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Short communication

Evaluation of optimal discharge current profile for planar electrodes to maximize the utilization

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Abstract

In this paper, optimization of operating conditions for electrochemical energy sources is attempted using a dynamic optimization approach. This rigorous approach is demonstrated using a nonlinear diffusion equation that governs the mass transport limitation from/to the planar electrode. The resulting differential-algebraic model is solved using piecewise constant control vector iteration method that uses vectorized discharge current. The results obtained using the optimal control profile is compared with constant current discharge method and also with another trial and error approach that uses linear current control. It is found that the optimal control method achieves 12% more state of discharge against constant current discharge method with better energy efficiency and battery use. The proposed approach can be extended to complex systems such as operating electrochemical energy sources in hybrid environments that require proper control of energy distribution among the hybrid components.

Keywords: Battery modeling; Process dynamics; Dynamic optimization; Hybrid environments; Electrochemical models

1. Introduction

Modeling and simulation issues in electrochemical energy sources such as batteries, fuel cells and super capacitors are gaining more attention these days. This is mainly because of the developments in hybrid power systems that have evolved as one of the major alternatives to using fossil fuels. An important topic in such hybrid environments is the power distribution among the hybrid components. Typically in many hybrid systems, an important component will be the electrochemical energy source, e.g., the batteries. Hence the optimization of operating conditions of electrochemical energy sources is important to control and share the power delivered by the batteries in hybrid environment. Many previous investigations have attempted to optimize electrochemical energy sources using various approaches. Shepherd derived a voltage–current and state-of-charge relationship for predicting discharge and charge curves particularly for lead-acid batteries [1]. Other forms of this relationship are derived [2] to relax the assumptions behind the Shepherd model. Another relationship used to predict remaining capacity of a battery was given by Peukert's empirical equation [3]. All these forms of simple relationships are not applicable to battery models in hybrid environments due to the fact that the battery can be studied only at limiting conditions under which these equations work. The main conclusion of a recent critical review paper is that the empirical equations cannot be used to predict state of charge accurately unless the electrochemical energy source is discharged under galvanostatic conditions at constant temperature [4].

Current or potential pulsing is another attempt to optimize the charge–discharge characteristics of electrochemical energy sources. Purushothaman et al. [5] discussed the application of battery charging process using various current waveforms. The model consists of a simple linear diffusion equation with an analytical solution to study the mass transport limitations under different pulse currents. However, there are some disadvantages of pulse charging, in particular a decrease in charge amp-hour and energy efficiencies and an increase in cell electrolyte temperature. The constant current charge method results in good energy efficiency with no significant heat effects. It shows that an optimal operating policy with respect to the operation of electrochemical energy source that offers an advantage over constant current charging/discharging is unknown at this point of time.

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Finding this optimal operating policy can provide the best way of utilizing electrochemical energy sources in any environment. This requires a more sophisticated way of keeping track of the remaining active material in the battery.

In this paper, the problem of finding the best operating conditions is solved offline using open-loop control policy by defining the model equations in the form of a dynamic optimization problem. To illustrate the approach a planar electrode system is considered. Here, the control variable is discharge current density and the state variables are active species concentration distribution at node points across a discretized planar electrode. The method used to solve the dynamic optimization problem is the piecewise constant control vector parameterization. The optimal operating conditions obtained are compared with constant current discharging and the converged results are also verified using another solution methodology which involves the assumption of trial function for the control variable. The authors [6–8] have already adopted this approach for evaluating optimal operating conditions for electrochemical reactors used in electro-organic synthesis process. The rigorous dynamic optimization approach [9,10] will later be extended to combine concentration and potential gradients within a porous electrode and henceforth for the rigorous model governing the entire battery.

