Battery aging and its influence on the electromotive force


Published in:
Journal of the Electrochemical Society

DOI:
10.1149/1.2742296

Published: 01/01/2007

Document Version
Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the author's version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

Citation for published version (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 15. Dec. 2018
Battery Aging and Its Influence on the Electromotive Force

V. Pop,1,4,8 J. H. Bergveld,3 P. P. L. Regtien,1 J. H. G. Op het Veld,1
D. Danilov,1 and P. H. L. Notten1,8,9

1University of Twente, Measurement and Instrumentation, 7500 AE Enschede, The Netherlands
2NXP Research, Mixed-Signal Circuits and Systems, 5656 AE Eindhoven, The Netherlands
3Philips Research Laboratories, System-in-Package Devices, 5656 AE Eindhoven, The Netherlands
4EURANDOM, Electrochemical Energy Storage, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Li-ion is currently the most commonly used battery chemistry in portable applications. Accurate state-of-charge (SOC) and remaining run-time indication for portable devices is important for user convenience and to prolong the lifetime of batteries. The actual SOC algorithms, which the main companies use in practice, make use of the so-called electromotive force (emf). In these SOC systems it is assumed that the emf of an Li-ion battery only depends on aging to a limited extent. In this paper, novel emf measurement and modeling efforts are presented as a function of battery aging. As will be shown, a better understanding of this dependence is useful for improving SOC accuracy.

The electromotive force (emf) of an Li-ion battery has been observed to be a useful battery variable for state-of-charge (SOC) determination by means of direct measurement.1−11 The battery emf is the difference in equilibrium potential of the positive and negative electrode and can be measured at the battery terminals when the battery is in equilibrium, i.e., when no external current is flowing and the battery voltage has been fully relaxed from the previously applied (dis)charge current. By measuring the battery voltage under equilibrium conditions the voltage can be translated into an SOC value via an emf-SOC relation stored in the system.1 This stored relationship can be obtained in a laboratory by the SOC-indication system manufacturer in several ways, including interpolation, extrapolation, and relaxation.1 Several emf determination methods have been evaluated in Ref. 11. Out of these, relaxation, has been recommended as the most accurate method for emf determination.

In addition, a mathematical model describing the emf function for an Li-ion battery has been developed.11−12 This model includes a variety of parameters whose values are changing during cycling of the battery. Therefore, to enable accurate SOC determination when the battery ages the variation of these parameters should be taken into account.

General Issues Concerning Battery Aging

During the lifetime of a battery, its performance or “health” tends to deteriorate gradually due to irreversible physical and chemical changes that take place with usage.1 Battery aging is a complex process that involves many parameters, e.g., impedance and maximum storage capacity.10 The state-of-health (SoH) is an indication of the point that has been reached in the battery life cycle and is a measure of its condition relative to a fresh battery. To deal with aging an adaptive system has to be used for SOC indication. For a good overview of existing adaptive systems for SOC indication the reader is referred to Ref. 10.

Li-ion battery aging.— Various degradation processes may contribute to battery aging, i.e., the electrolyte decomposition, the formation of surface films on both electrodes, compromised interparticle contact at the cathode, etc. In Ref. 12 it has been reported that during the battery lifetime the formation of the Co3O4 will also take place. This mechanism has been adopted by the authors of this article in an adaptive Li-ion model13 through which the aging effect has been explained. Consequently, this mechanism has been considered also in this work to explain the battery emf aging.

The decomposition of the LiCoO2 electrode in which xLi+ ions are intercalated may be represented as

\[
\text{Li}_x\text{CoO}_2 \rightarrow (1 - x)\text{Co}_3\text{O}_4 + \text{O}_2 / \text{Li}^+ + \text{e}^{-}
\]

where the active electrode material decomposes into inactive Co3O4 material, which will be formed at the surface of the LiCoO2 electrode and will contribute to the increase of the battery impedance or overpotential and to the decrease of the maximum storage capacity.

