Computers and Chemical Engineering 99 (2017) 31–39

Contents lists available at ScienceDirect

Computers and Chemical Engineering

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

Modeling the effect of aging on the electrical and thermal behaviors of a lithium-ion battery during constant current charge and discharge cycling

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ARTICLE INFO

Article history:
Received 27 September 2016
Received in revised form
14 December 2016
Accepted 3 January 2017
Available online 6 January 2017

Keywords:
Lithium-ion battery
Battery modeling
Battery aging
Cycling test

ABSTRACT

This paper reports a two-dimensional modeling to predict the aging effect on the variation of the electrical and thermal behaviors of a lithium-ion battery (LIB) cell under the constant current (CC) charge and discharge cycling over a long time. To account for the aging effects of the LIB cell due to cycling, the key modeling parameters are expressed as a function of cycling number. In order to validate the modeling methodology introduced in this paper, the modeling results towards the changes of the discharge curves and two-dimensional temperature distributions of the aged LIB cell during CC discharge at different C rates are compared with the experimental measurements after every thousand cycles. The electrical and thermal behaviors predicted by the modeling for the aged LIB cell show good agreement with the experimental data.

1. Introduction

Nickel-metal hydride (NiMH) batteries are successfully used in nonplug-in hybrid electric vehicles (Wikipedia contributors, 2016). Because a higher specific energy is required for plug-in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV) applications, most of the latest models of plug-in hybrid electric vehicle (PHEV) and battery electric vehicle (BEV) use lithium-ion batteries (LIBs) for onboard energy storage (Catenacci et al., 2013). The service life of LIB for PHEV and BEV applications is generally limited by aging, although it depends strongly on the usage conditions (Rezvanizaniani et al., 2014). The aging of LIB manifests itself in the variation of electrical and thermal behaviors such as capacity fade, cell voltage drop under load, and peak temperature rise during cycling (Cordoba-Arenas et al., 2015). It is, therefore, essential to predict the variation of electrical and thermal behaviors by including the effect of aging in the modeling and simulation tools of LIB for the optimal design and management of the vehicle electrical system in PHEV and BEV applications.

There have been many previous efforts concerning the aging mechanisms and the modeling to predict the aging for LIBs. The reviews on the aging mechanisms of LIBs are given in references (Arora et al., 1998; Aurbach, 2000; Wohlfahrt-Mehrens et al., 2004; Vetter et al., 2005; Barré et al., 2013; Nowak and Winter, 2015). Different models have been developed to account for various degradation mechanisms leading to the aging of LIBs (Darling and Newman, 1998; Arora et al., 1999; Broussely et al., 2001; Bloom et al., 2001; Spotnitz, 2003; Ramadass et al., 2003; Ramadass et al., 2004; Ploehn et al., 2004; Christensen and Newman, 2003; Christensen and Newman, 2004; Ning and Popov, 2004; Ning et al., 2006; Santhanagopalan et al., 2006; Subramanian et al., 2009; Safari et al., 2009; Delacourt and Safari, 2012; Deshpande et al., 2012; Doyle et al., 1993). Darling and Newman (1998) made the first attempt to model the influence of a side reaction on the operation of lithium intercalation electrode. Arora et al. (1999) presented a mathematical model to predict the conditions for the lithium deposition overcharge reaction on the carbon-based negative electrode of LIBs. Broussely et al. (2001) measured the long term calendar life of LIBs as a function of storage temperature. They fitted the experimental data to a model which relates capacity fade to time with a quadratic equation. Bloom et al. (2001) tested the accelerated calendar and cycle life of LIBs. They developed a semi-empirical life model of LIBs. Spotnitz (2003) reviewed the technical literature on the mea-

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http://dx.doi.org/10.1016/j.compchemeng.2017.01.006
0098-1354/