2. Planar electrodes

A mathematical model for planar electrodes that governs the mass transport to and from the electrode can be written as follows:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x}\left(D\frac{\partial c}{\partial x}\right) \tag{1}$$

subject to the initial condition

$$\text{at} \quad t = 0, \quad c = c_0 \tag{2}$$

and the boundary conditions

$$\text{at} \quad x = 0, \quad \frac{\partial c}{\partial x} = 0 \tag{3}$$

$$\text{at} \quad x = L, \quad \frac{\partial c}{\partial x} = -\frac{i(t)}{nFD} \tag{4}$$

where D is the diffusion coefficient of diffusing species from the electrolyte, c the electrolyte concentration and $i(t)$ is the applied discharge current density. The diffusion coefficient can be taken as constant in some cases, such as diffusion in dilute electrolyte solution. In other cases, such as diffusion in polymers, the diffusion coefficient depends very markedly on the concentration of diffusing substance, e.g., lithium-polymer. In this paper, the dependency of the diffusion coefficient is taken as

$$D = D_0\,(1 - 0.1c) \tag{5}$$

The above model is based on the assumptions that: (1) the electrode is planar, (2) the electrode is completely charged at time $t = 0$, i.e., 100% state-of-charge, (3) electrochemical reaction is taking place only at the surface of the electrode, (4) symmetry at $x = 0$ and (5) only the diffusion phenomenon is controlling the process compared to electrochemical kinetics and other competing phenomena. The following dimensionless variables are defined to make the above model equations dimensionless:

$$X = \frac{x}{L}, \quad C = \frac{c}{c_0}, \quad \tau = \frac{Dt}{L^2} \quad \text{and} \quad \delta(\tau) = \frac{i(t)}{nFD}\frac{L}{c_0} \tag{6}$$

Using Eq. (6), the dimensionless form of the model equation is

$$\frac{\partial C}{\partial \tau} = (1 - 0.1C)\frac{\partial^2 C}{\partial X^2} - 0.1\left(\frac{\partial C}{\partial X}\right)^2 \tag{7}$$

The boundary and initial conditions are

$$\text{at} \quad \tau = 0, \quad C = C_0 \tag{8}$$

$$\text{at} \quad X = 0, \quad \frac{\partial C}{\partial X} = 0 \tag{9}$$

$$\text{at} \quad X = 1, \quad \frac{\partial C}{\partial X} = -\frac{\delta(\tau)}{1 - 0.1C} \tag{10}$$

The nonlinear model equations given by Eq. (7–10) can be solved by applying any discretization method in the spatial coordinate. Using finite differences in X with N number of internal node points, the resulting differential algebraic form of the model equations are represented below:

At $X = 0$

$$\frac{-C_2 - 3C_0 + 4C_1}{2\Delta X} = 0 \tag{11}$$

For $0 < X < 1$, $i = 1$ to N

$$\frac{\mathrm{d}C_i}{\mathrm{d}t} = (1 - 0.1C_i)\left[\frac{C_{i-1} - 2C_i + C_{i+1}}{\Delta X^2}\right] - 0.1\left(\frac{C_{i+1} - C_{i-1}}{2\Delta X}\right)^2 \tag{12}$$

At $X = 1$

$$\frac{C_{N-1} + 3C_{N+1} - 4C_N}{2\Delta X} = \frac{-\delta(\tau)}{1 - 0.1C_{N+1}} \tag{13}$$

where $\Delta X = 1/(N+1)$ is the node spacing in X-direction. The initial conditions for differential equations (in Eq. (12)) are $C_i = 1$ at $\tau = 0$ for $i = 1,\ldots,N$. The resulting differential-algebraic equations (DAE) represented by Eqs. (11)–(13) can be solved for any given discharge current density $\delta(\tau)$. The values of the parameters used for the simulation are length of the electrode $L = 8.2 \times 10^{-3}$ m, diffusion coefficient $D_0 = 8.5 \times 10^{-8}$ m^2 s^{-1}, initial electrolyte concentration $c_0 = 10$ mol m^{-3}, constant discharge current $i(t) = 10$ A m^{-2}, equilibrium potential $E_0 = 4.1$ V, discharge time $t_f = 530$ s, number of electrons involved $n = 1$ and Faraday constant $F = 96487$ °C mol^{-1}.

The above set of model equations and set of parameters are simulated for the conventional case of constant current discharge, i.e., $\delta(\tau) = 1$. The resulting concentration variation across the planar electrode shows that the average concentration remains at a significant level of 62.11% state-of-discharge even after the end of discharge process. Obviously, the energy remaining inside the battery is critical and it should be utilized using an

effective alternate method of discharge other than an empirical relationship or pulse current. It is now clear that we need a profile based on the model equations and set of parameters, which can achieve a greater depth of discharge for the given time period.