The operational conditions determine whether an aged battery can still deliver acceptable remaining run-times (tR) to the user. A battery with high impedance may still deliver acceptable run-times for portable devices that require low discharge C-rate currents, e.g., a CD player or a wireless mouse. Portable devices that require high discharge C-rate currents, e.g., mobile phones, digital cameras or electrical vehicles (EVs), on the other hand, will deliver shorter than acceptable remaining run-times. As a result, the aged battery must be recharged more often compared to when it was new. This will lead to even more wear-out.

The formation of Co3O4 species at the surface of the LiCoO2 electrode contributes also to the decrease of the amount of active LiCoO2. In this case, the number of Li+ ions that can intercalate in the LiCoO2 electrode, i.e., the maximum capacity of the LiCoO2 electrode (Qmax), will decrease. Consequently, the battery maximum capacity (Qmax) will decrease. A battery with a low Qmax value may still deliver an acceptable tR for low discharge C-rate currents but the decrease in tR will become appreciable at higher C-rate currents. It can be concluded that Li-ion will lose performance during the lifetime due to the increase in the impendence and/or decrease in Qmax.

Experimental

Battery measurements.— The US18500G3 Li-ion batteries from Sony have been used throughout all experiments and simulations presented in this paper. The experiments have been carried out using a Maccor battery tester. The US18500G3 Li-ion battery consists of a LiCoO2 positive electrode and an LiC6 negative electrode. Table 1 presents the main characteristics of the US18500G3 Li-ion battery.

As discussed above, the changing rate of the battery impedance and maximum storage capacity is strongly dependent on the operational conditions. High C-rate (dis)charge currents, high temperatures, and voltage levels during charging will speed up the degradation of these two battery characteristics. To study the influence of the operational conditions on the battery degradation two different experiments have been carried out for two US18500G3 batteries.

During the operational conditions performed for battery 1, the battery was charged by means of the constant-current-constant-
battery characteristics.

<table>
<thead>
<tr>
<th>Battery</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical system</td>
<td>Lithium-ion</td>
</tr>
<tr>
<td>Cell type</td>
<td>US18500G3</td>
</tr>
<tr>
<td>Cell diameter</td>
<td>18.4 mm max</td>
</tr>
<tr>
<td>Cell length</td>
<td>49.3 mm max</td>
</tr>
<tr>
<td>Capacity (0.2 C-rate) typical</td>
<td>1180 mA (3.0 V cutoff)</td>
</tr>
<tr>
<td>Capacity (0.2 C-rate) minimum</td>
<td>1100 mA (3.0 V cutoff)</td>
</tr>
<tr>
<td>Cell weight</td>
<td>33 g</td>
</tr>
</tbody>
</table>

The voltage (CCCV) method until 4.3 V at 25°C. Clearly, the battery voltage rises during the CC period until the voltage value of 4.3 V is attained. Furthermore, the current decreases in the CV region. Charging was terminated when the current cutoff value had reached a current of 0.05 C-rate. During the CC step, a 4 C-rate current was applied. After a resting period of 30 min, the battery was always discharged at 0.5 C-rate. Discharging was terminated when a voltage of 3.0 V was reached. The discharge step was followed by a resting period of 30 min.

In the second case, the battery was partially (dis)charged between 30% and 70% SOC with 0.5 C-rate current at 25°C. The 40% SOC difference was calculated as a fraction of the maximum capacity \( Q_{\text{max}} \) for a fresh battery. Each 50 cycles, a complete (dis)charge was performed. During charging, the CCCV method was applied until the 4.2 V voltage level. Similar charge termination conditions and discharging cycles with those for battery 1 were considered.

\[ Q_{\text{max}} \] measurements.—To accurately calculate the maximum battery capacity both 0 and 100% SOC states must be defined for fresh and aged batteries. 0% SOC is considered in this paper when the battery emf has a value of 3.0 V, whereas a SOC of 100% is considered when the battery emf has a value of 4.175 V. This latter emf value is based on experimental considerations at 25°C. From repeated measurements, it has been observed that after applying the normal CCCV charging method at 0.5 C-rate current, the battery voltage has relaxed to 4.175 V at room temperature.

