Journal of Power Sources 206 (2012) 378–382

Contents lists available at SciVerse ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Short communication

Rate-based degradation modeling of lithium-ion cells

E.V. Thomas [a,*], I. Bloom [b], J.P. Christophersen [c], V.S. Battaglia [d]

[a] Sandia National Laboratories, Albuquerque, NM 87185-0829, USA
[b] Argonne National Laboratory, Argonne, IL 60439, USA
[c] Idaho National Laboratory, Idaho Falls, ID 83415, USA
[d] Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

ARTICLE INFO

Article history:
Received 14 October 2011
Received in revised form 11 January 2012
Accepted 12 January 2012
Available online 25 January 2012

Keywords:
Accelerated degradation testing
Life prediction
Non-isothermal stress

ABSTRACT

Accelerated degradation testing is commonly used as the basis to characterize battery cell performance over a range of stress conditions (e.g., temperatures). Performance is measured by some response that is assumed to be related to the state of health of the cell (e.g., discharge resistance). Often, the ultimate goal of such testing is to predict cell life at some reference stress condition, where cell life is defined to be the point in time where performance has degraded to some critical level. These predictions are based on a degradation model that expresses the expected performance level versus the time and conditions under which a cell has been aged. Usually, the degradation model relates the accumulated degradation to the time at a constant stress level. The purpose of this article is to present an alternative framework for constructing a degradation model that focuses on the degradation rate rather than the accumulated degradation. One benefit of this alternative approach is that prediction of cell life is greatly facilitated in situations where the temperature exposure is not isothermal. This alternative modeling framework is illustrated via a family of rate-based models and experimental data acquired during calendar-life testing of high-power lithium-ion cells.

1. Introduction

High-power lithium-ion batteries are being implemented in various transportation applications where there are stringent weight, energy, power, and cost requirements. A significant barrier that limits wide-spread commercialization of this technology is the requirement of long battery life, up to 15 years. The U.S. Department of Energy Office of Vehicle Technologies has sponsored a variety of projects to find solutions to these and other barriers that limit the commercialization of high-power lithium-ion battery technology. One related area of activity involves the development of methods to accurately predict the life of lithium-ion batteries in hybrid-electric vehicle (HEV) and plug-in hybrid vehicle (PHEV) environments with a high level of precision given short-term accelerated degradation testing.

Accelerated degradation testing with associated modeling and data analysis can effectively be used to predict failure-time distributions [1]. Information from such tests, usually obtained at relatively high levels of the accelerating factors (e.g., temperature), can be used to predict the long-term performance at normal use conditions. Typically, accelerated degradation testing involves exposing cells, in a collective sense, to a variety of thermal environments. However, individual cells are usually exposed to a single temperature. During the time of exposure, the state of health of each cell is measured periodically [2]. The measured performance at any given time for an individual cell is a combination of effects that can be related to the technology, to the unique behavior of the individual cell, and to the measurement process. Here, we focus on an approach for modeling the average cell performance that is indicative of a particular technology. The complete set of degradation data acquired across all cells over time is used to construct a degradation model (e.g., see [3,4]) that expresses the expected performance level versus the time and temperature under which a cell has been aged. Usually these models are cast in terms of cumulative degradation at constant stress conditions. Since cells are often deployed in applications where constant-stress conditions do not exist, there is motivation for the development and use of rate-based degradation models. By construction, such models can predict cumulative degradation under dynamic-stress conditions. Thus, the intent of this article is to present an alternative framework for modeling degradation that focuses on the degradation rate rather than the accumulated degradation.

The remainder of the paper is organized as follows. Section 2 discusses cumulative degradation models. Section 3 introduces rate-based degradation models and associated notation. Methods for estimating model parameters and predicting the cumulative degradation over any specified temperature profile are discussed. Section 4 illustrates the use of rate-based models with existing

* Corresponding author. Tel.: +1 505 844 6247; fax: +1 505 844 9037.
E-mail address: evthoma@sandia.gov (E.V. Thomas).

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doi:10.1016/j.jpowsour.2012.01.106

experimental data (obtained under constant stress) and presents a new model form that may be of general interest. An additional attribute of the rate-based framework (not applicable in the case of the illustrative example) is that degradation data acquired from cells under variable stress can be used for both estimating model parameters and model validation. Section 5 briefly discusses our current thoughts on how we might design future experiments to take advantage of the rate-based framework to use degradation data acquired from cells under variable stress.

