Energy 112 (2016) 294–306

Contents lists available at ScienceDirect

Energy

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

Application-specific electrical characterization of high power batteries with lithium titanate anodes for electric vehicles

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ARTICLE INFO

Article history:
Received 27 February 2016
Received in revised form
15 June 2016
Accepted 18 June 2016
Available online 5 August 2016

Keywords:
Butler-volmer equation
Lithium-ion batteries
Lithium titanate batteries
Electro chemical impedance spectroscopy
Hybrid pulse power characterization tests
Lithium

ABSTRACT

This study shows results of extensive experimental measurements performed on high power lithium titanate based batteries. Characterization tests are performed over a wide temperature range (−20 °C − +40 °C) by employing electrochemical impedance spectroscopy and modified hybrid pulse power characterization tests. Furthermore, the behavior of battery impedance parameters over the battery lifetime with regard to temperature, State-of-Charge and their influence on available battery power in an example of electric vehicles is discussed. Based on extracted parameters, a reduced order equivalent circuit model considering the nonlinearity of the charge transfer resistance is parametrized. The obtained results indicate that ohmic resistance increases with decreasing State-of-Charge while the shape of the curve remains almost constant over the battery lifetime. The total impedance determined at 1 mHz shows almost no dependence on State-of-Charge and remains constant over the whole State-of-Charge range. The necessity of considering the impact of the current dependence of the direct current resistance at least at low temperatures (i.e., below 0 °C) is confirmed. Moreover, by investigating the Butler-Volmer equation the behavior of exchange current density and symmetry factor is analyzed for various temperatures and State-of-Charges over the battery lifetime.

1. Introduction

Upcoming and existing regulations offered on national or international scale in order to reduce the local greenhouse emissions present new technical and economic challenges to the automotive industry. Partial or full electrification of the vehicle powertrains is one of the certain unfailing measures to reach particular targets in the aforementioned sector [1]. In this regard alternative energy storage systems (ESS) as a fundamental part of the vehicle powertrain play a key role in achieving the desired strategic objectives.

Lithium-ion batteries (LIBs) definitely belong to the most promising commercially available ESS for use in electric vehicles (EVs). The higher specific volumetric and gravimetric energy and power density, lower weight, higher cycle lifetime and lower self-discharge rate of LIBs [2] in comparison to settled ESS (e.g., Lead-acid batteries or Nickel-Metal hydride) either in automotive or in stationary applications make their entrance into the growth market much more attractive [3].

Nevertheless, there are still some drawbacks associated with LIBs which need to be addressed. First, LIBs still cost more than other ESS and up to now the aging mechanisms of LIBs are not sufficiently understood [4]. Second, on the one hand their lack of safety at high temperatures or in a crash case and on the other hand their limited performance at very low temperatures (e.g., especially challenging for hybrid electric vehicles (HEVs) with regard to cold cranking capability) belong to the main concerns of the vehicle manufacturer [5]. As a consequence, certain targeted improvements have to be made in terms of safety, developing innovative electrode and electrolyte materials yielding higher lifetime, cycle stability and more efficient power and capacity performance even at low temperatures [6].

LIBs using spinel lithium titanium oxide, $Li_4Ti_5O_{12}$ (LTO) anodes as a kind of zero strain insertion material [7] in combination with various cathode materials formed by a manganese-based compounds and olivine lithium metal phosphates, such as lithium

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http://dx.doi.org/10.1016/j.energy.2016.06.088
0360-5442/

manganese oxide, $LiMn_2O_4$ (LMO), lithium iron phosphate, $LiFePO_4$ (LFP) or lithium nickel cobalt manganese oxide, $Li(Ni_{1/3}Co_{1/3}Mn_{1/3})O_2$ (NMC), definitely belong to the most promising ESS in various aspects [8]. For HEVs where high power and cycling performance in a wide temperature range are required, LIBs using LTO anodes are proved with their excellent power performance. For example, LIBs using LTO anodes made by Toshiba Corporation are used in a 12 V ESS assisting the start-stop functionality in Suzuki's Wagon R and Wagon R Stingray compact HEVs [9].

Moreover, the LTO anode may not suffer from solid electrolyte interface (SEI) and dendrite formation [4]. Therefore, for LIBs using LTO anodes, the SEI phenomenon is mainly referred to the cathode [10]. Among the further advantages of LIBs using LTO anodes are their cyclability even at low temperatures, without the occurrence of lithium plating [11] and exfoliation of active materials, and their promising thermal stability at higher temperatures can be addressed [7]. During full lithiation the LTO anode reaches a theoretical capacity of 175–330 mAh g^{-1} [7]. Moreover, during the lithium insertion reaction process in the electrode a flat voltage of 1.55 V vs. Li/Li^+ appears while its spinel symmetry structure remains almost unaltered [12]. In contrast to LTO anodes, graphite anodes have a working potential of approx. 0.1 V and a capacity of approx. 370 mAh g^{-1}. All of this means that LIBs using LTO anodes show a reduction in operating cell voltage, electronic conductivity and theoretical capacity yielding less overall energy density [4] but high power density while the opposite is valid for graphite-based LIBs [7].