\( Q_{\text{max}} \) was determined for fresh and aged batteries by applying the following measurement method. Standard charging was first carried out with a constant maximum current at a 0.5 C-rate in the CC mode until the maximum charge voltage of 4.2 V was attained in the subsequent CV mode. Evidently, the charging currents dropped in the CV mode and charging was terminated at a predefined minimum current of 0.05 C-rate, after which the new battery was considered fully charged. After a resting period of 4 h, the batteries were discharged at 0.5 C-rate. Discharging was terminated when a voltage of 2.6 V was reached. The discharge step was followed by a resting period of 48 h and by a “deep-discharge” step at 0.001 C-rate until the battery voltage again reached 2.6 V. After this deep-discharge step a resting period of 96 h was applied. At the end of the rest period the battery voltage reached the equilibrium voltage of 3.000 V at which the SOC level was defined 0%. The long resting period was chosen to always reach the equilibrium voltage. The deep-discharge step at a low C-rate value was chosen to compensate for the overpotential effect. The maximum capacity was calculated by means of cumulative coulomb counting applied during the 0.5 and 0.001 C-rate discharging current steps.

\[ EMF \] measurements.—In Ref. 1-6 the emf of Li-ion batteries has been considered dependent on aging only to a limited extent. New emf measurements as a function of battery aging are presented here. The emf measurements were obtained by means of galvanostatic intermittent titration technique (GITT) for both fresh and aged batteries. New measurements regarding the emf hysteresis, as a function of battery aging are presented below.

To accurately determine the influence of battery aging on the emf, \( Q_{\text{max}} \) should be accurately calculated first. This calculation is necessary for a correct definition of SOC. Therefore, the \( Q_{\text{max}} \) experiment presented above was carried out for fresh and aged Li-ion batteries. It has been observed that although a deep-discharge step at a low C-rate value has been used for aged batteries, the increase of the battery overpotential still influenced the emf values, i.e., 3.000 and 4.175 V, at 0 and 100% SOC, respectively. This influence has been mainly observed at low and high temperatures, e.g., 5 and 45°C. Therefore, the measurements have been adjusted. For instance, if the battery emf reached a voltage level higher than 3 V, additional deep-discharge steps were applied after the 96 h relaxation period. A similar correction was applied also for charging where additional (dis)charging steps were applied to obtain the emf level of 4.175 V.

An example of correction through calculation may be considered when after the CCCV charging and the 4 h resting period the battery emf had a value of, e.g., 4.170 V. In this example, a 5 mV voltage and corresponding capacity must be added to the measured emf and capacity values. The corresponding capacity for the 5 mV emf value can be calculated from previous measurements, for which the capacity-emf relationship between 4.170 and 4.175 V has been measured. Similarly, a correction through calculation can be applied for discharging.

After the maximum battery capacity was accurately determined, GITT measurements were applied to determine the battery emf as a function of battery aging. The following measurement method was applied. First, the battery was charged from 3 V at 0.1 C-rate in 25 steps. For each step, a limit of 4.3 V in voltage and 4% SOC increase was considered. Each charge step was followed by a rest period. The rest period was chosen as a function of SOC, e.g., at low SOC long relaxation times of 24 h were required and at higher SOC shorter relaxation times of 12 h were sufficient. Subsequently, 25 discharge steps of 4% SOC were induced (0.1 C-rate) until the voltage level of 2.6 V was reached. Each discharge step was followed by a rest period. Similarly, the rest period was chosen as a function of SOC. As a result, 25 measured emf data points were obtained for both charging and discharging. The low C-rate current was selected to obtain an equilibrium voltage faster. The experiment was carried out at 5, 25, and 45°C.

\[ \text{Results} \]

\[ \text{Battery measurement results}.— \] The results obtained from the measurements presented above are presented here. As an example, the discharge capacity \( Q_d \) in mA for the operational conditions discussed above is plotted in Fig. 1 as a function of cycle number. In both examples, the discharge capacity has been inferred by means of coulomb counting from a complete discharge step at the 0.5 C-rate current. The decrease in discharge capacity can be expressed by

\[ Q_d(\%) = 100 \left( 1 - \frac{Q_f}{Q_{di}} \right) \]

where \( Q_d(\%) \) denotes the decrease in \( Q_d(\text{mA}) \) after \( j \) cycles and \( i \) the battery number. The discharge capacity after 220 cycles is 675 mA, whereas the initial storage capacity was 1165 mA. It can be concluded from this example that after 220 cycles the discharge capacity decreases with about 42%.

