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A study on the dependency of the open-circuit voltage on temperature and actual aging state of lithium-ion batteries

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HIGHLIGHTS

- Impact of temperature on OCV behavior is investigated.
- Impact of aging on OCV behavior is investigated.
- Impact of aging and temperature on OCV hysteresis is investigated.
- A simplified OCV model for Battery management systems is proposed.

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ABSTRACT

The knowledge of nonlinear monotonic correlation between State-of-Charge (SoC) and open-circuit voltage (OCV) is necessary for an accurate battery state estimation in battery management systems. Among the main factors influencing the OCV behavior of lithium-ion batteries (LIBs) are aging, temperature and previous history of the battery. In order to develop an accurate OCV-based SoC estimator, it is necessary that the OCV behavior of the LIBs is sufficiently investigated and understood. In this study, the impact of the mentioned factors on OCV of LIBs at different aging states using various active materials (C/NMC, C/LFP, LTO/NMC) is investigated over a wide temperature range (from −20 °C to +45 °C) comprehensively. It is shown that temperature and aging of the battery influence the battery's relaxation behavior significantly where a linear dependence between the required relaxation time and the temperature can be assumed. Moreover, the required relaxation time increases with decreasing SoC and temperature. Furthermore, we state that for individual LIB, the OCV and the OCV hysteresis change over the battery lifetime. Based on the obtained results a simplified OCV model considering temperature correction term and aging of the battery is proposed.

1. Introduction

In recent years, lithium-ion batteries (LIBs) have become the preferred choice for electric vehicles (EVs) mainly because of their high energy and power density (both gravimetric and volumetric), fast reaction time, low self-discharge rate and high cycle and calendar lifetime [1]. Many vehicle manufacturers, suppliers and research institutions worldwide have made an enormous effort to bring forward the research and development of LIBs.

Nevertheless, despite the mentioned advantages of LIBs, the application engineers are facing increasingly new challenges; in particular, understanding various aspects of battery aging mechanisms and developing reliable and robust battery monitoring algorithms that work accurately over the battery lifetime under varying conditions are still a challenging task [2]. Moreover, further requirements on monitoring algorithms resulting from different battery behavior on module and system level than on cell level become more important [3].

In modern monitoring algorithms, accurate estimation of battery State-of-Charge (SoC) and State-of-Available Power (SoAP) is often coupled with the knowledge of nonlinear monotonic SoC-open-circuit voltage (OCV) correlation [4]. The on-board

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estimation of battery SoC is always a part of battery management system (BMS). Battery SoC is equivalent to fuel gauge used in conventional vehicles and is often employed as a basis for reliable energy/power management strategy and residual driving mileage prediction in EVs [5]. SoC estimation definitely belongs to the most investigated battery states and it has often been discussed in many researches in the past. Comprehensive reviews on available SoC estimation techniques can be found, for example, in Refs. [5,6]. An inaccurate estimation of battery SoC influences the accuracy of State-of-Available Energy (SoAE) estimation or SoAP prediction that might have fatal consequences for vehicle manufacturers with regard to customer acceptance or safety failures (i.e., unwanted battery overcharge or battery over discharge etc.). In addition, an inaccurate SoC estimation leads to a change in operating SoC window that in short term has high impact on battery power capability prediction and in long term on expected battery lifetime [7].

The simplest and may be the most common technique for estimating the battery SoC is the so-called coulomb counting (CC) technique. The CC technique is based on integrating the current over time while it is often assumed that the actual battery capacity and initial SoC value are known or determined by other supporting algorithms. However, since the CC technique is an open-loop estimator, the SoC estimation accuracy is affected by measurement uncertainties (e.g., current measurement), disturbances or inaccuracies by setting the initial SoC or the battery capacity [8]. Therefore, in order to ensure long-term stability of the CC technique and compensate the mentioned disadvantages, the CC technique is often combined with other supporting techniques such as OCV-based estimation techniques.

Consequently, when the battery is in equilibrium state and all side reactions are finished, the nonlinear monotonic correlation between the OCV or strictly speaking, the electro motive force (EMF[1]) and the battery SoC is used. The OCV is always a function of SoC, OCV = f(SoC). Thereafter, this correlation is frequently employed to recalibrate the CC-based SoC estimation algorithm and setting the initial SoC value [9]. In fact, as a consequence of some external or internal issues such as temperature or aging of the battery, the SoC-OCV correlation changes under varying conditions [10] and long relaxation time resides in a range of some hours is necessary until the equilibrium state is reached [11].

