



# Electromotive force characterization of secondary battery cells using estimated electrolyte molality

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## ARTICLE INFO

### Keywords:

Secondary battery  
Electromotive force characterization  
Electrolyte molality  
Open-circuit voltage  
Temperature compensation

## ABSTRACT

Existing methods for electromotive force (EMF) characterization that make use of readily available data, such as terminal voltage and applied current, require a significant time commitment and a constant temperature environment. Both linear interpolation and extrapolation rely on state-of-charge (SOC) calculation by Coulomb-counting which only serves to reduce the accuracy of the resulting EMF-SOC curve(s). A battery management system requires accurate EMF-SOC data for periodic recalibration otherwise it cannot apply proper charge control. This paper presents an alternative concentration-based method for EMF characterization and the key lies in the fact that molality is not influenced by temperature. A modified version of the Nernst equation and temperature-compensated open-circuit voltage measurements are used to estimate the molality when the cell is at rest. During operation, the energy into or out of the cell is mapped to changes in the estimated molality to calculate the EMF as the cell charges or discharges. The concentration-based method is verified using experimental data from valve-regulated lead-acid cells and its EMF curves are compared to those of linear interpolation and extrapolation. The proposed method has less stringent practical requirements and validation results indicate a significant improvement in accuracy and applicability over the existing methods.

## 1. Introduction

The intense pace of battery research and development over the past few decades have been spurred by the ultimate goal of an inexpensive high-performance cell that is both safe and scalable [1,2]. As such, battery cells are available in a wide variety of chemistries, shapes and sizes with even more designs, such as aqueous redox flow batteries and non-aqueous metal air batteries, under active investigation [3,4]. Other research efforts try to improve our current understanding of cell behaviour and use these new insights to develop advanced charge control algorithms [5,6]. Regardless of the chemistry or construction of a specific battery cell, an intrinsic relationship between the cell's electromotive force (EMF) and the remaining useful capacity, called state-of-charge (SOC), exists [7,8].

On-board SOC estimation using traditional Coulomb-counting is problematic because the reference capacity can be different from the actual capacity and any errors in current measurement are amplified due to the integration operator [9,10]. The battery management system (BMS) makes use of the EMF-SOC relationship to periodically recalibrate the SOC estimate. This recalibration is achieved by taking stable open-circuit voltage (OCV) measurements and referring to a lookup

table describing the EMF-SOC curve to obtain the corresponding SOC [5,7,11]. The EMF-SOC curve for chemistries such as lithium iron phosphate can be problematic because the curve is flat for a significant range of the SOC [5]. The EMF-SOC curve is typically characterized at a constant temperature of 25°C before a cell is used in its intended application i.e. it is obtained offline in a temperature-controlled environment. Such a curve is also called an OCV-SOC curve and can sometimes be found on the manufacturer's datasheet.

The purpose of EMF (or OCV) characterization is to obtain a representative curve describing a cell's behaviour in terms of its EMF. Data such as voltage and current measurements are the norm in a typical battery energy storage application and, as such, characterization methods that make use of this readily available data are emphasized here [12]. The existing methods for EMF characterization under consideration in the current work are known as voltage relaxation, linear interpolation and linear extrapolation [13]. The voltage relaxation method is sometimes called the incremental OCV method [14]. These methods typically result in nonlinear monotonic curves with the SOC on the x-axis and the EMF on the y-axis. For exact details on these methods and their implementation to nickel-cadmium and lithium-ion batteries, the reader is referred to the work by Bergveld [13] and Pop [15,16].

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**Nomenclature**

AGM	Absorbed glass mat
BMS	Battery management system
CC	Coulomb-counting
COV	Cut-off voltage
EMF	Electromotive force
GOF	Goodness-of-fit
LAB	Lead-acid battery
OCV	Open-circuit voltage
SOC	State-of-charge
VRLA	Valve-regulated lead-acid
Subscript 1	Denotes time instant $t_1$
Subscript 2	Denotes time instant $t_2$
Subscript $c$	Denotes charging
Subscript $d$	Denotes discharging
Subscript $j$	Denotes time instant $t_j$
Subscript $k$	Denotes time instant $t_k$
$a$	Species activity
$c$	Molar concentration or molarity ( $\text{mol}\cdot\text{L}^{-1}$ )
$\Lambda$	Empirical constants for temperature coefficient calculation
$E$	EMF of an electrochemical cell (V)
$E^*$	Stable OCV measurements for a cell's EMF (V)
$E^\circ$	A cell's standard electrode potential at reference temperature (V)
$E_{\text{ext}}$	EMF from linear extrapolation (V)
$E_{\text{fit}}$	EMF curve as fitted from data (V)
$E_{\text{int}}$	EMF from linear interpolation (V)
$E_{\text{val}}$	Stable OCV measurements used for validation (V)
$F$	Faraday constant of $96,485 \text{ C}\cdot\text{mol}^{-1}$
$\gamma$	Activity coefficient
$i_d$	Applied current during discharge (A)