For battery 2 (dashed line in Fig. 1), the discharge capacity after 2000 cycles is 935 mA, whereas the initial storage capacity was 1150 mA. Therefore, the discharge capacity drops by 19% in 2000 cycles with respect to the initial storage capacity. Note that the decrease in the discharge capacity illustrated in Fig. 1 is a result of two combined battery processes, i.e., a decrease in battery capacity and an increase in battery impedance. A correct identification and separation of these two factors will be made below, where the battery maximum capacity is determined independently of the battery overpotential.

\[ \text{Qmax measurement results}.— \] By means of the described maximum capacity measurement a Qmax value of 1173 mA has been
Inaccuracy of −10.5%. A possible explanation of the emf for an aged battery, while the SOC value is actually 46.9% generated difference between the measured emf and SOC. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to 25.4% and 5.4%.

\[ Q_{\text{loss}} = 100 - \frac{Q_{\text{max}}}{Q_{\text{max,ref}}} \]  

**EMF measurement results.**—New emf measurement results as a function of battery aging are presented here. The emf measurements were obtained by means of the GITT method presented above for both fresh and aged batteries. New results regarding the emf hysteresis, as a function of battery aging are also presented.

The 25 emf points obtained by means of the GITT method have been fitted according to a mathematical equation. Note that the fitted emf curve passes through the 25 measured points. Figure 2 presents the emf inferred with GITT as function of aging during the discharge cycles at 25°C. The discharge emf retrieved for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

EMF measurement results. New emf measurement results as a function of battery aging are presented here. The emf measurements were obtained by means of the GITT method presented above for both fresh and aged batteries. New results regarding the emf hysteresis as a function of battery aging are also presented.

The 25 emf points obtained by means of the GITT method have been fitted according to a mathematical equation. Note that the fitted emf curve passes through the 25 measured points. Figure 2 presents the emf inferred with GITT as function of aging during the discharge cycles at 25°C. The discharge emf retrieved for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

**Figure 1.** Discharge capacity \( Q_c \) (mAh) as a function of cycle number, \( C_n \), \( Q_{d1} \) and \( Q_{d2} \), the discharge capacities measured for battery 1 and 2, respectively, under two different operational conditions. Battery 1 has been charged by means of the CCCV method until 4.3 V at 25°C. Charging has been terminated when the current cutoff value has reached a current of 0.05 C-rate. During the CC step a 4 C-rate current has been applied. After a resting period of 30 min, the battery was always discharged until 3.0 V at 0.5 C-rate. Battery 2 has been partially (dis)charged between 30% and 70% SOC with 0.5 C-rate current at 25°C. The 40% SOC difference has been calculated as a function of the maximum capacity (\( Q_{\text{max}} \)) measured for a fresh battery. measured for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

EMF measurement results. New emf measurement results as a function of battery aging are presented here. The emf measurements were obtained by means of the GITT method presented above for both fresh and aged batteries. New results regarding the emf hysteresis as a function of battery aging are also presented.

The 25 emf points obtained by means of the GITT method have been fitted according to a mathematical equation. Note that the fitted emf curve passes through the 25 measured points. Figure 2 presents the emf inferred with GITT as function of aging during the discharge cycles at 25°C. The discharge emf retrieved for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

EMF measurement results. New emf measurement results as a function of battery aging are presented here. The emf measurements were obtained by means of the GITT method presented above for both fresh and aged batteries. New results regarding the emf hysteresis as a function of battery aging are also presented.

The 25 emf points obtained by means of the GITT method have been fitted according to a mathematical equation. Note that the fitted emf curve passes through the 25 measured points. Figure 2 presents the emf inferred with GITT as function of aging during the discharge cycles at 25°C. The discharge emf retrieved for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

EMF measurement results. New emf measurement results as a function of battery aging are presented here. The emf measurements were obtained by means of the GITT method presented above for both fresh and aged batteries. New results regarding the emf hysteresis as a function of battery aging are also presented.