3. Linear current control

Here, instead of using a constant current for discharge a trial function is assumed for $\delta(\tau)$. This is done by assuming that the discharge current varies linearly as a function of time. The parameters for any assumed policy can be evaluated using parameter estimation algorithm or using the simplified model equations in Ref. [11], developed by the authors. Using this approach, the linear current control is evaluated and battery performance is investigated based on the model equations. It is found that a simple linear control can produce a depth-of-discharge equal to 69.11% which is 7% more than the depth-of-discharge achieved by the constant current control. Thus, this approach is interesting and further ensures existence of an optimal discharge current policy that needs to be evaluated using dynamic optimization technique.

4. Optimal control policy

The general statement for optimal control problem is as follows:

$$\min J[\mathbf{x}(t_f)] \tag{14}$$

subject to the differential constraints

$$\dot{\mathbf{x}} = \mathrm{f}(\mathbf{x}, \mathbf{u}) \tag{15}$$

where $\mathbf{x}$ is a vector of state variables and $\mathbf{u}$ is a vector of control variables. J is the objective functional that is to be optimized and t_f is the total process time. The specific objective function for planar electrode may be defined as maximize:

$$J_0[\delta(\tau)] = 1 - C_{ave}(\tau_f) \tag{16}$$

subject to the constraints represented as a system of DAE, Eqs. (11)–(13). Here, J_0 is a function of τ representing the performance index for dynamic optimization problem, C_{ave} is the arithmetic average of concentrations obtained at all the node points (both internal and external nodes) and τ_f is the duration of the discharge process.

There are several optimization techniques [9,10] for the solution of the above stated dynamic optimization problem, i.e., for solving Eq. (16) subject to the constraints Eqs. (11)–(13). Here, the method used for dynamic optimization of planar electrode is the piecewise constant control vector parameterization method. Since the problem considered does not have the nature of highly oscillatory control policy, a piecewise constant type of parameterization is sufficient with the advantage of simple and efficient computation scheme. In this method the total time of discharge τ_f is discretized and the constraints are evaluated at each time step as follows:

$$L = \frac{t_f}{p} \tag{17}$$

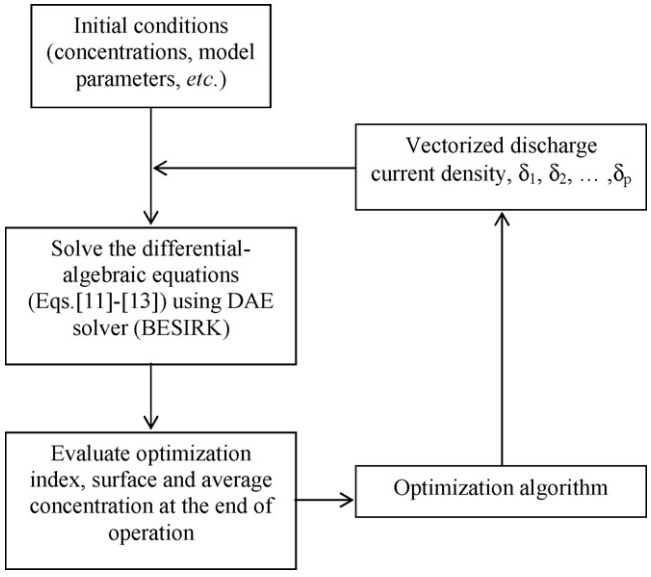

Fig. 1. Computation scheme for evaluating optimal operating conditions.

The computation starts at τ_0 where the initial conditions are known and ends at τ_p where p is the number of time steps. In each time step the control values to be used are determined by guesses that fall within the specified range for control variables. The strategy behind the random search in control domain is based on prior knowledge of the system. This search strategy can also enable quick convergence. Finally, the problem is also solved for different time steps, i.e., for $p = 10$, 15, 20, etc. to ensure convergence in control domain.

