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Capacity and power fade cycle-life model for plug-in hybrid electric vehicle lithium-ion battery cells containing blended spinel and layered-oxide positive electrodes

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H I G H L I G H T S

- Capacity and power fade aging model for lithium-ion cells containing NMC-LMO cathodes.
- Control-oriented cycle-life model for PHEV applications.
- Understanding of lithium-ion battery aging under realistic PHEV operation.

A R T I C L E I N F O

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A B S T R A C T

This paper proposes and validates a semi-empirical cycle-life model for lithium-ion pouch cells containing blended spinel and layered-oxide positive electrodes. For the model development and validation experimental data obtained during an aging campaign is used. During the campaign the influence of charge sustaining/depleting operation, minimum state of charge (SOC), charging rate and temperature on the aging process is studied. The aging profiles, which are prescribed in power mode, are selected to be representative of realistic plug-in hybrid electric vehicle (PHEV) operation. The proposed model describes capacity fade and resistance increase as function of the influencing stress factors and battery charge throughput. Due to its simplicity but still good accuracy, the applications of the proposed aging model include the design of algorithms for battery state-of-health (SOH) monitoring and prognosis, PHEV optimal energy management including battery aging, and the study of aging propagation among battery cells in advanced energy storage systems.

1. Introduction

A crucial step towards the large-scale introduction of plug-in hybrid electric vehicles (PHEVs) in the market is to reduce the cost of their energy storage devices. Lithium-ion (Li-ion) batteries are the preferred energy storage technology in PHEVs due to their high energy and power density [1]. One of the goals of U.S Department of Energy (DOE) Vehicle Technologies Program for hybrid electric systems is to, by 2022, reduce the production cost of Li-ion batteries by nearly 75% from 2012 costs. Currently, battery cycle and calendar life represents one of the greatest uncertainties in the total life-cycle cost of advanced energy storage systems [2].

Generally, battery aging manifest itself in a reduction in the ability to store energy and deliver power, performance metrics correlated with loss in capacity and increase in internal resistance [3,4]. Among the micro-mechanisms of Li-ion battery aging we cite active particle loss and metal sediment or SEI film accumulation. A review of today' s knowledge on the mechanics of aging in Li-ion batteries can be found in Refs. [3,5]. These physical-chemical mechanisms are enhanced by stress factors such as current severity (C-rate), operating temperature, state of charge (SOC), cycling rates, overcharge and over-discharge [3,4]. The generation of long-term predictions of the evolution of capacity and/or resistance to predict when it will reach a predetermined threshold is referred as battery prognosis. Prognosis helps in making informed

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and timely life cycle management decisions, reducing warranty and maintenance costs while improving serviceability, availability and safety. Prognosis is possible when an aging model describing the evolution of aging over time/cycle is available.

Battery aging models can be classified as physics-based [6–13] and semi-empirical models [2,14]. Due to its simplicity but still good accuracy, semi-empirical models have been used for on-line battery prognosis and state-of-health (SOH) estimation, and as part of other Battery Management System (BMS) tasks such as state-of-charge (SOC) estimation [4,15]. Recently, semi-empirical models have been also used for PHEV optimal energy management including battery aging [16,17] and for the study of aging propagation among cells in advanced battery systems [18]. Due to its potential applications, in this work, we choose to use the semi-empirical approach for the aging model development.

During the past years, the concept of blended electrodes composed of several active materials is attracting attention. Blended cathodes promise the combination of benefits of different metal-oxides into a hybrid electrode to allow performance optimization [19,20]. In particular, blended cathodes composed of layered-oxide positive electrodes such as $LiNi_{1/3}Nm_{1/3}Co_{1/}$ O_2 (NMC) and spinel oxide positive electrodes such as $LiMn_2O_4$ (LMO) have been considered as one of the most promising candidates for PHEV applications [21,22]. NMC positive electrodes have high specific capacity, good thermal stability and good cycle life. However, they have poor performance at high rates [21]. On the other hand, LMO positive electrodes, have a high rate capability and a low-cost. However, they have a low cycle life [19]. NMC-LMO blended positive electrodes have been reported to have the benefits of the two metal-oxides [23,21].

There have been substantial efforts to conduct experimental campaigns to understand the influence of different stress factors on battery aging for various cathode materials: $LiCoO_2$ (LCO) [24,25], LiNiO (LNO) [24], $Li(Ni,Co)O_2$ (NCO) [26–29], $Li(Ni,Co,Al)O_2$ (NCA) [30,25,31,32], $LiFePO_4$ (LFP) [2,14,32], NMC [33–35]. The majority of these studies have also included efforts to develop semi-empirical aging models. The main stress factors investigated have been SOC, ΔSOC, C-rate, and Temperature. Recently, other PHEV related stress factors such as vehicle-to-grid services (V2G) [36], charging protocol [37] and SOC equalization [38] have been included.

