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A study of the open circuit voltage characterization technique and hysteresis assessment of lithium-ion cells

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HIGHLIGHTS

- Lithium-ion cell open circuit voltage is directly related to charge/discharge capacity.
- Discharge capacity of the cell changes with step discharge.
- OCV is path dependent, i.e. exhibit hysteresis, for all lithium-ion cell chemistries.
- Hysteresis is highest for LFP cell and lowest for LTO cell.
- Dynamic hysteresis model correctly predicts OCV.

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ABSTRACT

Among lithium-ion battery applications, the relationship between state of charge (SoC) and open circuit voltage (OCV) is used for battery management system operation. The path dependence of OCV is a distinctive characteristic of lithium-ion batteries which is termed as OCV hysteresis. Accurate estimation of OCV hysteresis is essential for correct SoC identification. OCV hysteresis test procedures used previously do not consider the coupling of variables that show an apparent increase in hysteresis. To study true OCV hysteresis, this paper proposes a new test methodology. Using the proposed methodology, OCV hysteresis has been quantified for different lithium-ion cells. The test results show that a battery's OCV is directly related to the discharge capacity. Measured battery capacity can vary up to 5.0% depending on the test procedure and cell chemistry. The maximum hysteresis was found in a $LiFePO_4$ (LFP) cell (38 mV) and lowest in the LTO cell (16 mV). A dynamic hysteresis model is used to show how better prediction accuracy can be achieved when hysteresis voltage is a function of SoC instead of assuming as a constant. The results highlight the importance of the testing procedure for OCV characterisation and that hysteresis is present in other Li-ion batteries in addition to LFP.

1. Introduction

Introduction of lithium-ion batteries to electric vehicles (EV), including hybrid electric vehicles (HEV), plug-in hybrid electric vehicles (PHEV), battery electric vehicles (BEV), is enabled by their high energy and power capability, long cycle life and a low purchase price [1–4]. Electrical equivalent circuit models (ECM) are commonly used to evaluate electrical performance (e.g. current, voltage, power, energy) of the battery in real world operating conditions. ECMs have a wide range of applications, varying from on-board State-of-charge (SoC) estimation [5–7] to long-term ageing estimation [8–10]. A substantial amount of research has been done on equivalent circuit modelling of the lithium-ion battery [5,6,11–14]. ECMs of the simplest form [11] to very complex form [12] have been proposed which represent the electrical and electrochemical behaviour of the cell.

A commonly used structure of ECM is shown in Fig. 1. The values of resistances and capacitances in ECM can be determined using different techniques such as Electrochemical Impedance Spectroscopy (EIS) and pulse power test etc. [10]. These techniques are well understood and general relationships of these circuit parameters exists for different real world operating conditions like varying temperature [5,10,15–19] and SoC [5,6,10].

Open circuit voltage (OCV) is present in all forms of ECMs. The OCV is the battery thermodynamic equilibrium potential when not under a current load. The OCV as a function of SoC is an important

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Abbreviations and notations

BEV	battery electric vehicle
BMS	battery management system
CC–CV	constant current constant voltage
DoD	depth-of-discharge
EV	electric vehicle
ECM	equivalent circuit model
HEV	hybrid electric vehicle
LFP	lithium iron phosphate
LTO	lithium titanate
NCM	nickel cobalt manganese oxide
OCV	open circuit voltage
ODE	Ordinary Differential Equation
PHEV	plug-in hybrid electric vehicle
RV	rest voltage
RV_c	charge rest voltage
RV_d	discharge rest voltage
$(\overline{RV})$	average rest voltage between charge and discharge
SoC	state-of-charge
z (t)	SoC at time t
w (t)	DoD at time t
Q_c (t)	capacity during charge
Q_d (t)	capacity during discharge
Q_r (t)	cell remaining capacity
Q_e (t)	extracted capacity from cell
$Q_{(e,max)}$	maximum extracted cell capacity in Ampere-seconds

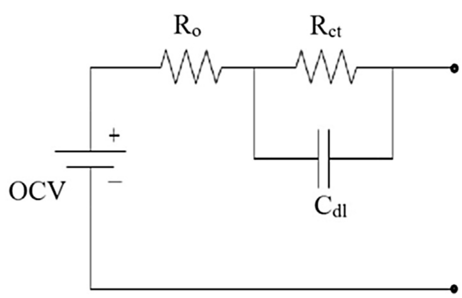

Fig. 1. An equivalent circuit model showing open circuit voltage (OCV), ohmic resistance R_o, charge transfer resistance R_{ct} and double layer capacitance C_{dl}.

characteristic for ECMs. It acts as an ideal but variable (e.g. with SoC) voltage source in the model to which over-potential is added by the remaining resistor and capacitor elements of the ECM.