Impedance characteristics of ESS, in particular LIBs, depend mainly on the following factors [13]:

- State-of-Charge (SoC),
- Temperature,
- Actual battery aging state [14].

Electrochemical impedance spectroscopy (EIS) measurement and hybrid pulse power characterization (HPPC) test are powerful techniques for characterizing the ESS and investigating the dependence of the battery impedance parameters on SoC or temperature and its influence on battery power capability [15]. In addition, some other works in the literature show results of extensive accelerated calendar and cycling aging tests at various temperatures and Depth-of-Discharge (DoD) discussing the change of impedance parameters over the battery lifetime and how this information can be used for predicting the battery's remaining useful lifetime (RUL) [16]. In Ref. [17], the authors present an aging model considering the battery capacity loss that is used as a basis control algorithm that provide the vehicle energy management system with valuable information in order to find an optimum tradeoff between fuel consumption and battery aging in an example of HEV.

In Ref. [15], the authors show results of experimental investigations over a wide temperature range using LIBs in a new state with $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ cathode and graphite anode materials. High dependence of ohmic resistance (R_0) on temperature is shown while dependence on SoC is less pronounced. In addition, an increase of the charge transfer resistance (R_{ct}) with decreasing SoC is observed. Furthermore, the low temperature power capability of LIBs using $LiCoO_2$ (LCO) cathodes and graphite anodes is investigated by performing three electrode measurements and the simulation of the equivalent circuit model (ECM) in Ref. [18]. The main contribution of R_{ct} and its increase by decreasing temperatures is noted as a major source of cell polarization at low temperatures.

A cycle life analysis of LIBs using LTO anodes and NMC cathodes materials is performed in Ref. [19]. The authors report a higher capacity fade due to active material loss in the cathode than the degradation that occurred in the anode. For degradation analysis, the incremental capacity analysis technique is consulted. In Ref. [20], the same results are obtained by investigating LIBs using LMO and LCO cathode and LTO anode materials. According to the authors, for the cycle-aged LIBs, the loss of cyclable lithium and the loss of positive electrode active material are identified as the main aging contributor. Results indicate minor loss of negative electrode active material and negligible aging for calendar-aged LIBs.

In Ref. [10], impedance measurement results of LIBs using LTO anode and LCO cathode materials in a new state for various temperatures and DoDs are shown. An ECM employing passive elements (resistances, capacitances, inductance etc.) representing cathode and anode is used for parameterization of the cells. The main focus lies on understanding the capacity fade mechanism on both electrodes. The results indicate that the increase of the R_{ct} and the capacity fade of the cathode are major degradation mechanisms.

However, most of the researches published in literature explore the impedance characteristic of LIBs using graphite anodes. Up to now, few works have investigated the aging mechanism and especially the behavior of impedance characteristics of the LIBs using LTO anodes under different conditions. Within this study, LIBs using LTO anodes at different aging states are characterized in order to determine the influence of SoC, temperature and current rate on impedance characteristics and battery power capability, respectively. Kinetic processes described by the Butler-Volmer equation (BVE) with regard to the current dependence of direct current resistance (R_{dc}) and the behavior of BVE parameters, namely exchange current density and symmetry factor (I_0, α), are analyzed. The Butler-Volmer behavior has been mainly examined for a certain temperature and SoC or when the battery was in a new state in the past. In this study, a full evaluation of the Butler-Volmer behavior of investigated LIBs is performed over a wide temperature and SoC range at different aging states.

The remainder of this study is organized as follows: In Section 2, the basic theory of EIS and HPPC tests and the performed measurement procedures are discussed. A selection of measured impedance spectra for LIBs under different conditions and the influence of temperature and SoC on battery impedance characteristics and Butler-Volmer behavior are described in Section 3. Finally, this work is summarized and the impact of temperature and SoC on impedance characteristics is discussed in the conclusion.

2. Theory of electrochemical impedance spectroscopy and hybrid pulse power characterization tests

EIS and HPPC techniques are often used for offline characterization of ESS. As a main difference between both measurement techniques, the experimental setup and employed excitation signals may be addressed. In this Section the basic theory of EIS measurements and HPPC tests for parametrizing battery models and the performed measurement procedures is discussed briefly.

2.1. Electrochemical impedance spectroscopy

The measurement technique based on EIS is often used as a promising non-invasive technique for parameter identification and investigation of a battery's dynamic behavior. Performing EIS measurement allows deep insight into electrochemical processes occurring inside the cell over a wide frequency range. This yields a very simple and accurate parameter and process identification from very low (some μHz) up to high frequencies (some kHz and even more) [21]. The complete impedance spectrum can be obtained