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A physics based reduced order aging model for lithium-ion cells with phase change

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HIGHLIGHTS

- Reduced order model for cells with phase change electrodes.
- Two phase coexistence described using a concentration dependent diffusivity.
- Easy implementation of degradation to study the cycle life.
- Model captures experimentally observed signatures of phase transition and aging.

ARTICLE INFO

ABSTRACT

The electrochemical model has the potential to provide a robust and accurate battery management system, but is not the preferred choice as it involves solving non-linear, coupled partial differential equations. In the present work, a model order reduction of the complete electrochemical model for a lithium ion cell with phase change electrodes is carried out. The phase change phenomenon is described using a simple, concentration-dependent diffusivity derived from mixture rules. This reduced order model (ROM) is validated with experimental data from literature. The applicability of the model to capture the atypical behavior of the phase change electrode system is demonstrated. Using the cell response from ROM, charge−discharge asymmetry and path dependence in a lithium iron phosphate (LFP) cell are explored in detail. In addition, side reaction kinetics and solid electrolyte interphase formation are included in the ROM framework to enhance its capability to predict cell aging. The model is used to investigate capacity losses occurring in a phase change electrode cell. Insights from these results are used to suggest cell operating guidelines for maximizing utilization.

1. Introduction

With the advent of alternate energy automobiles such as electric and hybrid electric vehicles, into the commercial market, there is an ever increasing need for a robust Battery Management System (BMS). Within the numerous functions of a BMS, the most important is the accurate prediction of battery state and life. Conventional state estimators make use of equivalent circuit models (ECMs) [1]. In spite of their high speed and accuracy, these state estimators are weighed down by their non-predictive nature and use of a large number of empirical parameters. In the quest for longer lasting batteries, better electrodes involving phase change [2] or engineered composite materials [3] are developed. As ECM based estimators work best within the range of data for which they are tuned, it is difficult to incorporate the atypical behavior inherent to the novel electrode materials using these methods.

Physics based models are more generic than the equivalent circuit models as the processes occurring within the cell are represented accurately in the former. In this context, the electrochemical model (EM) proposed by Doyle et al. [4] is applied to a wide variety of electrochemical systems, including the lithium ion cells. The strength of this approach lies in its applicability to novel electrode materials that show atypical behaviors, like the multiphase coexistence. Intercalation/deintercalation of lithium in certain electrode materials can lead to the formation of one or more new phases. This phase changing property of the electrode most

often manifests as a non-monotonic response of the cell voltage. This feature attracts considerable research intrigue and hence is a widely studied area. For certain electrodes such as lithium iron phosphate (LFP) the two phase coexistence results in a constant discharge voltage [2] which holds considerable industrial interest. Widely used negative electrode material, graphite, is also known to transform to a number of phases during cycling [5] adding to the importance of this phenomenon in the electrochemical model.

A variety of approaches are adopted in the literature to include the phase change phenomenon within the electrochemical model. These range from simple physical models which assume the phase formation to be isotropic to complex thermodynamics based models which take into account the anisotropy in phase formation. In one of the pioneering efforts, Srinivasan and Newman [6] represent the new phase formation using the shrinking core physics. Instead of an active material sphere with a single phase, this model assumes a shell and core with the phase boundary at an equilibrium concentration. This approach is applied to model the discharge of an LFP half-cell and an LFP/Carbon (C) full cell [7–9]. The extension of the shrinking core approach to model the charge part of the cycle is proposed via a generalized moving boundary model by Khandelwal et al. [10]. Using this approach, features of the phase transformation in LFP, namely, an asymmetry in the charge and discharge cycles, path dependence of the response and the tangential phase propagation within the LFP material are captured. Motivated by the experimental evidence of anisotropic lithium insertion [11,12], phase field models have been proposed [13–16]. These models are most useful to understand detailed aspects of the phase transformation physics but can prove difficult to translate to onboard algorithms. A major difficulty with the phase change system is to track multiple phase boundaries formed during cell cycling. This is addressed in the generalized moving boundary approach [10] within the shrinking core family of models, while it is obtained as wave solution of the phase field parameter in the phase field family [13] of models, both involving complicated solution schemes.