From electrochemical point of view, when no current flows and the electrode potentials are in equilibrium state, the OCV of a full cell can be determined as follows (Eq. (1)):

$$\mathrm{OCV} = V_{\mathrm{positive}}^{\mathrm{eq}} - V_{\mathrm{negative}}^{\mathrm{eq}} \tag{1}$$

The OCV of each electrode depends on temperature and concentration of lithium-ions in the electrode that is normalized by the SoC of the respective electrode [12]. However, since in real life depending on respective application (e.g., taxis etc.) such long relaxation periods are rarely given, the battery OCV can be estimated under load based on an equivalent circuit model (ECM) by applying adaptive joint or dual filters (e.g., Kalman/H_∞) filter, least-square-based filter or similar observer techniques [13,14]. Within the aforementioned technique, the OCV is directly viewed as a part of the ECM parameters and is estimated on-board along with other impedance parameters such as ohmic resistance (R_0) etc. However, for an accurate OCV estimation, the employed ECM should be able to reproduce the nonlinear behavior of LIB as precisely as possible. In fact, because of limited computational power of BMS in EVs, the employed ECMs are simplified significantly. As a result, the obtained OCV is not necessarily equal to battery voltage in equilibrium state as it consists of overvoltages referring to time constants in range of some hours (e.g., solid-state diffusion overvoltages etc.). The OCV of LIBs depends mainly on the following factors [11,15–18]:

- Applied current rate before current interruption,
- Battery temperature,
- Previous history,
- Cell-to-cell variation,
- Actual aging state of the battery etc.

Deep understanding of the impact of the above mentioned factors on relaxation behavior of the battery is of great interest as it can make a significant contribution to improving the SoC estimation accuracy. Prior researches on the above mentioned factors and theirs impact on OCV of the LIBs are limited in amount and scope. Up to now, most of the researches published in the literature have explored the OCV behavior of LIBs either under nominal condition or when the battery was in a new state. Unfortunately, the impact of aging or temperature of the battery is often neglected or assumed to be negligible. In Refs. [19,20], the authors investigate the OCV behavior of lithium iron phosphate, $LiFePO_4$ (LFP)-based LIBs in new state. Special emphasis is put on investigating the OCV hysteresis of the aforementioned LIBs; in this regard a hysteresis model for BMS applications is presented and verified. Moreover, in Ref. [16], the OCV behavior of LIBs using various active materials in new state is investigated comprehensively. The authors present results with regard to determined OCV gradient, OCV hysteresis and OCV behavior of the investigated LIBs at different temperatures. However, in the latter reference the impact of battery aging is neglected and not considered further. In Ref. [21], the authors propose an accurate normalized OCV modeling technique considering the impact of aging and temperature of the battery. According to the authors, the SoC-OCV correlation remains unchanged over the battery lifetime for various temperatures.

The main contribution of the present study is to discuss the importance of precise battery OCV characterization procedure and examine various factors influencing the battery OCV behavior. A special emphasis is put on understanding the impact of temperature and aging on battery's relaxation behavior. The qualitative discussion should give the readers an overview and possible explanation of the OCV behavior of the investigated LIBs and potentially clarify the origin of the found dependences. To this end, LIBs at different aging states using various active materials (graphite (C)/lithium nickel cobalt manganese oxide, $Li(NiMnCo)O_2$ (NMC), C/LFP, lithium titanium oxide, $Li_4Ti_5O_{12}$ (LTO)/NMC) are investigated. The OCV measurements are performed over a wide temperature range (−20 °C … 0 °C … +10 °C … +23 °C … +45 °C).

The remainder of this article is organized as follows: In Section 2, the characteristics of the investigated LIBs and the performed measurement procedure are described. In Section 3, the results of OCV measurements performed under nominal conditions are profoundly discussed. Thereupon, the impact of battery temperature on OCV curves and OCV gradients are analyzed in Section 4. Moreover, in Section 5, the impact of aging, temperature and SoC on required relaxation time and voltage relaxation curves after current interruption are investigated. Furthermore, based on the measurement results a simplified OCV model including temperature correction term and actual aging state of the battery (State-of-Health (SoH)) is proposed in Section 6. Finally, this study is summarized in the conclusion.

[1] The term EMF refers to the battery voltage under open-circuit condition when the thermodynamic equilibrium potential of the main and side reactions is reached [2]. In this study, the OCV is employed as an equivalent to the EMF.