surements and models for predicting the capacity fade of LIBs. He developed polynomial expressions to estimate the capacity losses due to solid electrolyte interphase (SEI) growth and dissolution. Ramadass et al. (2003) developed a capacity fade prediction model for LIBs based on a semi-empirical approach. They used correlations for variation of the film resistance with cycling. Ramadass et al. (2004) developed a first principles-based model to simulate the capacity fade of LIBs through incorporation of side reactions with the existing Li-ion intercalation model. Ploehn et al. (2004) presented a one-dimensional solvent diffusion model to explain the capacity loss of LIBs during storage under float potentials at various temperatures. Christensen and Newman (2003) simulated the side reactions that lead to a change in the total amount of cyclable lithium and the effect of SEI resistance on the cycling of an LIB. They presented a mathematical model to estimate the SEI film growth rate, film resistance rise, and irreversible capacity loss due to film formation in LIBs (2004). Ning and Popov. (2004), Ning et al. (2006) developed a first principles base charge-discharge model to simulate the cycle life behavior of LIBs. Santhanagopalan et al. (2006) reviewed various models to predict the cycling performance of LIBs. Subramanian et al. (2009) presented the mathematical analysis for the reformulation of physics-based LIB models to improve computational efficiency. Safari et al. (2009) developed a multimodal physics-based aging model considering a solvent-decomposition side reaction leading to the growth of an SEI film at carbonaceous anode material for the life prediction of LIBs. Delacourt and Safari (2012) developed an aging model of a commercial graphite/$LiFePO_4$ cell that takes into account side-reaction kinetics and solvent-diffusion limitations across growing passive film at both anode and cathode. Deshpande et al. (2012) proposed a cycle life model of a graphite/$LiFePO_4$ cell to describe the lithium loss caused by coupled chemical degradation and fatigue mechanics. Methekar et al. (2011) discussed the potential for coupling the kinetic Monte Carlo model with the continuum model based on porous electrode theory to arrive at a multiscale model for analyzing capacity fade. Ramadesigan et al. (2012) reviewed the development of multiscale models at different length and time scales for the improved predictability of the capacity fade of LIBs from a systems engineering perspective. Ramadesigan et al. (2011) proposed an alternative approach to estimate the capacity fade of LIBs by extracting the effective kinetic and transport parameters from past measured voltage-discharge curves. Barré et al. (2013) reviewed the mechanisms, factors, and estimation methods of the aging of LIBs. According to their summary on the aging effects of LIBs, the SEI growth induces the loss of cyclable lithium and electrolyte decomposition. Furthermore, the solvent interaction with the graphite in the negative electrode may cause the graphite exfoliation and create gas which can crack the SEI. In terms of battery performance, both of the losses of cyclable lithium and active materials lead to the battery capacity fade and the battery resistance increase is engendered by the passive film growth at the surface of active material. Suthar et al. (2014) incorporated the contribution of intercalation induced stress generation as one of the main reasons for the capacity fade of LIBs to derive an optimal charging profile. Cordoba-Arenas et al. (2015) proposed semi-empirical capacity and power fade aging models for LIBs based on PHEV aging cycles. Most of the aging models for LIBs mentioned above (Ramadass et al., 2003, 2004; Arora et al., 1999; Ploehn et al., 2004; Christensen and Newman, 2003, 2004; Ning and Popov, 2004; Ning et al., 2006; Santhanagopalan et al., 2006; Subramanian et al., 2009; Safari et al., 2009; Delacourt and Safari, 2012; Deshpande et al., 2012) basically adopted a porous electrode model founded on the concentrated solution theory developed by Doyle et al. (1993) and altered the model of Doyle et al. (1993) to account for the degradation mechanisms leading to the aging of LIBs. Kwon et al. (2006) introduced a modeling strategy different from the rigorous porous electrode model (Doyle et al., 1993) to account for the effect of electrode configuration on the discharge performance of an LIB cell. They presented a model to compute the two-dimensional distributions of the potential and current density on the electrodes of an LIB cell. By not computing the potential distribution of electrolyte phase and the transport phenomena of lithium ion, the model of Kwon et al. (2006) cuts down considerable computation time in comparison with the rigorous porous electrode model (Doyle et al., 1993), while preserving the validity of the model. Kim et al. (2008, 2009, 2011b, 2013) carried out a two-dimensional modeling to compute the thermal behaviors of an LIB throughout charge and discharge processes based on the distributions of potential and current density on the electrodes acquired by following a similar procedure of Kwon et al. (2006). They reported that the thermal modeling results agree well with the experimental IR measurements. Kim et al. (2011a) and Yi et al. (2013) improved their model (Kim et al., 2008, 2009) to include the dependence of the discharge performance of an LIB on environmental temperature. Yi et al. (2015) enhanced the previous works (Kwon et al., 2006; Kim et al., 2008, 2011b, 2013, 2011a; Yi et al., 2013) to unravel the short time effects of the abrupt change of charge and discharge currents such as rest periods and pulse currents during the dynamic cycling of an LIB cell.

The modeling approach cited above (Kwon et al., 2006; Kim et al., 2008, 2011a,b, 2013; Yi et al., 2013, 2015) is useful for the modeling to analyze the electrical and thermal behaviors of a new LIB cell, because it requires much less computational burden than that of the rigorous porous electrode model (Doyle et al., 1993). It is, however, indispensable to make the previous modeling approach (Kwon et al., 2006; Kim et al., 2008, 2011a,b, 2013; Yi et al., 2013, 2015) accommodate the aging effects in order to model the performance decay of an aged LIB cell under the dynamic cycles for PHEV and BEV applications. In this work, a two-dimensional modeling is carried out to predict the effect of aging on the variation of the electrical and thermal behaviors of an LIB cell during cycling over a long time. The cycling tests are performed under the protocol of the constant current (CC) charge and discharge. Modeling results for the variation of the electrical and thermal behaviors of the LIB cell due to aging as a function of cycling number are to be compared with the experimental data collected from the cycling tests in order to show the validity of the modeling approach introduced in this work.

2. Mathematical model

A 14.6 Ah LIB fabricated by LG Chem. is modeled in this work. The LIB consists of $LiMn_2O_4$ positive electrodes, graphite negative electrodes, and porous separators impregnated with plasticized electrolyte. The modeling procedure used in this work for a new LIB cell at the beginning of cycling is similar to that of Yi et al. (2015). From the continuity of the current on the positive and negative electrodes during discharge, the Poisson equations to compute the potential distributions on the positive and negative electrodes are derived as follows:

$$\nabla^2 V_p = -r_p J \text{ in } \Omega_p \tag{1}$$

$$\nabla^2 V_n = +r_n J \text{ in } \Omega_n \tag{2}$$

where V_p and V_n are the potentials (V) on the positive and negative electrodes, respectively, r_p and r_n are the resistances (Ω) of the positive and negative electrodes, respectively, and J is the current density (current per unit area ($\mathrm{A\,m^{-2}}$)) flowing from the negative electrode to the positive electrode. Ω_p and Ω_n denote the computational domains of the positive and negative electrodes, respectively.

To account for the short time effects of the abrupt change of charge and discharge currents such as rest periods and pulse cur-