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Evaluation on Performance of Lithium-ion Batteries Based on Internal Physical and Chemical Parameters

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In this work, a new method for evaluating performance of Lithium-ion batteries by finding the association between internal physical/chemical parameters and batteries' degradation is developed. The research is divided into three stages: preparation, off-line analysis and online application. Achievements have been made on simulation model computation and simplification, parameter identification and parameter sensitivity analysis. This paper addresses the achievements and ongoing works involved in the three stages in brief.

1. Introduction

Evaluation on performance of Li-ion batteries, which includes the estimation of charge/discharge ability (state of charge) and the prognostic of remaining number of cycle life (state of health), is one of the most important functionalities of battery management system (BMS).

In the process of using batteries, only terminal voltage, loop current, shell temperature and electrochemical impedance spectroscopy (EIS) can be tested. It is easy to see that batteries behave differently when load or temperature change (Marc and John, 1996). Many applications of BMS estimate the status of batteries according to empirical and phenomenological models, Bayesian methods, etc.

A weighted Ah aging model is based on the assumption that the impact of a given Ah throughput on the lifetime depends on the details of the conditions during the Ah throughput, and the degradations under nonstandard conditions are the weighted forms of the degradation under standard condition (D.U. Sauer, 2003). An event-oriented aging model adds up the incremental loss of lifetime caused by different events for lifetime prediction in electrochemical systems (D.U. Sauer, 2008). The impact of either "different conditions" or "events" on lifetime must be identified experimentally or evaluated based on expert knowledge.

In most cases, SOC/SOH estimation needs to contend with multiple sources of errors, like modeling inconsistencies, system noise and degraded sensor fidelity. The Bayesian theory of uncertainty management provides a way to contain these problems. The relevance vector machine (RVM), the Bayesian treatment of the well known support vector machine (SVM) is incorporated into a particle filter (PF) framework, where statistical estimates of noise and anticipated operational conditions are used to provide estimates of remaining useful life (RUL) in the form of a probability density function (H. Wenzla, 2005).

One disadvantage of these applications is that the experimental testing work is tremendous due to various combinations of charge/discharge rates and temperatures. Besides, it is found that the empirical data is inconvenient to be used especially when load changes, which may cause non-ignorable errors. In fact, in many situations the loads of batteries, which are used in electric vehicles or portable electronics, do not remain unchanged, and even change dramatically. Therefore, people are increasingly aware that the lack of available information reflecting behavior changes of batteries is hindering the BMS from raising its level.

Some researchers managed to look into the interior of batteries to see what factors influence the performance of batteries in nature and how they play their roles. Ning et al. (2006) pointed out that side reactions and the increase of film resistance on anode lead to the loss of batteries' capacity. Ramadass et al. (2003), Zhang and Ralph (2008) revealed that SOH is mainly affected by the decrease of active

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material and “cyclable” Li-ion, while the degradation of capacity at higher charge/discharge rates is caused by the increase of resistance of solid electrolyte interface film and the decrease of diffusion coefficients of electrodes. Cai et al. (2013) also found that the disproportionation reaction would lead to the spinle-based cathode dissolving into the electrolyte and the formation of an inactive material layer which causes a resistance increase. In addition, some phenomena such as decomposing, deoxidation and transesterification will occur in electrolyte during the ageing process, which lead to extra capacity fade of the battery (Ein-Eli et al, 1997).
It is a pity that no quantitative descriptions of these relationships are given and the internal physical or chemical characteristics of batteries are hard to get when batteries are in service. Further researches also show that the mechanisms of different failure patterns interplay each other in the process of performance evolution, which makes the situation more complicated (Salking et al. 1999).
This paper presents a novel solution to extracting internal physical and chemical parameters of Lithium-ion batteries as their extended PHM characteristics. Figure 1 shows the roadmap of our research work.

