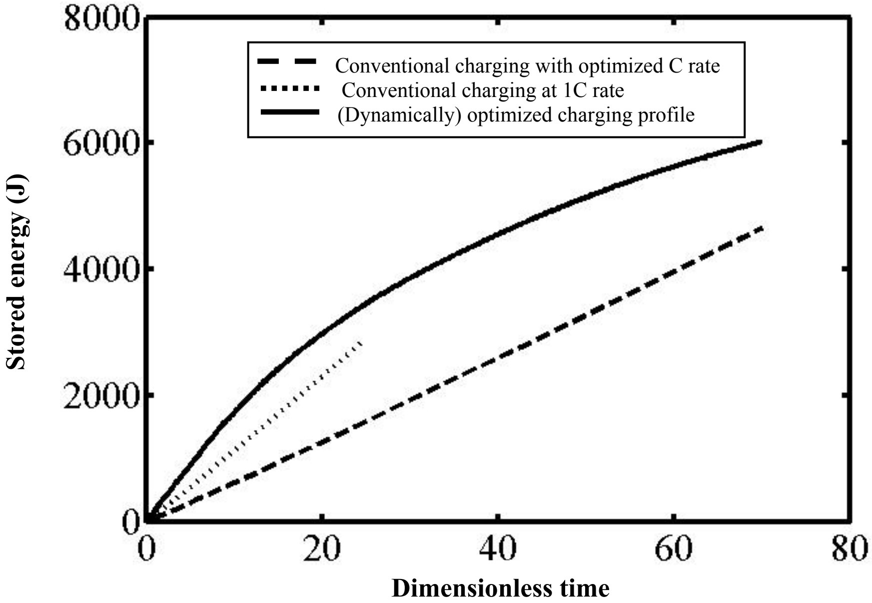

Figure 3: Comparison of energy stored in lithium ion battery for three different types of charging protocol.

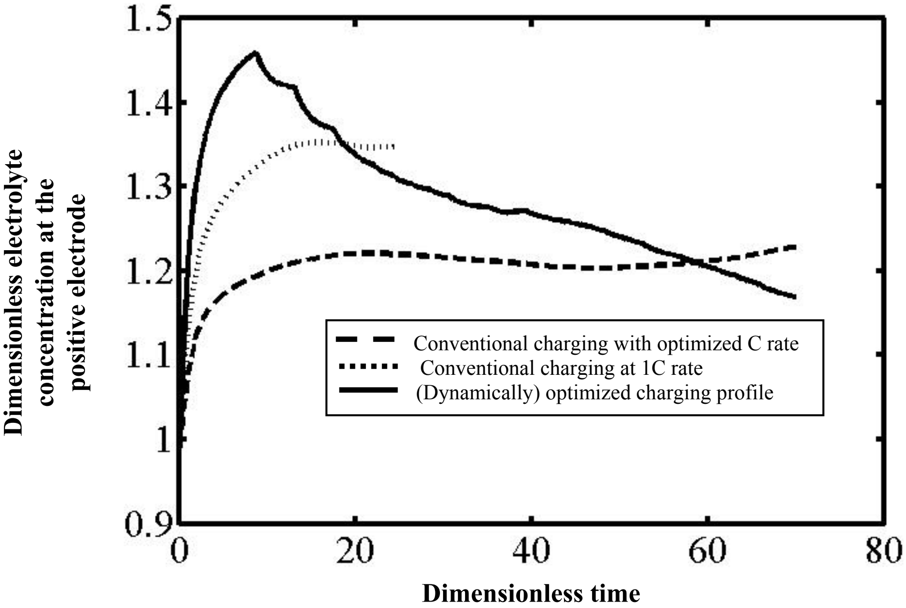

Figure 4: Dynamic analysis of electrolyte concentration at the positive electrode for the three different types of charging protocol.