Fig. 1 shows the algorithm for developing the computer program. The model equations (Eq. 11–13) are solved using the DAE solvers DASSL in FORTRAN environment and BESIRK [12,13] in Maple® environment (for stability verification two different solvers are used). The number of internal node points used for the solution is 100 for better accuracy. The tolerance limits for the solver are also set high at 10^{-8} for absolute tolerance and 10^{-5} for relative tolerance. The total number of equations needed to be solved for constant and linear current controls are 100 and 2 for the boundaries. But for the case of evaluating the optimal control profile, for each iteration, solution of 102 differential-algebraic equations are needed. The final converged optimal profiles are obtained by using 10 runs with 40 steps in time. This means that the solver has to stop at each time step and recalculate the state variables 40 times. Thus, one run requires the solution of 102×40 equations and for the optimal profile it is 102×400 equations. An executable code that calculates the electrode performance using different operating conditions is available upon request from the corresponding author (VS).

5. Discussion

Fig. 2 shows the different operating profiles obtained using various approaches, i.e., constant, linear and optimal current controls. It also shows the corresponding potential variation

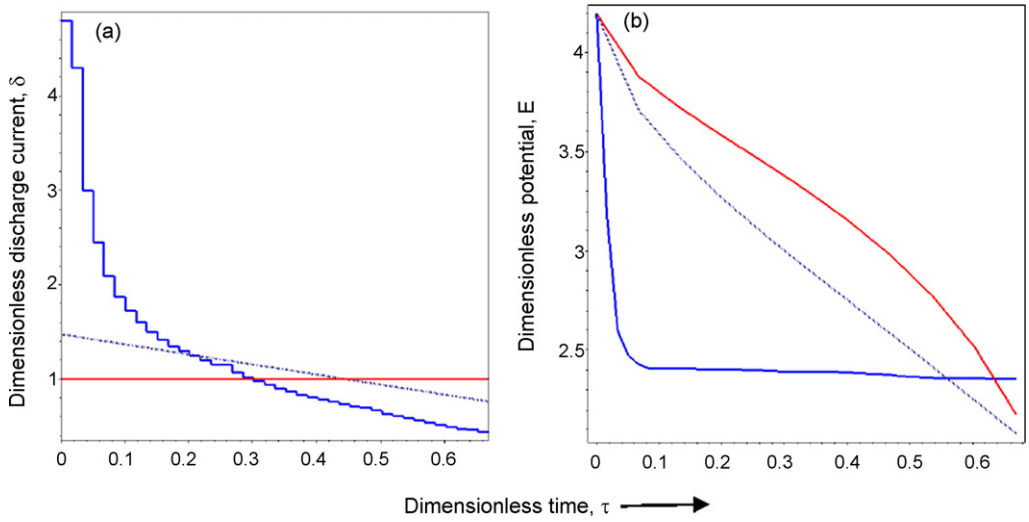

Fig. 2. Optimal discharge profile (a) and its corresponding potential profile (b) for a planar electrode. (i) Horizontal line, constant current; (ii) dotted line, linear current and (iii) continuous line with steps, optimal control.

inside the planar electrode as a result of different controls. The electrolyte potential plot is made by using the Nernst relationship for surface concentration and electrolyte potential with an equilibrium potential assumed as 4.1 V. From these plots it is clear that a maximum load can be applied during the initial stages of discharge and then the capacity decreases gradually. The maximum level and the dynamic profile of gradual decrease in load sharing are obtained by keeping track of the active material remaining inside the battery. Absence of such an implied constraint prevents the constant current (or the other profiles) to achieve a greater depth of discharge in the same amount of time. Fig. 3 shows the concentration distribution obtained across the planar electrode at different time steps during discharge. Fig. 4 shows the average and surface concentration variations by following different operating modes in comparison with constant current control. It can be seen that the conventional constant current discharge method cannot utilize the active electrode material at the center of the electrode (x = 0) due to transport limitations. But, a simple linear current control can yield better utilization than constant control and thus reiterates the existence of an optimal discharge profile that can exploit the battery effectively and completely.