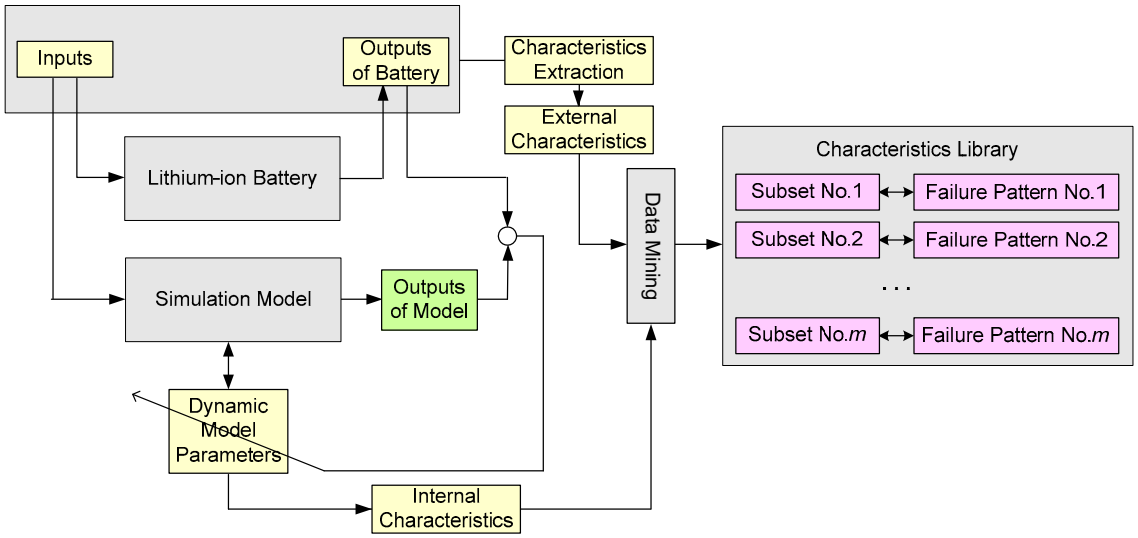

Figure 1: Diagram of the roadmap.

The keys to this roadmap are as below:
(1) *Simulation model for Li-ion battery* is the computer implementation of mathematical description for physical and chemical processes inside batteries.
(2) *Dynamic model parameters* include the physical and chemical parameters of batteries (or simulation model). These parameters either change with time during one charge/discharge cycle, or shift with number of cycles in a battery’s life span. Load and ambient temperature are regarded as the *inputs* of both the battery and the simulation model. Terminal voltage, loop current and shell temperature can be the outputs of a battery. The model parameters are adjusted so that the outputs of simulation model approach the tested outputs of the real battery.
(3) *External characteristics* are extracted from the inputs and outputs of the battery. Dynamic model parameters are also seen as *internal characteristics*.
(4) The relationship between these characteristics and the concerned failure modes are analyzed through *data mining* method. The characteristics are divided into subsets and their roles in certain failure modes are described in a quantitative way.
The research work in the roadmap can be divided into three stages. The first is the stage of preparation, including selection of suitable math model that simulates the battery performance precisely and how to solve it in a computer, and grouping of model parameters (i.e. fixed parameters, sensitive parameters, and non-sensitive parameters). The second is the stage of off-line analysis, in which the external tested data of batteries in different experimental conditions is recorded, then the concerned parameters inside the model are identified using the least square method or genetic algorithm. And the associations between the parameters and the performance of batteries (SOC or SOH) are also found. Finally is the online application stage, including the simplification of simulation model, the development of more efficient parameter identification method and real-time evaluation method. This paper presents some details in the above three stages.

2. Stage one: preparation

2.1 Mathematical models and their numerical solutions

Mathematical modeling of lithium ion batteries involves defining the dependant variables and their respective governing equations (usually a combination of partial differential equations) along with necessary boundary and initial conditions (Vinten, 2009). The rigorous math model of Li-ion batteries is called P2D since the battery model is pseudo 2-dimention (Marc et al, 1993). The simplest version of P2D is single particle model (SPM) with a set of reasonable assumption (Bala et al, 1998; Guo et al, 2011). There are also other versions of math models between P2D (Paul et al, 2011; Cai and Ralph, 2012) and SPM (Alexander et al, 2010; Saeed et al, 2013). Generally speaking, the numerical solution is more accurate and less efficient if the model is more complicated.

There are many numerical solvers that can solve these PDEs. They are generally divided into three categories: finite differences, finite elements and finite volumes (Vinten, 2009), and we have tried several forms of FDM and FEM methods.

COMSOL is a kind of FEM commercial solver that computing rigorous P2D model (Cai and Ralph, 2011). The solutions of COMSOL are used as virtual experimental data in the early stage of our work due to the accuracy of P2D. But COMSOL solver is not very effective and does not support further development for future embedded online applications.

FDM method converts the governing equations to a set of differential algebraic equations by discretizing in the spatial co-ordinate (Gerardine et al, 2000). FDM is easy for programming realization in computer, and finally adopted in this work. By now we have developed a series of solver code in versions of FORTRAN, MATLAB, MAPLE and C, either acquired from the web or programmed by our own. Besides, we also take temperature into account, which were usually omitted in the previous simulations.

2.2 Grouping of model parameters based on parameter sensitivity examination

For a P2D model, there are 33 basic parameters altogether. It is very difficult to obtain so many parameters all in only one identification process. Besides, the convergence speed of identification algorithm may be also intolerable.

Some parameters almost don't change during cycling. The values of these fixed parameters can be offered by manufacturers (if lucky enough) or we can measure them through destructive test of battery samples.