The 25 emf points obtained by means of the GITT method have been fitted according to a mathematical equation. Note that the fitted emf curve passes through the 25 measured points. Figure 2 presents the emf inferred with GITT as function of aging during the discharge cycles at 25°C. The discharge emf retrieved for a fresh battery. This value will be further considered as maximum reference capacity, \( Q_{\text{max}} \). The aged batteries discussed in section 3.1 have a \( Q_{\text{max}} = 875 \text{ mAh} \) and \( Q_{\text{max}} = 1110 \text{ mAh} \). The difference between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values and between the measured \( Q_{\text{max}} \) and \( Q_{\text{d}} \) values, 200 and 175 mAh, respectively, are explained by the influence of the battery overpotential in the emf measurement. The capacity loss is calculated using Eq. 3. For the aged batteries, the capacity losses amount to \( Q_{\text{loss}} = 25.4\% \) and \( Q_{\text{loss}} = 5.4\% \).

**Figure 2.** EMF for fresh (f) and aged (a) batteries during discharging at 25°C as function of SOC. \( \text{emf} \) corresponds to battery 1 and \( \text{emf} \) corresponds to battery 2. The emf measurements have been obtained by means of GITT for both fresh and aged batteries. The maximum capacity for both fresh and aged batteries equals the capacity taken out from the battery during a complete discharge cycle performed between the 4.175 and 3.0 emf levels.

Figures 4 and 6 show the measured emf dependencies for fresh and aged batteries during the discharge cycle at 5 and 45°C, respectively. The differences between the “fresh” and “aged” emf at 5 and 45°C are plotted in Fig. 5 and 7, respectively.

These figures show that at all temperatures, a similar increase in the emf difference can be observed when the battery ages. For instance, a difference of about −48 mV is obtained at 57.4% SOC for all considered temperatures. The small difference between the emf measured at different temperatures and at low SOC is explained by the low number of interpolation points chosen at low SOC in the experiments. It can be concluded that the chosen GITT measurement method does not influence the emf determination during discharge.

Until now, the emf measured by means of GITT has been considered during discharge only. However, as shown in Ref. 11 the discharge and charge emf curves are different due to a so-called hysteresis effect.

The emf at 25°C for fresh and aged batteries during charging and discharging is illustrated in Fig. 8. The difference between the corresponding emf curves is plotted in Fig. 9. It appears that a maximum emf difference of 39 mV is obtained for the 5.4% capacity loss.
battery at 4.7% SOC. Ignoring this emf difference leads to an error of −0.7% SOC. This effect will be more pronounced at low temperatures and in the flat region of the emf-SOC curve where even small differences in emf will cause larger errors in SOC. For instance, a difference of about 24 mV is calculated between the emf measured during the charge and discharge cycle for the 5.4% capacity-loss battery at 28.0% SOC. In this case, ignoring the difference between the charge and discharge emf will lead to an error in SOC of −6.7%.

Moreover, the difference between the fresh and aged emf is consistently the same at all temperatures. The emf difference between charge and discharge (see Fig. 8 and 9) may be explained by hysteresis (H). This hysteresis may be introduced by the \( \text{LiCoO}_2 \) electrode. Tentatively, it may be concluded that a possible cause for the hystereses are phase transitions \( \text{ph} \). For further reading on electrochemical hysteresis the reader is referred to Ref. 11 and 14-16.

It can be concluded from the above-described situations that the charge/discharge emf dependence on aging should be taken into consideration to enable accurate SOC determination. Another important conclusion is that although the emf during, e.g., discharge changes with the aging effect (see Fig. 3, 5, and 7), the hysteresis form does not change (see Fig. 9). Therefore, it can be concluded that the aging effect has a similar influence on the charge and discharge emf.