2. Cumulative degradation models

The battery literature contains a number of model forms that express the cumulative degradation of the response of interest (that measures state of health) as a function of time and the stressing factors(s). A wide variety of model forms have been proposed (e.g., see [3]). These forms can be mechanistic, empirical, or mixed. Aging temperature is a common stress factor. Discharge impedance is commonly used to measure state-of-health and, therefore, can be used to measure degradation [2]. In such cases, the expected cumulative degradation of a cell (measured by increasing impedance) is often represented by a model of the form $\mu(T;t) = a + k(T)\cdot f(t)$, where $\mu(T;t)$ represents the expected value of cell impedance after exposure to temperature T for time t. In general, we assume that $\mu(T;t)$ is an increasing function of both t and T. In some cases, we use the convention that $\mu(T;t=0)=1$. This convention would pertain to the case where the response variable is expressed as a value that is relative to the observed response at $t=0$. For example, Thomas et al. [4] considered a model of the form,

$$\mu(T;t) = 1 + \exp\left\{\beta_0 + \beta_1 \cdot \frac{1}{T}\right\} \cdot t^{1/2}.$$

Note that cumulative degradation models are generally formulated in terms of exposure to a constant stress level. Thus, such models are often only used to predict degradation at, for example, isothermal conditions. This is significant, since cells are often deployed in applications where isothermal conditions do not exist. While the instantaneous degradation rate can be derived by differentiating the cumulative degradation models, it may be difficult to concisely express the rate in terms independent of t. In such cases, it may be difficult to predict the level of degradation in cases where the stress level (temperature) is not constant. Thus, there is motivation to develop rate-based degradation models which, by construction, can predict the cumulative degradation at non-isothermal conditions.

3. Rate-based degradation models

Often, it can be more natural to conceptualize a degradation model in terms of a rate rather than in terms of accumulated degradation. Chan and Meeker [5] describe a general approach for evaluating degradation-based reliability that is based on a degradation-rate model. The integration of the degradation rate with respect to time gives the cumulative degradation as a function of the stressing history. We also consider models that can be expressed in a differential form. As in the case of cumulative degradation models, the form of rate-based models can have a physical, empirical, or mixed basis. Here, we restrict rate-based models to cases where the rate of degradation depends only on the current stress and the current level of degradation, but not the detailed history of the degradation process. This is somewhat analogous to the "cumulative exposure" model for accelerated life tests discussed by Nelson [6] in which "the model assumes that the remaining life of specimens depends only on the current cumulative fraction failed and current stress – regardless how the fraction accumulated." Peng and Tseng [7] extends the cumulative exposure concept to accelerated degradation testing in which it is assumed that "the degradation path has a memoryless property, which means the rate of degradation depends only on the current stress, and not on the history of the process." The general form of the degradation-rate model described by Chan and Meeker [5] also assumes that the degradation rate depends only on the current level of stress. Here we allow the rate of degradation to also depend also on the current level of degradation. For example, in the case with a temperature as the sole stress factor, $d\mu/dt = g(\mu, T(t))$. The cumulative degradation over the temperature profile $T[0, t]$ is therefore given by

$$\mu(T[0,t]) = \int_0^t g(\mu(\tau), T(\tau); \alpha_1, \alpha_2, \ldots, \alpha_p)d\tau,$$

where g also involves model parameters (α_1, α_2, ..., α_p) that must be estimated. The model parameters are generally estimated using nonlinear regression with the observed degradation data. The observed degradation data used to estimate the model parameters could be acquired as a consequence of non-isothermal stress. The resulting fitted model can then be applied to predict the degradation behavior over some user-specified temperature profile that can be constructed to match any particular application environment.

3.1. Estimating model parameters

The experimental data are typically acquired by repeatedly measuring a number of cells. To illustrate, consider the following notation. Let

Y_{ij} = the jth measurement of the ith cell (for $i = 1{:}N$ and $j = 1{:}n_i$)
t_{ij} = time at which Y_{ij} was acquired, and
$T[0,t_{ij}]$ = temperature profile experienced by the ith cell through t_{ij}.