Optimal control profile (curve c in Fig. 2) yields the best state of discharge of 74.93%. It is possible due to the dynamic current applied over the period of discharge that minimizes transport as well as kinetic limitations by having proper control over the amount of coulombs removed at any particular time step. Moreover, the optimal control policy ensures the depletion of active material perpendicular to the electrode till the other end at $x = 0$ and discharges the electrode more efficiently. Figs. 3c and 4b show the concentration distribution for optimal operating conditions. From these results, it is evident that this method of keeping track of the availability of charged species cannot be properly achieved using heuristic controls like linear or constant current. The maximum states of discharge achieved using different methods are: constant current profile 62.11% and linear current 69.11%. Table 1 shows the state of discharge obtained using different time steps in optimal control problem. It shows the convergence of optimization approach and its results in time domain. Fig. 5 shows the resulting power and energy distribution using all

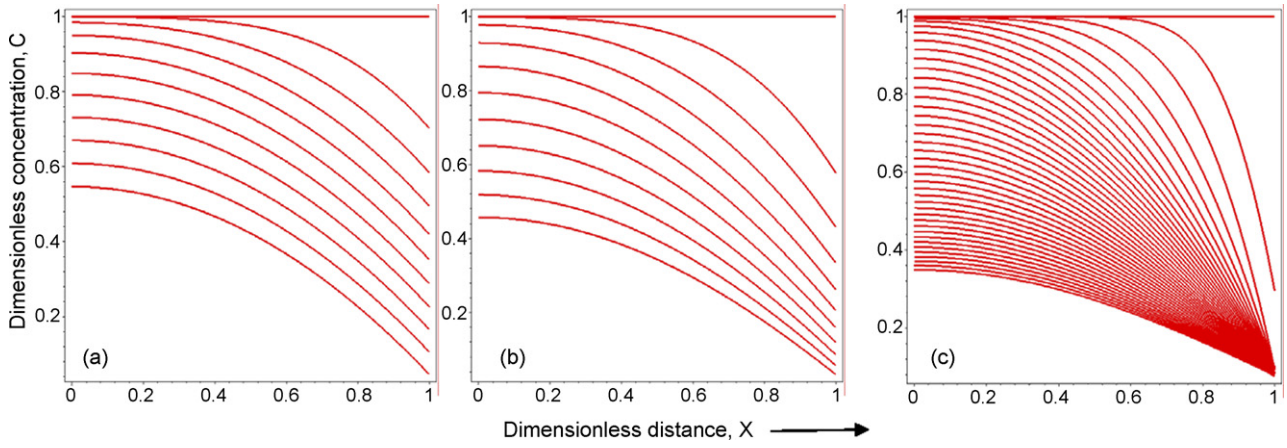

Fig. 3. Concentration distribution inside the planar electrode at different times during discharge process: (a) constant current, (b) linear current and (c) optimal control.