$m$	Molal concentration or molality ( $\text{mol}\cdot\text{kg}^{-1}$ )
$\hat{m}$	Estimated molality ( $\text{mol}\cdot\text{kg}^{-1}$ )
$m_{\text{total}}$	Total change in molality during operation ( $\text{mol}\cdot\text{kg}^{-1}$ )
$m_{1\text{OR}m_2}$	Molality at that time instant ( $\text{mol}\cdot\text{kg}^{-1}$ )
$m_k$	Molal concentration or molality at time instant $t_k$ ( $\text{mol}\cdot\text{kg}^{-1}$ )
$n$	Number of electrons transferred
$Q$	Reaction quotient
$Q_R$	Rated charged capacity (Ah)
$R$	Universal gas constant of $8.3144 \text{ J}\cdot(\text{mol}\cdot\text{K})^{-1}$
$rmse$	Root mean squared error
$rsq$	R-square adjusted for degrees-of-freedom in the error
$rmse_v$	Root mean squared error on validation data
$sse$	Sum of squares due to error
$sse_v$	Sum of squares due to error on validation data
$T$	Absolute temperature (K)
$T_{\text{ref}}$	Reference temperature of $298.15\text{K}(25^\circ\text{C})$
$t$	Time (s)
$t_1$	Time instant before operation starts (s)
$t_2$	Time instant after operation has ended (s)
$v_d$	Measured discharge voltage (V)
$v_{c,l}(t)$	Voltage profile number $l$ during charging (V)
$v_{d,l}(t)$	Voltage profile number $l$ during discharging (V)
$w$	Electric work from the power delivered or absorbed by the cell over a specified period of time (Wh)
$w_{\text{max}}$	Maximum electric work (Wh)
$w_{\text{total}}$	Total change in electric work done by the cell during discharge (Wh)
$w_{1\text{OR}w_2}$	Sum of the work done by the cell up until that time instant (Wh)
$w_k$	Sum of the work done by the cell up until some instant $t_k$ (Wh)

The shortcomings of the existing methods for EMF characterization will now be explained. The voltage relaxation method requires a significant time commitment and favours the use of the other two methods: linear interpolation and linear extrapolation [17–19]. However, both the voltage relaxation and the linear extrapolation methods result in two EMF-SOC curves wherein hysteresis can be observed: one valid for charge and the other valid for discharge [13]. The linear interpolation method produces a single EMF curve and incorrectly assumes that the cell's internal resistance is symmetric during charge and discharge [20]. Without hysteretic information, control algorithms in a BMS cannot achieve their purpose in terms of monitoring and diagnosis [21]. Challenging requirements common to all three methods are the use of sufficiently low charge or discharge rates and a constant temperature environment [1].

In addition, Coulomb-counting is employed in all three existing methods to obtain the SOC data for the  $x$ -axis of these curves, which in itself reduces the accuracy of the resulting curve(s) [14]. The SOC calculations involved in the existing methods rely on predefining the battery as either full before starting a discharge, or as empty before a charge. Without these reference values, the SOC cannot be calculated [13]. As mentioned earlier, the three existing methods rely on SOC calculations which are known for integrating errors over time along with the charge into or out of the battery [15]. The BMS will not be able to apply proper charge control without accurate SOC information obtained from an EMF-SOC curve [22,23]. Even slight inaccuracy in SOC indication can be severely detrimental to battery electrode and electrolyte materials over time because the BMS then regularly operates outside of the recommended SOC range. Other approaches avoid the issues associated with SOC calculation and use analytical descriptions to model the EMF but involve a large number of parameters [6].

It is worth noting that on-board SOC estimation based on Coulomb-counting can be sufficiently accurate when more complex techniques other than lookup tables are employed. Advanced signal processing can compensate for sensor noise and online parameter identification enables adaptive battery models [3,24]. Online parameter identification has also been combined with Kalman-filter observers, amongst others, in model-based SOC estimation to monitor capacity loss in real time [25,26]. However, estimation accuracy deteriorates when the ambient temperature changes because the EMF-SOC curve is influenced by temperature. On-board implementation of these adaptive filter approaches is possible because they are less complex than state estimation techniques that try to model electrochemical processes during operation [9].

In the current work, an alternative method for EMF characterization of secondary cells is investigated. The aim is to develop a method that does not rely on SOC calculations or a temperature-controlled environment. Sophisticated approaches using expensive equipment, such as electrochemical impedance spectroscopy, or advanced signal processing are not considered. The resulting method makes use of a few simple equations to obtain estimates of the electrolyte molality and maps the energy into or out of the cell to changes in the estimated molality during operation. The estimated molality during operation is used to obtain the EMF when the cell is not in an open-circuit condition. As such, this method is called the concentration-based method for EMF characterization.

Section 2 starts by explaining the theoretical foundation of the concentration-based method for EMF characterization followed by the details of temperature compensation. The concentration-based method is then applied to a valve-regulated lead-acid (VRLA) cell with an absorbed glass mat (AGM) separator as an example. The particulars for

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