**EMF Modeling**

A model for the emf-SOC relationship is presented here. This emf model is a part of the Li-ion battery model presented in Ref. 1.
molfraction of Li+ ions inside the positive electrode corresponding molfraction of the Li+ ions inside the negative electrode. In the
tion energy between the intercalated Li+ ions from a value realized in the present physical model by the change in the interac-
phase 1 to a value $/H_{20851}$/ given by

\[
\xi = (U_j^+ - U_j^-)x_{\text{ph}} + \xi_j^-,
\]

in which $E_{\text{eq}}^0$ is the standard redox potential of the LiCoO_2 electrode in [V], $U_j^+$ denotes the dimensionless interaction energy coefficient in the LiCoO_2 electrode, $\xi_j$ is a dimensionless constant, $x_{\text{Li}}$ is the molfraction of Li^+ ions inside the positive electrode corresponding to the SOC of the LiCoO_2 electrode, $R$ is the gas constant [J (mol K)^{-1}], $F$ is the Faraday constant [C mol^{-1}], and $T$ is the (ambient) temperature in [K]. In Eq. 6 a phase transition (ph) occurs at $x_{\text{Li}} = x_{\text{ph}}$ that results in a curvature change. According to modern literature on Li-ion batteries with an LiCoO_2 electrode (see, e.g., Ref. 1 and 22) the main phase-transition point is located nearby $x_{\text{ph}} = 75$. A phase transition is noticed as a change in the slope of the equilibrium potential as a function of $x_{\text{Li}}$. This change in slope is realized in the present physical model by the change in the interaction energy between the intercalated Li^+ ions from a value $U_j^+$ in phase 1 to a value $U_j^-$ in phase 2. The values of the dimensionless constants $\xi_j$ and $\xi_j^-$ in phases 1 and 2 are chosen so that a continuous transition in equilibrium potential between phase 1 and 2 is obtained (see Eq. 6).

The negative electrode is modeled similarly

\[
E_{\text{eq}}^- = E_0^- - \frac{RT}{F} \left[ \log \left( \frac{x_{\text{Li}}}{1 - x_{\text{Li}}} \right) + U_j^- x_{\text{Li}} - \xi_j^- \right]
\]

where $E_0^-$ is the standard redox potential of the LiC_6 electrode in [V], $U_j^-$ denotes the dimensionless interaction energy coefficient in the LiC_6 electrode, $\xi_j^-$ is a dimensionless constant, and $z_{\text{Li}}$ is the molfraction of the Li^+ ions inside the negative electrode. In the negative electrode, a phase transition occurring around $z_{\text{ph}} = 0.25$ has been modeled. Under normal operational conditions $x_{\text{Li}}$ will cycle between 0.5 and 1 and $z_{\text{Li}}$ between 0 and 1. To model the emf-SOC relationship in a practical SOC indication system, in addition to the parameters characterizing the electrode electrochemistry, parameters related to the battery design are also required. As schematically indicated in Fig. 10, a fresh Li-ion battery can be characterized by the maximum capacity of the positive electrode ($Q_{\text{max}}$), the maximum capacity of the negative electrode ($Q_{\text{max}}^{-}$), the amount of electrochemically active Li^+ ions inside a fresh battery ($Q_0$), and the amount of Li^+ ions inside the negative electrode in a fully (under standard operational conditions) discharged battery ($Q_{\text{f}}$). Finally, $Q_j$ denotes the charge stored in the negative electrode for a given SOC.

For a fresh battery, the amount of the electrochemically active Li^+ ions inside the battery $Q_{\text{max}}$ will equal the maximum capacity of the positive electrode $Q_{\text{max}}^+$. Note that because $x_{\text{Li}}$ cycles between 0.5 and 1 only half of the maximum capacity of the positive electrode $Q_{\text{max}}^+$ is cyclable. In this case the number of the cyclable electrochemically active Li^+ ions is equal to $Q_{\text{max}} - Q_{\text{max}}^-/2$. During the first activation cycles, a part of the amount of the Li^+ ions will remain in the negative electrode (represented by $Q_0$ in Fig. 10) and another part will be consumed in the solid electrolyte interface (SEI), which is an irreversible process. The $Q_0$ capacity can be explained by the Nernstian decrease of the LiC_6 electrode equilibrium voltage when its SOC is going to zero. The SEI suppresses the decomposition of the electrolyte at the electrode surface. For simplicity, the SEI has not been illustrated in Fig. 10 and is not consid-
ered in the present physical model. Given the parameters of Fig. 10 and the experimentally determined SOC values, $x_{\text{Li}}$ and $z_{\text{Li}}$ can be determined from

\[
z_{\text{Li}} = \frac{Q_0}{Q_{\text{max}}^+}
\]

where $Q_j$ is the SOC of the LiCoO_2 electrode, $Q_j$ is the SOC of the LiC_6 electrode, and $Q_{\text{max}}$ is the maximum capacity of the battery. The measured charge/discharge emf difference $U_{\text{ab}}$ between fresh (f) and aged (a) batteries at 25°C as function of SOC (see also Fig. 8).