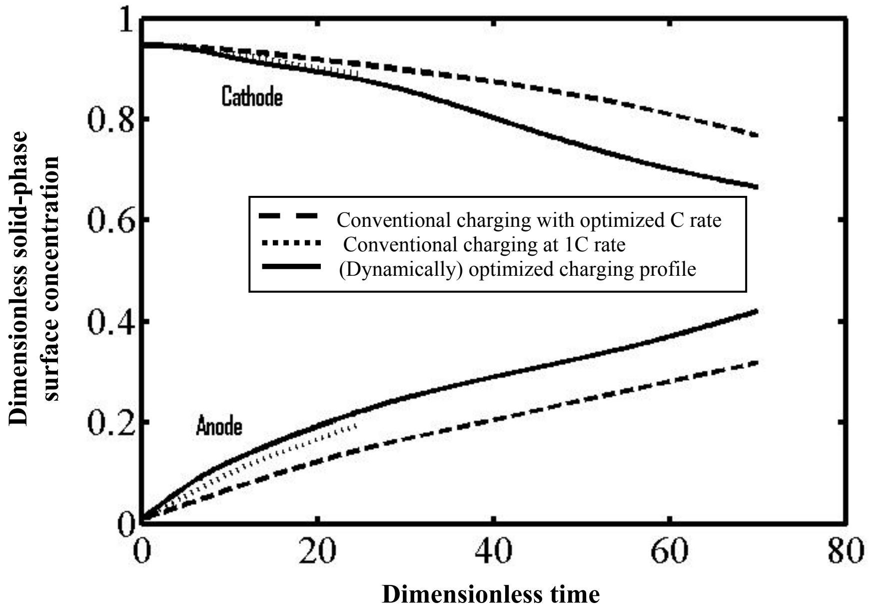

Figure 5: Solid-phase surface concentration at the current collector interfaces for the positive and negative electrodes for the three different types of charging protocol.

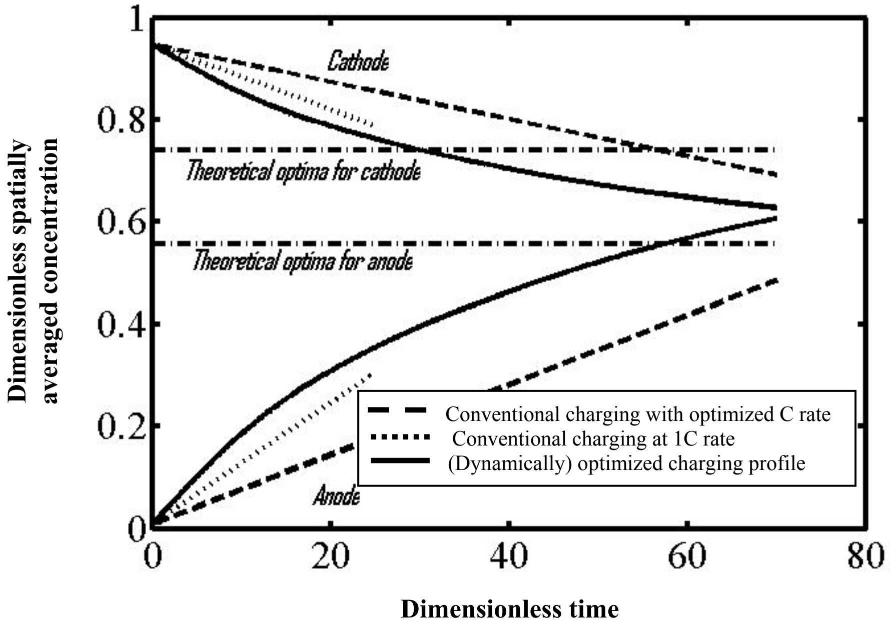

Figure 6: Spatially averaged concentration in the anode and cathode $\int c_{s,ave} dx$. (The theoretical maximum is estimated by charging the Li-ion battery at a very low rate (approx. C/100) without time limitation) for the three different types of charging protocol.