The collection of data can be compactly expressed by

$$\begin{array}{l}
\{Y_{11}; t_{11}, T[0, t_{11}]\}, \{Y_{12}; t_{12}, T[0, t_{12}]\}, \ldots, \{Y_{1n_1}; t_{1n_1}, T[0, t_{1n_1}]\} \\
\{Y_{21}; t_{21}, T[0, t_{21}]\}, \{Y_{22}; t_{22}, T[0, t_{22}]\}, \ldots, \{Y_{2n_2}; t_{2n_2}, T[0, t_{2n_2}]\} \\
\ldots \\
\{Y_{i1}; t_{i1}, T[0, t_{i1}]\}, \{Y_{i2}; t_{i2}, T[0, t_{i2}]\}, \ldots, \{Y_{in_i}; t_{in_i}, T[0, t_{in_i}]\} \\
\ldots \\
\{Y_{N1}; t_{N1}, T[0, t_{N1}]\}, \{Y_{N2}; t_{N2}, T[0, t_{N2}]\}, \ldots, \{Y_{Nn_N}; t_{Nn_N}, T[0, t_{Nn_N}]\}
\end{array}$$

The parameter estimation process will likely involve nonlinear regression. Inherent in the nonlinear regression process is a kernel function (h) that predicts Y_{ij} by numerically integrating the degradation rate-based model over the temperature profile $T[0, t_{ij}]$ conditioned on the current set of model parameter values, i.e., $\hat{Y}_{ij} = h\{t_{ij}, T[0, t_{ij}]; \alpha_1, \alpha_2, \ldots \alpha_p\}$. For example, when using MATLAB (MathWorks, Natick, MA) we let the kernel function be an input to the nonlinear regression module, *nlinfit*. The nonlinear regression procedure searches for the set of model parameter values that optimizes some objective function that is expressed in terms of the differences between $\hat{Y}_{ij}$ and Y_{ij}. Within the nonlinear regression procedure, the kernel function is computed many times for various sets of the model parameter values. Each computation of $\hat{Y}_{ij}$ involves proceeding through the temperature profile at an appropriate time step, Δt, using the recursive relationship $\hat{Y}(k) = \hat{Y}(k-1) + g(\hat{Y}(k-1), T(k)) \cdot \Delta t$ that is illustrated in Table 1.

Estimates of the model parameters ($\hat{\alpha}_1, \hat{\alpha}_2, \ldots, \hat{\alpha}_p$) are obtained at the end of the iterative nonlinear regression process resulting in a fitted rate-based model denoted by

$$\frac{d\mu}{dt} = g(\mu(t), T(t); \hat{\alpha}_1, \hat{\alpha}_2, \ldots, \hat{\alpha}_p).$$

Note that the cost of computing the kernel function for rate-based models with non-isothermal profiles can be expensive when

Table 1
Construction of $\hat{Y}_{ij}$.

$\delta=t/\Delta t$	$T(\delta)$	$\hat{Y}(\delta)$	$\frac{d\hat{Y}(\delta)}{dt}$
0	$T(0)$	$\hat{Y}(0)$	$g(\hat{Y}(0), T(0))$
1	$T(1)$	$\hat{Y}(0)+\frac{d\hat{Y}(0)}{dt}\cdot\Delta t$	$g(\hat{Y}(1), T(1))$
2	$T(2)$	$\hat{Y}(1)+\frac{d\hat{Y}(1)}{dt}\cdot\Delta t$	$g(\hat{Y}(2), T(2))$
.	.	.	.
.	.	.	.
.	.	.	.
$m=t_{ij}/\Delta t$	$T(m)$	$\hat{Y}(m-1)+\frac{d\hat{Y}(m-1)}{dt}\cdot\Delta t$	$g(\hat{Y}(m), T(m))$

compared to computing the analogous kernel function for cumulative rate-based models with isothermal profiles (where $\hat{Y}_{ij}$ can be computed directly).

3.2. Predicting the degradation behavior over an application-specific temperature profile

Given the fitted rate-based model, one can predict the cumulative degradation over an application-specific temperature profile (ASP), $T[0, t]_{ASP}$, using a numerical approximation to evaluate $\hat{Y}(T[0,t]_{ASP})=\int_0^t g(\hat{Y}(T[0,\tau]_{ASP}), T(\tau);\hat{\alpha}_1,\hat{\alpha}_2,\ldots,\hat{\alpha}_p)d\tau$ (e.g., see Table 1).