Some other parameters change with SOC and/or SOH, the values of which determine the simulation results obviously, and play very important roles in PHM applications. So these parameters can be seen as the internal characteristics relating to SOC and/or SOH and are called sensitive parameters, which should be identified by non-invasive method. Simulation experiments are conducted at different temperatures, discharge rates and depths of discharge (DODs). When the experimental conditions are set fixed, change the value of a certain concerned parameter within its range, and then observe if this parameter is sensitive or not by plotting the terminal voltage curves. Thus each parameter has a 3-D sensitivity value matrix as the quantitative description of its sensitivities to different experimental conditions. Each parameter also has a greatest value of sensitivity, the corresponding experimental condition of which is the "Best Condition for Identification" (BCI) of this concerned parameter. To identify each parameter on its BCI is obviously not operable. The parameters which have the same or similar BCIs can be identified on the same condition. All sensitive parameters are divided into four categories by using Fuzzy C-Means clustering method. The four clustering centers are then the suitable experimental conditions for the four clusters of parameters respectively.

3. Stage two: off-line analysis

3.1 Parameter identification

Parameter identification off-line is done by analyzing data of four kind of suitable experiments according to former parameter sensitivity analysis.

The open circuit potential (OCP) and incremental capacity analysis (ICA) curves are both used as two sub-objectives in a multi-objective genetic algorithm (MOGA). The ICA curve, which transforms the voltage plateaus into distinctly identifiable $\Delta Q/\Delta V$ peaks and has been used in capacity fade analysis, has greater parameters sensitivity than an OCP curve. It is used to make voltage plateaus of OCP curves more obvious, so that the genetic algorithm converges easily to the global optimum.

In fact, multi-objectives can be synthetized by weighting the two objectives according to both OCP and ICA. The weights of both objectives are dynamically adjusted in the iteration process of genetic algorithm.

For identifying the full set of parameters, an advanced MOGA (e.g. NSGA-II) will be used, in which both the terminal voltage and shell temperature will be the sub-objects. So the model results with the optimal parameter set could fit the experimental data very well.

3.2 Finding associations between parameters and failure modes

The parameters of battery model are called internal characteristics. Features extracted from the terminal voltage, loop current and shell temperature of batteries are then called external characteristics. The hidden relationships between characteristics and the evolution of battery performance are to be discovered for future PHM purpose. Restricted by the time-consuming aging test, which is the critical aspect of battery performance, this part of work has not been carried out yet. Even so, a research proposal is given here.

We can use APRIORI algorithm, which is a classic algorithm for frequent itemset mining over databases, to identify the frequent individual items in the database and extend them to larger and larger subsets composed of characteristics at certain failure modes as long as those item sets appear sufficiently often in the database. The frequent subsets determined by APRIORI can be used to find out the association rules between subsets of characteristics and all the failure patterns. The support level of each association relationship is calculated. If the support level of a subset to a certain failure pattern is greater than a recommended threshold, then the association between the subset and the pattern is confirmed. The characteristics that relate to no patterns are considered to be redundant.

The process above is roughly demonstrated in Figure 2.

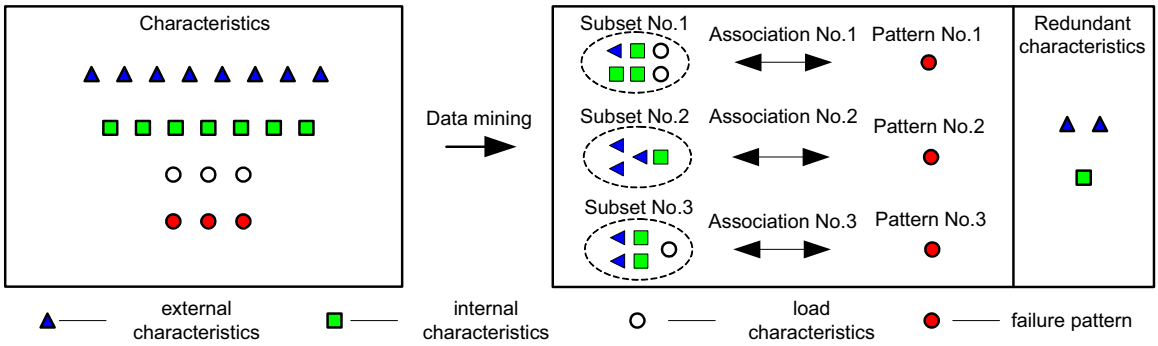

Figure 2: Data mining of associations between parameters and failure modes.

There are also the third type of characteristics named load characteristics, which are some forms of the stress accumulation of applied current and temperature. For example, after we manage to obtain the characteristics in Subset No.1 and the Association No.1, we can predict the evolution of Failure Pattern No.1 more precisely. The associations can be acquired by methods of multiple regression.