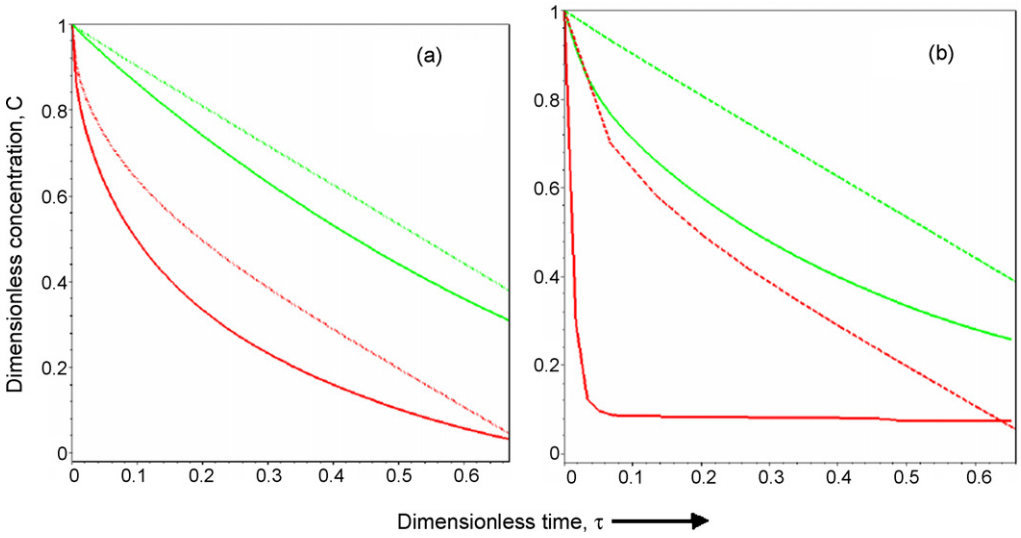

Fig. 4. Average and surface concentration variations during discharge of a planar electrode using time-varying controls in comparison with constant current discharge. Continuous line denotes surface concentration and dotted line denotes average concentration: (a) linear current and (b) optimal control.

Table 1
State-of-discharge obtained using various time steps in control vector parameterization approach

Number of time steps, N	$C_{ave}(t_f)$	SOD
10	0.2953062825	70.46937%
15	0.2712546656	72.87453%
20	0.2653962833	73.46037%
25	0.2530673100	74.69327%
30	0.2507845663	74.92154%
40	0.2507498113	74.92502%

these controls. The maximum power and energy from a battery can safely be extracted by using optimal control profile followed by the linear and constant currents. Thus, the constant current discharge is not a suitable method for using electrochemical energy sources in varying load environments like hybrid power systems and some portable power applications with constant load fluctuations. For a given objective function, the optimal charge–discharge policy once evaluated using the physics based model can provide a proper control over varying load hence improving performance and extending the life of the battery.

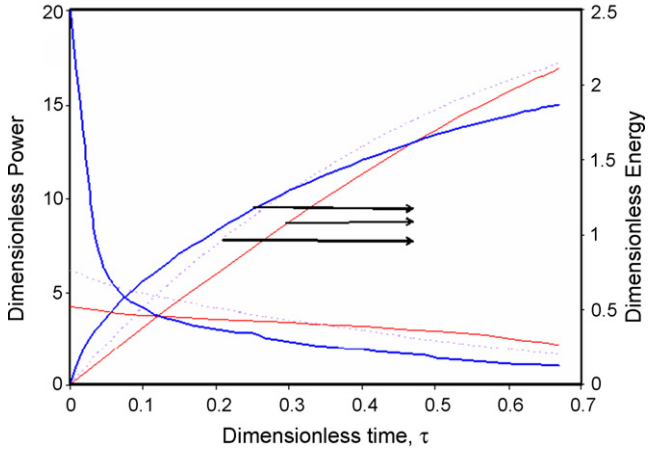

Fig. 5. Power and energy distribution during discharge of planar electrode obtained using various controls. Continuous line, constant current; dotted line, linear current; continuous dark line, optimal control.

6. Future directions

This paper introduces a rigorous dynamic optimization algorithm for operating electrochemical energy sources particularly suitable in hybrid environments. To illustrate this approach a planar electrode system is considered and good performance improvement of up to 12% for state of discharge is demonstrated. The results are encouraging and the approach will be extended to porous electrodes governed by a rigorous battery model. Since temperature variation is one of the adverse effects in lithium-based batteries, it can be studied and optimized as another control variable using this approach. Such a study can provide new directions for the efficient operation of lithium-based batteries in hybrid cars. The nonlinear model considered for the demonstration is simple and it does not impose much computational burden. If we extend this approach to porous electrode or the entire cell model, more attention should also be paid for choosing an efficient solver in FORTRAN or other computation environments. Also, the full battery model has 10 partial differential equations that cannot be directly used for dynamic optimization studies. This is because, if we choose 100 internal node points for discretization in both spatial and radial directions then the model equations will be converted to a system of 4800 DAE [14]. During the process of optimization all these equations have to be solved at each time step and for each run covering the entire time domain. This may need the solution of at least $10 \times 4800 \times 100$ DAE.

To overcome this computation difficulty, an efficient simplified battery model is being developed [11,14] to extend this optimization approach to a lithium-ion battery consisting of cathode/separator/anode. Incorporation of additional constraints related to power management is needed to set up an automated hybrid environment [15]. These and many other factors in implementing dynamic optimization procedure for battery models

will be identified and discussed in further publications using the approach introduced in this work.

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