4. Illustrative example

Here we illustrate the use of rate-based models by using experimental data discussed in [4].

As described in [4], the experimental data were acquired from high-power SAFT VL7P lithium-ion cylindrical cells. The purpose of the experiment was to estimate the mean lifetime of this cell technology via their observed degradation in performance. Briefly, nine cells were exposed to each of the following three temperatures: 40 °C, 47.5 °C, and 55 °C. Three additional cells were exposed to 30 °C. Prior to initiating the experiment and at an interval of every 31.5 days following initiation, the cells were subjected to a reference performance test (RPT) at 30 °C to assess performance degradation. As part of each RPT, the discharge resistance was measured at a state-of-charge of 62% SOC. The test continued for about 221 days resulting in eight RPT's (including the initial RPT).

Thomas et al. [4] represented the experimental data with the cumulative degradation model,

$$\mu(T;t)=1+\exp\left\{\beta_0+\beta_1\cdot\frac{1}{T}\right\}\cdot t^{1/2},$$

where $\mu(T;t)$ represents the expected relative resistance (resistance at time t divided by the initial resistance). The model matched the experimental data reasonably well. However, based on a bootstrap procedure [4], there was some indication of lack-of-fit. Based on this cumulative degradation model, the expected relative resistance ($\hat{\mu}$) is the solution to the equation, $(1/2)\hat{\mu}^2-\hat{\mu}+(1/2)=(1/2)\int_0^t \exp\{2\cdot(\hat{\beta}_0+\hat{\beta}_1\cdot(1/T(\tau)))\}d\tau$. For this particular model form, we are able to obtain a relatively simple expression for cumulative degradation over a non-constant stress profile. However, other model forms may not be amenable to such a compact expression.

We have found an alternative model form that provides a closer fit to the experimental data. This rate-based model is of the form $d\mu/dt=k(T)\cdot\mu^{-\rho}$ with the initial condition $\mu(T;0)=1$, where $k(T)=\exp\{\beta_0+(\beta_1/T)\}/(\rho+1)$ and $\rho>0$.

The general form of the model, $d\mu/dt=k(T)\cdot\mu^{-\rho}$, was motivated by observing a decreasing rate of degradation with time where at a particular degradation state (μ), the rate depends on temperature. The Arrhenius form of the effect of temperature was assumed. This model form is designed to provide a flexible family of rate models

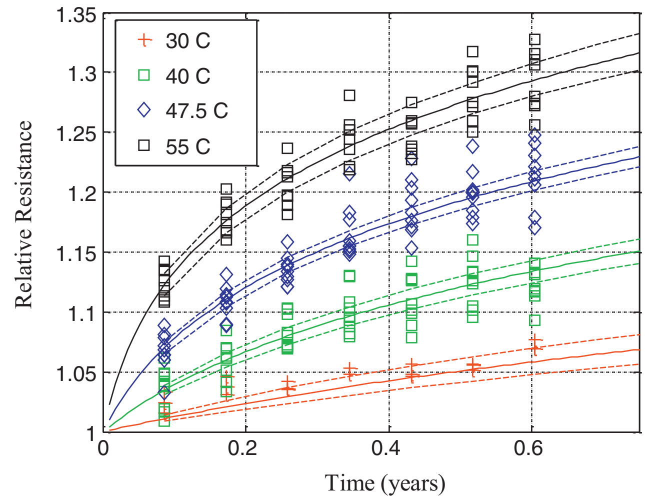

Fig. 1. Fitted degradation model with 95% confidence intervals and data.

that depend on the current state and exposure temperature such that the rate of resistance growth decreases with increasing resistance. This model, which might have application elsewhere, could apply to a linear decay rate where a reaction was independent of the thickness of a film, or a square root of time dependence that mimics resistance of a film growing via diffusion limitations, or something else. The Arrhenius term, $k(T)$, also gives this model form some physical/chemical basis.

Estimates of the model parameters could be obtained using the method described in Section 3.1.