Figure 10. (Color online) Schematic representation of a “fresh” Li-ion battery parameters related to the battery design. Under normal operational conditions, the positive electrode will cycle between 0.5 and 1 and the negative electrode between 0 and 1.
Equations 9–11 can be understood as follows. It follows from Fig. 10 that the Li+ ions move from the cobalt-oxide electrode to the graphite electrode during charging. At the end of charging, the battery SOC is defined to be 100%, i.e., $Q_c^-$ is equal to $Q_{max}$ and $Q_c^+$ equals $Q_{max} - Q_{max}/2$ (Eq. 10). It follows from Eq. 9 and 11 that at 100% SOC $x_{Li} = (Q_{max} - Q_{max} - Q_{max}/2)/Q_{max} = 0.5$ and $z_{Li} = 1$. During discharge the Li+ ions move from the graphite electrode to the cobalt-oxide electrode. At the end of discharging under standard operational conditions, $Q_c = Q_0$. As can be calculated from Eq. 9 and 11, the $x_{Li} = (Q_{max} - Q_0)/Q_{max}$ will be a somewhat smaller than 1 and $z_{Li} = Q_c/Q_{max}$ will be a little bit larger than 0.

$E_{eq}^+$ and $E_{eq}^-$ are calculated from Eq. 5 and 6 and Eq. 7 and 8, respectively. However, from the emf measurements can be shown that the phase transition does not take place instantaneously but in a certain interval around the phase transition points. To achieve a smooth phase transition the following approximation is considered

$$E_{eq}^+ = E_0^+ - \frac{RT}{F} \left\{ \log \left( \frac{x_{Li}}{1 - x_{Li}} \right) + \Phi \left( \frac{x_{Li} - x_{ph}}{\sigma_x} \right) \left( U_{eq}^+ x_{Li} - \xi^+ \right) + \left[ 1 - \Phi \left( \frac{1 - x_{Li}}{\sigma_x} \right) \right] \left( U_{eq}^+ x_{Li} - \xi^+ \right) \right\}$$

$$E_{eq}^- = E_0^- - \frac{RT}{F} \left\{ \log \left( \frac{z_{Li}}{1 - z_{Li}} \right) + \Phi \left( \frac{z_{Li} - z_{ph}}{\sigma_z} \right) \left( U_{eq}^- z_{Li} - \xi^- \right) + \left[ 1 - \Phi \left( \frac{1 - z_{Li}}{\sigma_z} \right) \right] \left( U_{eq}^- z_{Li} - \xi^- \right) \right\}$$

where $\Phi$ denotes a standard normal cumulative distribution function and the parameters $\sigma_x$ and $\sigma_z$ determine the smoothness of the phase transitions in the positive and negative electrode, respectively.

To include the temperature influence in the emf-SOC relationship a linear dependence of each model parameter (par) has been assumed according to

$$par(T) = par(T_{ref}) + (T - T_{ref}) \Delta par$$

where $T_{ref}$ is the reference temperature (in this case 25°C) and $T$ is the ambient temperature. $\Delta par$ is the sensitivity to temperature of each parameter.

Different values for the model parameters can be used for the charge- and discharge-emf to deal with the hysteresis effect. Also, when another type of Li-ion battery with a different emf-SOC curve chemistry is used the model can be adapted by fitting, leading to new parameter values. In this way, this model is not limited to the present Li-ion battery type. Taking into account hysteresis and temperature, the presented method is considered to be the best solution for a practical emf implementation.

**EMF Modeling as Function of Battery Aging**

A physical model for the emf-SOC relationship for fresh batteries has been presented above. For a given emf and temperature, the corresponding SOC can be calculated. However, the measured emf curve is also dependent on battery aging as presented above. Here, the physical emf model developed above is used to explain the emf dependence on battery aging in a qualitative way.

