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Approximate analytical solutions for a shrinking core model for the discharge of a lithium iron-phosphate electrode by the Adomian decomposition method

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ABSTRACT

In this paper, we solve the mathematical model that describes the variation of lithium concentration in a lithium iron-phosphate ($LiFePO_4$) particle during the process of lithium intercalation into the particle with shrinking core during the discharge process. The model is composed of a second-order linear partial differential equation satisfied by the distribution function of lithium concentration with an unknown moving boundary function and an ordinary partial differential equation satisfied by these two unknown functions. An approximate analytic solution for the partial differential equation with undetermined parameters is first given by the Adomian decomposition method (ADM) and then we require it to satisfy the moving boundary condition to determine these parameters in order to obtain the solution for the model. We need not transform the moving boundary into a fixed boundary as in prior research. Our new approach in solving the model shows that the ADM is an efficient method for solving moving boundary problems. Based on the algorithm provided by the ADM, we decompose the complex operation of solving the model into a sequence of sub-operations which are easily implemented by using the numerical and symbolic operations in MATLAB. By completing these sub-operations, we obtain an accurate expression of the approximate analytic solution for engineering simulations.

1. Introduction

Partial differential equations (PDEs) or systems of such equations, which are subject to a free or moving boundary, are known as Stefan problems [1–3]. As a particular kind of boundary value problem for a partial differential equation, Stefan problems are relatively uncommon in mathematics. But considerable mathematical models arising in applied science and engineering, which are characterized by a phase boundary moving with time, belong to the class of Stefan problems such as the models describing solidification of metals, freezing of the ground and water, melting ice, etc. Shrinking core models subject to a moving boundary often appear in chemical and electrochemical engineering, such as the model for the fluid–solid uncatalyzed reaction [4] in chemical reaction engineering and the discharge model for the negative electrode of the lead-acid battery [5] in electrochemical engineering, etc.

In recent years, $LiFePO_4$ has been used extensively as a cathodic material in the iron phosphate-based lithium-ion secondary battery due to its many advantages such as a high theoretical capacity, thermal stability, relatively low environmental

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impact, etc. Meanwhile, much theoretical research has been done on the $LiFePO_4$ porous cathode which consists of carbon black, $LiFePO_4$ particles and binder. For modeling the discharge behavior of the porous cathode, Srinivasan and Newman [6] adopted two characteristic scales, namely the electrode scale and the $LiFePO_4$ particle scale to deal with the mathematical model, while Dargavillez and Farrell [7] adopted three characteristic scales, namely the electrode and particle scales as well as a scale of a small cluster gathered by carbon black and $LiFePO_4$ particles.

The key scale is the smallest scale, the $LiFePO_4$ particle scale because the electrochemical cell reaction only occurs on the particle scale. During the discharge, the processes of lithium intercalation into a $LiFePO_4$ particle will exert fundamental influence on the performance of the battery. As evidenced from X-ray diffraction patterns of the material at various stages of lithiation, Srinivasan and Newman [6] developed a mathematical model for lithium intercalation and phase change in a particle in the secondary battery to understand the cause for the low power capability of the material. The juxtaposition of the two phases is assumed to be in the form of a shrinking core, where a shell of one phase covers a core of the second phase. Diffusion (i.e. intercalation) of lithium through the shell and the movement of the phase interface are described.

We divide the processes of lithium intercalation into three stages (see Fig. 1). In the first stage, after a very small fraction of the lithium (Li) from the surface of the particle intercalates into the iron-phosphate ($FePO_4$) solid lattice, a Li-deficient single phase Li_yFePO_4 (y is close to zero) forms in the whole spherical particle. As the lithiation reaction continues at the particle surface, a thin spherical shell of Li-rich phase $Li_{1-x}FePO_4$ (x is close to zero) covers a core of the Li-deficient phase. As the electrode is discharged further, more lithium is transported to the Li-deficient core through the shell region and this leads to the continual shrinking of the two-phase interface towards the center of the particle. In the second stage, the Li-deficient phase and Li-rich phase coexist in the particle region. As discharge continues in the last stage, when the radius of the core reaches approximately $\frac{1}{100} \sim \frac{10}{100}$ of the radius of the particle, the two-phase interface disappears and the whole particle is now composed of the single Li-rich phase. Further discharging results in the complete intercalation of the Li into the solid lattice and the conversion of the particle to the fully lithiated form.

Neglecting the initial single-phase region, the second stage dimensionless concentration of lithium in the iron-phosphate lattice $\theta = \theta(\xi, \tau)$ and the dimensionless radius of the two-phase interface in the iron-phosphate particle $\xi_i = \xi_i(\tau)$ [6,7] satisfy

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial\xi^2} + \frac{2}{\xi}\frac{\partial\theta}{\partial\xi}(\xi_i < \xi < 1, 0 < \tau < \tau_1), \tag{1}$$

$$\frac{\partial\theta}{\partial\xi}(1,\tau) = I^*, \tag{2}$$

$$\theta(\xi,\tau) = \theta_0(0 \leqslant \xi < \xi_i, 0 < \tau < \tau_1), \tag{3}$$

$$\theta(\xi_i,\tau) = \delta(0 \leqslant \tau \leqslant \tau_1), \tag{4}$$

$$(\theta_0 - \delta)\frac{d\xi_i}{d\tau} = \frac{\partial\theta}{\partial\xi}(\xi_i,\tau)(0 < \tau < \tau_1), \tag{5}$$

$$\xi_i(0) = \xi_0, \tag{6}$$

where τ_1 is the time when the two-phase interface disappears, I^* is the current, θ_0 is the initial concentration of lithium in the iron-phosphate lattice, δ is the concentration of lithium in the shell at the phase-interface, ξ_0 is the initial radius of the two-phase interface, where all of these are dimensionless, positive parameters.

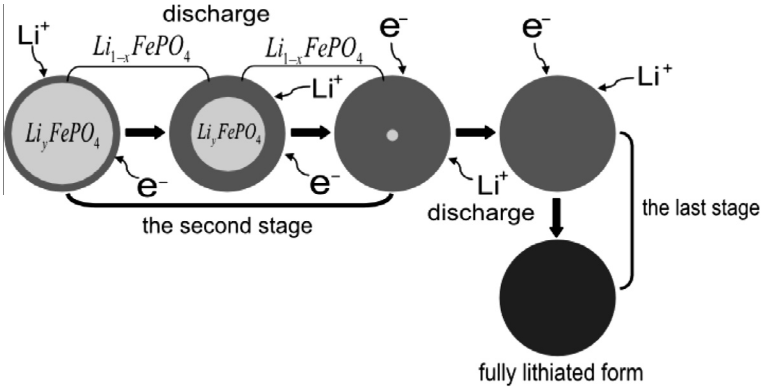

Fig. 1. The processes of the intercalation of lithium into a $FePO_4$ particle and the formation and disappearance of the moving boundary of the two phases during discharge.