However, since the individual cells were exposed to isothermal conditions, one can use a simpler approach in this case. First, integrate the rate-based model assuming that T is constant. This yields the cumulative degradation model $\mu(T, t)=[\exp\{\beta_0+(\beta_1/T)\}\cdot t+1]^{1/(\rho+1)}$. The model parameters can be estimated by using nonlinear regression with the data

$$\{Y_{ij};t_{ij},T_i\},\ i=1:N, j=1:N_i.$$

Following [3], robust nonlinear regression was used with the 40 °C, 47.5 °C, and 55 °C data in order to estimate the model parameters. The estimated model parameters (with standard errors) are:

$$\hat{\beta}_0=40.73\quad(2.2)$$
$$\hat{\beta}_1=-12,194\quad(680),\quad\text{and}$$
$$\hat{\rho}=11.03\quad(0.48).$$

Confidence intervals for the model parameters can be obtained by adding and subtracting multiples of the standard errors to the respective parameter estimates. An approximate 95% confidence interval for a given parameter is the estimate plus or minus twice the respective standard error. For example, an approximate 95% confidence interval for β_0 is [36.3, 45.1]. The fitted degradation model (with data) is illustrated in Fig. 1. Confidence intervals (at the 95% level) representing the uncertainty in the average performance (across the cell population) over time and temperature are also provided. One can compare this model with the model that was presented in [4]. As seen in Fig. 1, the current model generally seems to pass closer to the middle of the observations in each time/temperature group than the model presented in [4] (compare with Fig. 2 in [4]). While the rate-based model seems to underpredict the resistance increase at 30 °C, the apparent discrepancy is well within what might be expected given a relative measurement error of about 1% (see below).

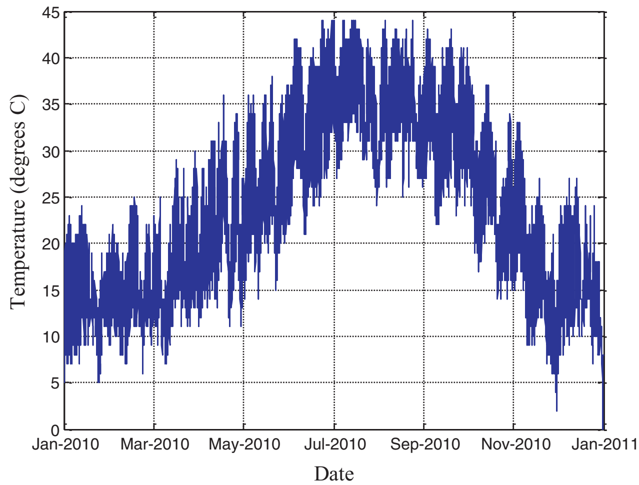

Fig. 2. Hourly temperature profile: Phoenix, AZ, Calendar year 2010.

Differences between the observed data and model predictions were assessed in the context of the error model described in [4]. Briefly, the error model is of the form $Var(Y_i(X;t)) \approx \sigma_\delta^2 \cdot (\mu(X;t)-1)^2 + 2\cdot\sigma_\varepsilon^2$, where σ_ε^2 is the measurement error and σ_δ^2 is a random cell-specific effect. The estimates of the error model parameters are $\hat{\sigma}_\delta^2 = 3.6\times10^{-3}$ and $\hat{\sigma}_\varepsilon^2 = 1.2\times10^{-4}$, respectively. Thus, the cell-specific proportional effect is estimated to have a standard deviation of about 0.06 and the measurement error is estimated to have a relative standard deviation of about 0.01. When the using the bootstrap procedure [3] (which incorporates the error model), there was no indication of lack of fit.

For this illustrative example, the assumption of "lack of memory" in the degradation process cannot be evaluated due to the fact that cells were exposed only to isothermal stress. Nevertheless, using the "lack of memory" assumption, it is interesting to apply the fitted rate model to predict the degradation for a hypothetical temperature profile. To illustrate, consider the hourly ambient temperature profile of Phoenix, AZ during 2010 that is exhibited in Fig. 2 [8]. Using the method discussed in Section 3.2 and based on the fitted degradation model, if we expose cells to this annual profile five consecutive times we predict the degradation profile illustrated in Fig. 3. The predicted degradation profile based on the cumulative degradation model from [4] is also displayed for