3.3 Battery testing platform

The Battery testing platform is shown in Figure 3. The platform is composed of four battery testers, an electrochemical workstation, a thermostatic chamber and a NI PXI system. The Battery testers are responsible for the charge/discharge experiments of battery cells with current range of 2μA~20A. The electrochemical workstation is used to test and analyze the EIS of batteries. The thermostatic chamber and PXI system are indispensible for setting ambient temperature and acquisition of shell temperature of battery.

4. Stage three: online application

Real-time acquisition of concerned internal characteristics is the critical point for the above methods to be used in on-line applications, which may be installed in the BMS of electric vehicles, portable electronics and even space stations. The parameter identification algorithms usually work in an iterative way. On each iteration, the model parameters are adjusted, and the numeric calculating program of simulation model is run at least once. The outputs of model are compared with those of real batteries to decide if the iteration converges. So it is concluded that the effectiveness of simulation models is of most importance.

P2D model is too complex to be used on-line (Vijayasekaran et al, 2008). The outputs of SPM are only comparable with those of P2D at lower charge/discharge rates. If the load current rate is high or changes dramatically, the simulation results of SPM deviate from their real values too much.

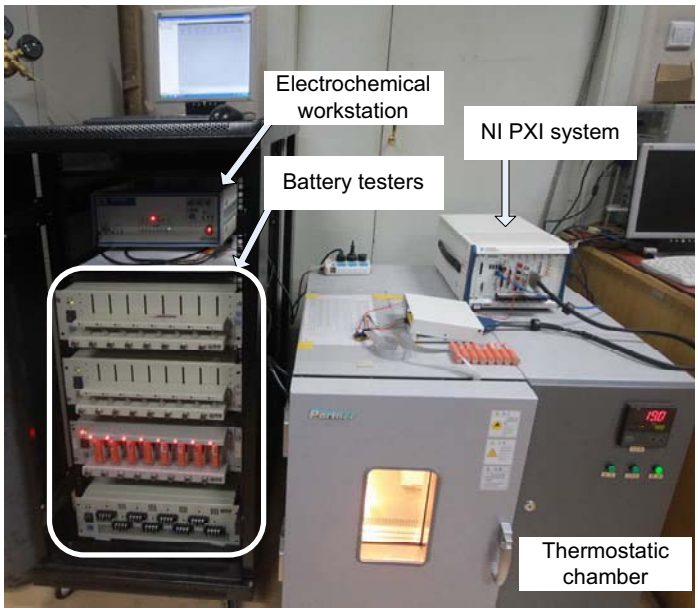

Figure 3: Photograph of battery testing platform

For the reasons above, we developed an extension of SPM (ESP) for higher charge/discharge rates taking the spatial nonuniform of electrochemical reaction and the overpotential of concentration polarization into account. Simulation results show that the greatest difference of terminal voltage between ESP and P2D is only 20mV at charge/discharge rate of 4C. The difference is even smaller if the rate is below 4C. Besides, the computational efficiency of ESP is also excellent. With the same computer configuration, the time consumption of ESP, SPM and P2D models are compared in Table 1. The simulation time of ESP is about one thousandth of that of P2D, while about only 13 times of that of SPM.

Table 1: Time consumption of ESP, SPM and P2D models

Operating condition	SPM	ESP	P2D	Ratio(ESP/P2D)	Ratio(ESP/SPM)
1C discharge	0.758ms	10.55ms	11.15s	1/1057	13.9
2C discharge	1.421ms	15.56ms	16.85s	1/1083	11.0
3C discharge	4.534ms	56.31ms	59.18s	1/1051	12.4
4C discharge	6.777ms	91.09ms	94.34s	1/1036	13.4
0.5C CCCV charge	2.901ms	33.61ms	31.75s	1/945	11.6
4C DST	1.601ms	22.08ms	19.91s	1/902	13.8
4C FUDS	35.247ms	527.43ms	530.77s	1/1006	14.9

5. Conclusion

This paper sketches the blueprint of a novel method for Li-ion battery PHM research. The prominent difference between this roadmap and previous work is the effort of extracting internal parameters of batteries as the characteristics reflecting the evolution of SOC or SOH.

The contribution of this work lies in:

(1) Dividing the research work of the roadmap into three stages.

(2) The internal, external and load characteristics altogether contain the most comprehensive information on battery performance.

(3) Finding the balance point between accuracy and efficiency by presenting ESP model.

(4) Grouping of model parameters based on parameter sensitivity examination reduces the risk of failure of the parameter identification.

Most of the accomplished work mentioned in this paper is by means of simulation, from which the focus should transit to experimental study of real batteries from low capacity cells to power battery packs, so that the not yet completed parts of the roadmap are supplemented.

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