Conversely, the SoC of a cell, which is crucial for a vehicle battery management system (BMS), can be determined if the cell's OCV is known. This however assumes a one-to-one relation between OCV and SoC allowing the SoC to be known via the OCV. If, however, hysteresis is present, the cell OCV during charge is different from discharge at the same SoC. The presence of any hysteresis therefore implies that knowledge of the cell open circuit potential alone is insufficient to determine the SoC without also knowing the charge–discharge history of the cell. In recent literature, the importance of hysteresis in SoC estimation using ECM has been shown [20].

OCV hysteresis can have significant influence on SoC estimation accuracy [21,22]. An inaccuracy in SoC will be reflected as inaccurate range estimation, leading to decrease of user satisfaction/trust; which in turn is a potential business risk to the OEMs. On the other hand, the inaccuracy in SoC can lead to change of operating SoC window of EV's battery packs. To maintain minimum available power assist and regenerative capability, HEV battery packs operate within a SoC window, avoiding high and low SoC [23]. A SoC window is also used for other types of EVs to extend battery life and avoid safety failures due to overcharge and overdischarge [23,24]. An inaccurate measurement of SoC can change the operating SoC window which will be reflected as short term (e.g. regenerative power capability) and long term performance drop (e.g decrease of expected battery life). Therefore, it is important that the ECM used by BMS should incorporate any cell hysteresis accurately.

The first step toward accurate assessment of hysteresis is the accurate assessment of OCV. As the OCV-SoC relation is typically determined empirically it is important that the experiment and subsequent calibration are performed with care. The OCV cannot be used to establish the SoC. When investigating the level of hysteresis, the SoC is determined via Coulomb counting for which an initial SoC is required. An incorrect initial SoC value can offset the charge and discharge OCV-SoC curves and incorrectly indicate that hysteresis is present.

Cells with lithium iron phosphate electrodes or nickel hydroxide electrodes are known to have stable hysteresis [20,25,26]. However, existing battery test standards [27–29] do not include a test procedure for OCV measurement and the identification of OCV hysteresis. Therefore, different methodologies (i.e. low current charge/discharge, incremental charge/discharge) have been used by researchers to measure OCV and OCV hysteresis [20,22,26,30–35]. However, these papers too, did not provide a robust and consistent methodology to assess OCV and OCV hysteresis. Therefore, an erroneous assessment of OCV and OCV hysteresis could be present historically, and will be discussed in detail in Section 2 of this paper.

In this study the authors investigate the influence of step size on OCV measurements to establish an ideal testing protocol. This testing protocol will be used to identify OCV and OCV hysteresis of different chemistry lithium-ion cells. Lastly, the hysteresis data will be incorporated into a hysteresis transition model, to provide an example of how a better estimation of SoC can be achieved when accurate hysteresis data is used. In Section 2, a review of the origin of OCV hysteresis, previously used test procedures, issues with these procedures, and hysteresis modelling methods are introduced with reference to the relevant published work. Subsequently, the experimental method used as part of this research is shown in Section 3. In Section 4, results, analysis of the results and their implications to the model are presented. Finally, the key findings are summarised in Section 5.

2. Background

2.1. *Origin of hysteresis: a thermodynamic explanation*

Hysteresis in a battery corresponds to the existence of several possible thermodynamic equilibrium potentials at the same SoC of the cell. Positive electrodes with lithium iron phosphate as the active material are known to exhibit a hysteretic phenomenon [30,34]. Srinivasan and Newman [26] provided an explanation for hysteresis based on the existence of a lithium rich and lithium deficient phase within an active particle. They termed the explanation as the *path dependent shrinking core model*, whereby during discharge a shrinking particle core of Li_yFePO_4 and a growing outer crust of $Li_{(1-x)}FePO_4$ occurs, while during charge a shrinking core of