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Generalized moving boundary model for charge–discharge of $LiFePO_4$/C cells

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HIGHLIGHTS

- Generalized moving boundary model for lithium ion cells with phase change electrode.
- Numerical implementation is obtained using a pseudo 2D approach.
- Model captures tangential phase front movement and phase separation in $LiFePO_4$.
- Simulation shows charge–discharge asymmetry and path dependency in $LiFePO_4$.

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ABSTRACT

Lithium ion cells with electrode materials that undergo phase transitions, like $LiFePO_4$, have unique charge–discharge characteristics. In this work a generalized framework of moving boundary approach is proposed to model the path dependent charge–discharge response of porous electrodes that exhibit multi-phase coexistence. Using the Landau transformation the governing equation in moving coordinate is transformed to fixed coordinate and a suitable path dependent algorithm is devised and is implemented in a multi-physics environment. Simulation results show that tangential propagation of the phase front, often seen in experiments, can be addressed by this model. Incorporation of multi-phase diffusion predicts the characteristic phase separation in $LiFePO_4$ particles. The proposed model successfully captures the charge–discharge asymmetry of $LiFePO_4$ based cells. Efficacy of the proposed approach to model the path dependence of cells with phase change electrodes is demonstrated by simulating the response of $LiFePO_4$/graphite cell subjected to a charge–discharge pulse. Numerical studies are performed to study the effect of important model parameters to enhance cell design and to bring out unique features in the cell response due to multi-phase coexistence.

1. Introduction

Lithium iron phosphate ($LiFePO_4$, LFP) is increasingly deployed as positive electrode material in lithium ion cells owing to its high thermal stability, cost effectiveness, non-toxic nature and long cycle life [1–3]. Given these advantages, it however suffers from limitations [4–6] due to low electronic conductivity resulting in higher Ohmic drop in the electrode and low rate capability leading to reduced active material utilization. Several research efforts over the last decade have enabled significant improvements by enhancing properties of the material through suitable modifications. Some of the prominent ideas pertain to coating of LFP particles with carbon to improve electronic conductivity [7,8], decrease in particle size for reduction in transport losses [9,10], use of LFP nano-crystals to increase the surface area [11], solid–solution doping by supervalent metals [12] etc. Because of these developments, LFP based cells have found applications in mobile, automotive and other industries.

The wide spectrum of applications of LFP based cells encourages electrochemical modeling to understand the underlying cell processes. In addition to optimized cell design, electrochemical models enable robust battery management systems (BMS) development for on-board applications. A critical challenge in developing BMS algorithm for cells with LFP based electrodes is the non-monotonic dependence of open circuit potential on capacity. This behavior is

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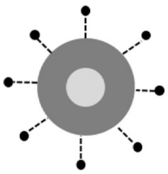
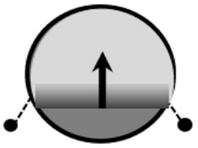
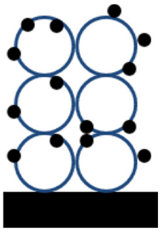
also observed in other electrode materials, mainly due to the underlying crystallographic solid–solid phase transformation. Therefore, modeling phase change is an active area of research that enables development of a complete electrochemical model [8] for lithium based cells. These models are proposed at various length scales varying from crystalline level to continuum level. Existing approaches in electrochemical modeling of LFP electrodes can be classified into three categories viz., (a) shrinking core models [13–18], (b) phase field models [19–23], and (c) resistive reactant models [24–28]. A brief overview of these models is provided in Table 1.

An electrochemical model based on a core–shell approach was first proposed for LFP electrode by Srinivasan and Newman [14] and later developed [15] for an LFP/C cell. As mentioned in Table 1, this approach captures the discharge behavior by considering intercalation coupled mass transport due to diffusion in a Li rich β phase and movement of two-phase interface. In this framework however, the diffusion in Li-poor phase (α) is neglected. The underlying construct of this model assumes diffusion in a particle causing lithium flux movement normal to the phase boundary. On the contrary, experimental studies [1] reveal Li movement in a tangential direction. The diffusion under phase transition is modeled using sharp interface model which predicts a fast Li transfer across the phase boundary between α and β phase. Followed by this work, a more sophisticated version of the core–shell model in which diffusion in both phases of $LiCoO_2$ cathode [13] is developed. Also, Wang and co-workers in Ref. [16], proposed a model for LFP, where the interface movement between the two coexisting phases was considered to be sluggish by incorporating a mobility term in the interface movement equation. Kasavajjula [17] further enhanced this model by considering the Li diffusion in both phases together along with the interface mobility. Recently, a multi-scale approach proposed by Dargaville and Farrell [18] employed the shrinking-core model of Srinivasan and Newman [14] to represent the three size scales present in a porous LFP cathode, namely crystals, agglomerates, and the porous cathode itself.

Above developments show that the core–shell approach provides a mathematically consistent framework to incorporate effects of phase transitions in a complete electrochemical model. The existing models [13–18] do not however account for factors such as diffusion in the Li-poor LFP phase (α), Ohmic drop due to carbon coating to model inhomogeneous current distribution etc. As a result, the application of the shrinking core approach is limited to represent discharge behavior only. Safari and Delacourt [26,27] recently proposed a reduced order electrochemical model using the resistive reactant concept without incorporating the details of phase transformation in LFP electrode. It successfully captures the charge–discharge asymmetry but does not represent the features due to phase transformation in terms of tangential front propagation, phase separation and path dependence. Hence, development of a suitable electrochemical approach that models the multi-phase coexistence during charge and discharge consistently is highly desirable. Considering the simple and robust framework of shrinking core model an extension of this approach to represent multiple charge–discharge cycle is yet to be attempted. Such a general framework would also enable detailed investigation of charge–discharge asymmetry and path dependence [29] frequently reported for LFP electrodes.

In the present work a general electrochemical framework is proposed that identifies the mechanisms governing voltage response in cells with phase change electrodes. In the following sections, a generalized path dependent moving boundary model is developed and subsequently modified as a cell design tool. Section 2 describes the phase transformation processes in LFP which brings

Table 1
An overview of existing electrochemical models for LFP.

Technique	Shrinking core	Phase field model	Resistive reactant
			
Principle	Concept of shrinking core is used to model phase transition	Non-local chemical potential is used to ascribe diffusion	Non-uniform current distribution due to resistive reactant Ohmic drop
Seminal Work	Padhi, Nanjundaswamy, and Goodenough [1], Srinivasan and Newman [14]	Singh, Ceder and Bazant [19]	Thomas Alyea [24]
Pros	1. Provides physical insight of phase transition 2. Models discharge curves 3. Sharp interface model	1. Models observed tangential phase front propagation 2. Diffused interface description	1. Models characteristic charge–discharge asymmetry 2. Well suited for multiple cycle application
Cons	1. Normal phase front propagation 2. Inconsistent charge–discharge asymmetry [29] 3. Not suited for multiple cycles	1. Computationally elaborate 2. Not suited for multiple cycles 3. Needs further development for integration with EM	1. Phase transition is not considered 2. More number of parameters