In an alternate approach, instead of considering a physical boundary, researchers make use of a concentration dependent diffusion coefficient [17,18]. The concentration dependence manifests as a thermodynamic factor/activity correction multiplying the constant diffusion coefficient. But, as electrolyte effects are not considered, this model is applicable only at rates until 1C. Safari and Delacourt [19] also make use of a concentration dependent diffusion coefficient albeit of empirical origin. The advantages of this model include a simplified approach to modeling the phase change whilst considering the highly resistive nature of the LFP material using a resistive-reactant model [20]. The model is validated with experiments on an LFP half-cell [19] and an LFP/C commercial cell [21]. Although the model successfully captures and explains features such as charge–discharge asymmetry and path dependence in LFP, the transport coefficients are obtained by fitting the model results to experiments increasing the dependency on cell data.

A lithium ion cell undergoes degradation from a variety of sources [22]. Electrodes are known to change in volume during the insertion/deinsertion process leading to fatigue and/or cracking while certain positive electrode materials are known to dissolve into the electrolyte [23]. The most common and well-studied mechanism is the occurrence of side reactions within the cell. This involves reduction of the electrolyte at the negative electrode leading to the formation of a Solid Electrolyte Interphase (SEI). The electrochemical model has been used extensively to predict the degradation of lithium ion cells. Studies incorporating just the solvent decomposition reaction [24] or combined with the SEI formation [25] have been carried out in the past. The use of empirical equations to model the capacity loss [26] or the use of

first principles based equations describing the SEI growth [27] are incorporated in the aging models. Models predicting calendar life [28] or cycle life [27] of lithium ion cells are also studied. Safari et al. [25] present a multimodal aging model for the lithium cobalt oxide (LCO) cell, valid for cycle life and both constant voltage and OCV storage. In all of the above studies the degradation model is included in one form or the other but is valid for cells with single phase active material electrodes. In terms of modeling the degradation/aging of a phase change electrochemical cell, Safari and Delacourt [29] model the aging of a commercial LFP/C cell. The phase change electrode is modeled using the earlier approach [19] of a concentration dependent diffusivity and the resistive-reactant model. The degradation is included in the form of an SEI evolution equation while considering solvent diffusion as the limiting step to the SEI formation. Although it incorporates phase change, degradation and uses the single particle model approach, the applicability of this model is limited to low and nominal rates as electrolyte effects are not included.

In order to make the electrochemical model amenable for on-board use, it needs to be combined with a certain order reduction methodology. Also, cell aging studies involve long time simulations of the electrochemical degradation models. This proves time consuming for a high number of cycles. Therefore, most often researchers try to incorporate simplified models which can reduce the simulation run time. The single particle model (SPM) proposed by Subramanian et al. [30] and applied by Safari and Delacourt [19] to study degradation of LFP/C cells, is a widely used approach. It is, however, found to be valid only until a current rate of 1C. A number of reduced order models have been proposed by various groups. These reduced order models include but are not limited to the following: enhanced single particle model [31,32], reformulated models [33], state variable models [34] and proper orthogonal decomposition (POD) based models [35]. Of these models, apart from the single particle model, the rest make use of various complicated mathematical techniques for model order reduction. The state variable models need a post processing step such as residue grouping which involves sophisticated mathematics. In addition, the reformulated model and the POD based model require an initial guess of variables and initial data for ensemble, respectively. In the enhanced SPM, the physical basis of the SPM is maintained while the electrolyte effects are included via parabolic [32] or Galerkin approximations [31].

In an alternate approach to reduce the model order, Kumar [36] propose a completely physics based methodology developed using volume averaging. The solid phase equations and the electrolyte profiles are obtained consistently using profile based approximations following the volume averaging. This reduced order model (ROM) approach has a greater range of applicability in terms of current rates, when compared to the SPM and a higher predictability than the numerical model order reduction techniques. On the same lines, Kumar et al. [37] propose an algebraic ROM developed for linearly varying currents motivating that any complicated current profile can be built of smaller linear current segments. These studies are however, confined to single phase electrode cells. Also, prediction of degradation upon cycling or storage is not studied using this model.

A model for a phase change system should incorporate the phenomenon in a simple yet generic way, should be able to predict the cell capacity loss due to aging, should not require extensive tuning to experimental data and should be amenable for onboard implementation in devices. Although the electrochemical model is an ideal approach to predict accurate cell response, to incorporate it in a BMS algorithm a reduced order model is required. The aim of the present work is to develop a physics based reduced order electrochemical model which can predict the response of fresh and