As expressed in Eq. 1, the LiCoO2 electrode will decompose during aging and an inactivator layer may be formed at the LiCoO2 electrode surface. As a result, the amount of cyclable electrochemically active Li+ ions in the battery will reduce. For this reason, the emf model parameters related to the battery design (Fig. 10) will also change, whereas the emf parameters related to the battery thermodynamics will remain the same. This situation is schematically indicated in Fig. 11 where the aged Li-ion battery is characterized by a similar set of parameters as for the fresh battery (Fig. 10). To make a comparison, the defined parameters related to the battery design for a fresh battery are also represented.

It follows from Fig. 11 that the amount of electrochemically active Li+ ions inside an aged battery $Q_{max}$ is higher than the maximum capacity of the positive electrode $Q_{max}$. This situation can be explained by the LiCoO2 electrode decomposition or CoO2 layer formation at the electrode surface (see Eq. 1). In this case, for an aged battery, an amount of electrochemically active Li+ ions will remain stored in the LiCo electrode which will contribute to a higher $Q_{max}$ than $Q_{max}$. The formation of the CoO2 at the LiCoO2 electrode surface will also contribute to the increase of the battery overpotential. Therefore, during the battery lifetime, the amount of Li+ ions that will remain inside the graphite at the end of discharge executed under the same operational conditions will increase. This situation is illustrated in Fig. 11 by $Q_c$ and $Q_{max}$.

Figure 12 illustrates the $E_{eq}^+$ and $E_{eq}^-$ dependence on SOC for a fresh and aged battery. $E_{eq}^+$ may have a voltage value between 3.6 and 4.3 V whereas $E_{eq}^-$ ranges between 0.1 and 0.6 V. In this case, the emf calculated for the fresh battery has a voltage value between 3 and 4.2 V. These emf limits correspond to 0 and 100% SOC, respectively. During the battery lifetime the LiCoO2 electrode will decompose and an amount of the cyclable Li+ ions will remain stored inside the LiCo electrode. Therefore, $Q_{max}$ will be lower than $Q_{max}$/2 a result, $E_{eq}^+$ or an aged battery will have a emf value lower than 0.6 V at the 0% SOC level (see Fig. 12b). Consequently, to reach the defined 3 Vemf level at 0% SOC the positive electrode is discharged under the 3.6 V emf level (see Fig. 12b). In this case, the emf for the aged battery will be calculated as a difference between different equilibrium potential levels with respect to the emf calculated for a fresh battery. Therefore, the emf calculated for the aged battery will be different from the emf calculated for a fresh battery. Also the battery degradation process, mainly induced by the LiCoO2 electrode, will be accelerated.

To further investigate the emf dependence on the aging effect the
battery model presented in Ref. 13 has been simulated. During these simulations, similar aspects to the ones presented above have been taken into account. For this case, a good agreement between the qualitative explanation given in Fig. 12 and simulations has been obtained. Furthermore, several batteries have been opened and measurements with reference electrodes have been performed.\textsuperscript{23} These measurements confirmed that the positive electrode decomposition mechanism is mainly responsible for the emf aging effect. This enhances the confidence level of the emf dependence on the aging process presented in this paper.

**Conclusions**

New emf measurements and models as a function of battery aging have been presented for Li-ion batteries. The emf can be used as input for an accurate and adaptive state-of-charge algorithm.

The emf has been measured by means of GITT. The effects of the temperature and hysteresis on the emf-SOC curve as a function of battery aging and the influence on the SOC indication accuracy have been investigated. The results show that the emf of an Li-ion battery depends on aging. This dependence leads to more than 10% SOoC inaccuracy prediction when only the emf for a fresh battery is considered. Therefore, to enable accurate SOC indication, this dependence must be taken into account.

A mathematical model for the emf-SOC relationship that also takes the temperature into account has been presented. With this model, the emf dependence on the battery aging has been explained. The difference between fresh and aged battery emfs has been attributed to the LiCoO\textsubscript{2} electrode decomposition.

In future publications, solutions used to improve the SOC indication by including the aging effect will be addressed.

*University of Twente assisted in meeting the publication costs of this article.*

**References**