Though NMC-LMO cathodes are considered an excellent candidate for PHEV applications, only few aging campaigns using this composite material have been published [39–41,13]. In Ref. [39] the effect of temperature and SOC on calendar-life and charge sustaining/depleting cycle-life are studied within a large aging campaign. In Ref. [40], cycle-life is studied under two scenarios. In the first one, the effect of thermal cycling superimposed to charge sustaining/depleting operation is studied. In the second one, the magnitude and randomness of constant power pulses is investigated. None of these studies have included the development of suitable aging models for BMS and prognostics schemes.

Despite the efforts reported in the literature, there is still the need to understand battery aging under more realistic PHEV operation. In particular, the development of accurate aging models able to assess and prognose the life of the most advanced li-ion cathode candidates under realistic automotive scenarios is critical. This paper proposes semi-empirical capacity and power fade aging models for Li-ion pouch cells with NMC-LMO positive electrodes based on PHEV aging cycles. During the aging campaign that provided data for the proposed model, the influence of charge sustaining/depleting operation, minimum SOC, charging rate and temperature on the aging process was studied [13].

This paper is organized as follows. Section 2 describes the design of experiments and the methodology used during the periodic state of health assessments. Sections 3 and 4 present the capacity fade experimental data and describe the development and validation of an aging model based on empirical relations of the stress factors with capacity fade. Sections 5 and 6 present the resistance increase experimental data and describe the development and validation of a power fade model. In Section 7, the conclusions are presented.

2. Experimental campaign

The United States Advanced Battery Consortium (USABC) defines two operational modes for PHEVs, Charge-Depleting (CD) and Charge-Sustaining (CS) [1]. In CD mode the vehicle is allowed to operate in electric mode (i.e. the vehicle powered by the electric drive and onboard electric energy storage) and hybrid mode (i.e. the vehicle is powered by the electric drive and/or engine), with a net decrease in battery state-of-charge (SOC). Where the battery SOC is defined as the available capacity expressed as a percentage of rated capacity. In CS mode the vehicle is only allowed to operate in hybrid mode with a relatively constant battery SOC. Fig. 1 shows an schematic of a typical SOC profile under PHEV cycle operation. During CD the battery is depleted starting from a battery SOC of SOC_{max} and until reaching a predefined SOC_{min}. During CS the battery SOC is kept within a window UE_{CS} with an average value of SOC_{min} [1], see Fig. 1. We define t_{CD} as the time spent in CD, t_{CS} as the time spent in CS, and $(t_{CD} + t_{CS})$ as the total operating time. The ratio of CD to the total operating time is then defined as the ratio of t_{CD} to $(t_{CD} + t_{CS})$,

$$Ratio = \left(t_{CD} : \left(t_{CD} + t_{CS}\right)\right) = \frac{t_{CD}}{t_{CD} + t_{CS}} \quad (1)$$

which indicates the fraction of time spent in CD mode over the total operation time. Therefore, $Ratio = 1$ corresponds to CD operation i.e. all the operating time is spent in CD. $Ratio = 0$ corresponds to CS operation, i.e all the operating time is spent in CS. *Ratios* such that $0 < Ratio < 1$ correspond to mixed operation i.e. the total operating time is divided between CD and CS. For example, the SOC profile shown in Fig. 1 corresponds to mixed operation with a *Ratio* of 1/2, i.e, half of the CD-CS operation time is spent in CD while the other half is spent in CS.

Battery charging is typically done through CC-CV protocol [37]. That is, a constant current (CC) is used until the battery voltage reaches a predetermined limit, followed by a constant voltage (CV) until the current declines to a predetermined value. In this work we

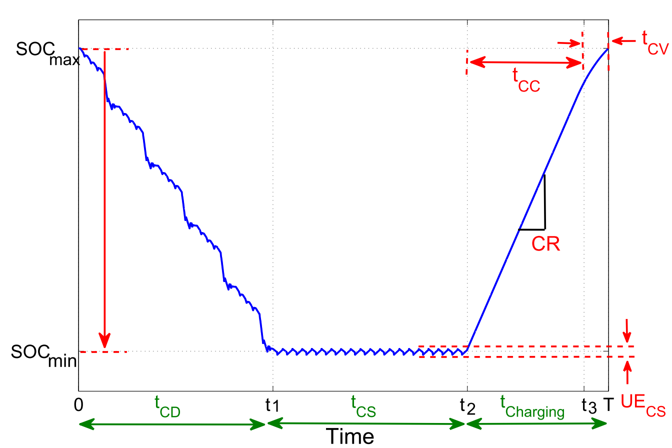

Fig. 1. Schematic of SOC profile under PHEV operation: charge depleting (CD), charge sustaining (CS) and charging.