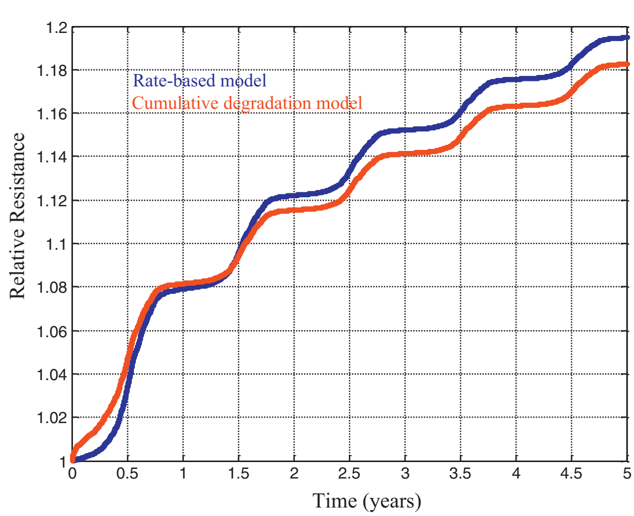

Fig. 3. Predicted degradation profiles for rate-based and cumulative degradation models.

purposes of comparison. Note that the plateaus in the predicted relative resistance relate to the low-temperature portion of each annual cycle. While the resistance profiles produced by the two models are grossly similar, the rate-based model begins with a gentler increase but reaches higher levels of resistance. The unavailability of variable stress data makes it impossible to rigorously compare the two models. Note that the predicted lifetime of the cell would be determined by the predicted time required to reach a certain level of cumulative degradation.

5. Experimental design and model validation

To date, due to the focus on accumulated degradation models, most calendar life experiments involve constant stress. Consideration of rate-based models can motivate a number of alternative experimental designs to assess calendar-life. While one might continue to expose some cells to isothermal stress, other cells could be targeted to experience non-isothermal exposure. Due to the nature of the parameter estimation process described in Section 3.1, the data acquired from all cells (independent of the nature of temperature exposure – isothermal versus non-isothermal) could be used either to estimate the model parameters or to validate a model. It would be desirable to subject some of the cells to increasing stress levels and others to decreasing stress levels. The temperature profiles could be discrete (e.g., step changes) or continuous (e.g., sinusoidal). One could also vary the frequency and amplitude of the temperature variations. We are currently investigating experimental designs containing various combinations of stress profiles for studying other cell technologies.

One could opt to develop degradation models with data acquired from cells exposed to isothermal environments and validate the models with data acquired from cells exposed to non-isothermal environments. However, true validation of degradation models requires that cells be tested at stress profiles that are similar to use conditions.

In cases where the validation data are inconsistent with predictions from the developed model, one needs to modify the form and/or assumptions of the model. If the current degradation rate does depend on the detailed past history of the degradation process, then the degradation measure does not adequately represent the state of health. Other performance measures (possibly in combination) may be needed to represent the state of health. For example, the growth of a solid electrolyte interphase (SEI) layer may be accompanied by an increase in resistance. Suppose the resistance of the existing SEI layer is a function of the circumstances under which it was formed, and, in turn, affects the nature of the layer and kinetics of further layer growth. In such a case, the current degradation rate would likely depend on the detailed prior history of the degradation process. Full characterization of the state of health of the cell might require higher-dimensional data (e.g., electrochemical impedance spectroscopy [9,10]). In such a case, the degradation model would be more complex and likely involve a set of equations of the form:

$$\left\{ \frac{d\mu_1}{dt} = g_1(\mu_1, \mu_2, \ldots, \mu_q; T(t)), \ldots, \frac{d\mu_q}{dt} = g_q(\mu_1, \mu_2, \ldots, \mu_q; T(t)) \right\}.$$

where q is the dimension of the state-of-health measure. We plan to incorporate such measurements in our future degradation studies.

6. Conclusion

This paper provides methodology for constructing rate-based degradation models. By construction, such models can provide predictions of degradation accumulated over variable stress conditions. Thus, this methodology can be beneficial when the stress conditions in the application of interest are variable such as in the case of lithium-ion technology used in transportation applications. While the methodology was illustrated with lithium-ion cells under thermal stress, it can be applied more generally to situations involving other technologies with other degradation measures and stress factors.

Acknowledgements

This work was performed under the auspices of the Office of Energy Efficiency and Renewable Energy within the United States Department of Energy. Sandia National Laboratories is a multi-program laboratory managed and operated by Sandia Corporation, a wholly owned subsidiary of Lockheed Martin Corporation, for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000. The authors also acknowledge DOE support under Contract No.'s DE-AC02-06CH11357, DE-AC07-05ID14517, and DE-AC03-76SF00098.

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