A Novel Method for the In Situ Determination of Concentration Gradients in the Electrolyte of Li-Ion Batteries

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Abstract: An electrochemical method has been developed for the in situ determination of concentration gradients in the electrolyte of sealed Li-ion batteries by measuring the potential difference between microreference electrodes. Formulas relating the concentration gradient and the potential difference between the microreference electrodes were derived from the Nernst–Planck equation. The concentration gradients in Li-ion batteries are theoretically and experimentally proven to be linear at steady state under galvanostatic charging and discharging conditions. Based on this finding, both the diffusion coefficient of the lithium ions in the electrolyte and the diffusion overpotential related to the concentration gradient have been calculated. It was found that the concentration gradient is proportional to the applied current over a wide current range and that the obtained diffusion coefficient of lithium ions is almost constant. For the batteries studied in this work, the diffusion overpotential is already noticeable at 0.30 A and the limiting current is estimated to be 1.1 A, corresponding to a C-rate of 3.7.

Keywords: concentration gradient · electric potential · electrochemistry · lithium · lithium-ion battery

Introduction

Li-ion batteries are now a widely accepted power source for a huge variety of portable electronic devices, due to their high energy density and excellent cycle life. To gain a better understanding of the electrochemical characteristics of Li-ion batteries, intense research has taken place over the last decade. Of special interest is the electrochemistry of the electrode materials used in such batteries. The electrochemical charge-transfer kinetics and the diffusion coefficient of lithium ions in both the positive and negative electrode have been extensively studied.[1–6] In contrast, the electrochemistry involving the electrolyte attracts much less interest despite its important role in the performance of Li-ion batteries. For instance, Bergveld et al. have simulated that the diffusion overpotential from the electrolyte in Li-ion batteries is comparable to the kinetic overpotentials.[7] Sawai et al. have studied the factors affecting the rate capability of graphite electrodes for Li-ion batteries and have found that the dominant influential factor is not the diffusion of lithium ions in the graphite electrode, but the diffusion of lithium ions in the electrolyte.[8]

One aspect involving the electrolyte is the diffusion and migration of species under the influence of concentration gradients in the electrolyte when currents are flowing through the battery.[9] This diffusion/migration process may result in a diffusion overpotential contributing to the total battery overpotential, which has a great impact on the rate capability of the battery. The total overpotential is usually made up of charge transfer overpotentials and diffusion overpotentials. According to Vetter,[10] calculation of the diffusion overpotential from the electrolyte is possible by means of the Nernst equation, using the concentration of the relevant species directly adjacent to the electrode surface. This surface concentration can be obtained from the established concentration gradient. Consequently, the determination of the concentration gradient in the electrolyte can help to provide some quantitative information about the total battery overpotential, thereby advancing the operation of Li-ion batteries.

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The concentration gradient in the electrolyte is also important for battery modeling, which nowadays forms a key part of battery management systems.[7,11] Battery models are very helpful for predicting the behavior of batteries under a wide variety of operating conditions and a good battery management system induces more efficient battery operation.[7,12]

In spite of its importance for battery performance, knowledge about the concentration gradient in the electrolyte of Li-ion batteries is very limited in the literature. The lack of knowledge might be due to the difficulties of in situ measurement of the concentration gradients in sealed batteries. Some work has been done in this field,[13–16] but this was based mainly on optical methods and is not applicable to sealed battery systems due to the complexity of the measurements and the experimental equipment.

In this paper, an electrochemical method is presented for in situ determination of the established concentration gradients in the electrolyte of sealed Li-ion batteries under galvanostatic charging and discharging conditions. Based on the measured concentration gradients, both the diffusion coefficient of lithium ions in the electrolyte and the diffusion overpotential contributed by the electrolyte can be calculated. The limiting charging and discharging currents of the batteries investigated in this work has also been estimated.

Theory

General: The passage of current through batteries induces ionic mass and charge transport in the electrolyte. For prismatic Li-ion batteries, it is reasonable to assume that the ionic transport in the electrolyte is a one-dimensional process, which can be described by Equation (1), the Nernst–Planck equation,[9] in which $J_j(x)$ is the flux of species j ($\mathrm{mol\,m^{-2}\,s^{-1}}$) at a distance x from the electrode/electrolyte interface, D_j is the diffusion coefficient of j ($\mathrm{m^2\,s^{-1}}$), $\partial c_j(x)/\partial x$ is the concentration gradient at a distance x ($\mathrm{mol\,m^{-4}}$), $\partial\phi(x)/\partial x$ the potential gradient ($\mathrm{V\,m^{-1}}$), z_j and c_j are the valence state (dimensionless) and the concentration ($\mathrm{mol\,m^{-3}}$) of species j, respectively, $v(x)$ is the velocity ($\mathrm{m\,s^{-1}}$) with which a volume element in solution moves along the axis, F is the Faraday constant ($96485\ \mathrm{C\,mol^{-1}}$), R is the universal gas constant ($8.314\ \mathrm{J\,K^{-1}\,mol^{-1}}$) and T is the absolute temperature (K). The three terms on the right-hand side of Equation (1) represent the contributions of diffusion, migration and convection, respectively, to the ionic flux.

$$J_j(x) = -D_j\frac{\partial c_j(x)}{\partial x} - \frac{z_jF}{RT}D_jc_j\frac{\partial\phi(x)}{\partial x} + c_jv(x) \qquad (1)$$

The electrolyte employed in this work contains $\mathrm{LiPF_6}$ as a salt, therefore the species j are $\mathrm{Li^+}$ and $\mathrm{PF_6^-}$ in the present paper. Since $\mathrm{Li^+}$ and $\mathrm{PF_6^-}$ ions are charged moieties, the current I_j associated with the ionic transport of species j in the electrolyte is given by Equation (2),[9] in which A is the geometrical electrode surface area through which the flux passes.

$$I_j = -z_jFAJ_j(x) \qquad (2)$$

The total current, I, at any location in the electrolyte of a Li-ion battery consists of contributions from all species and, assuming that the contribution of the convection flux to the total current is negligible [see Eq. (1)], can be expressed by Equation (3).

$$I = I_{\mathrm{d,Li^+}} + I_{\mathrm{d,PF_6^-}} + I_{\mathrm{m,Li^+}} + I_{\mathrm{m,PF_6^-}} \qquad (3)$$

The parameter $I_{\mathrm{d,Li^+}}$, which is the diffusion-related current carried by $\mathrm{Li^+}$ ions, can be represented by Equation (4).

$$I_{\mathrm{d,Li^+}} = z_{\mathrm{Li^+}}FAD_{\mathrm{Li^+}}\frac{\partial c_{\mathrm{Li^+}}}{\partial x} \qquad (4)$$

Similarly, the diffusion-related current of $\mathrm{PF_6^-}$ ions ($I_{\mathrm{d,PF_6^-}}$) can be given by Equation (5).

$$I_{\mathrm{d,PF_6^-}} = z_{\mathrm{PF_6^-}}FAD_{\mathrm{PF_6^-}}\frac{\partial c_{\mathrm{PF_6^-}}}{\partial x} \qquad (5)$$

The migration-related currents of $\mathrm{Li^+}$ ($I_{\mathrm{m,Li^+}}$) and $\mathrm{PF_6^-}$ ions ($I_{\mathrm{m,PF_6^-}}$) can be represented by Equations (6) and (7), respectively.

$$I_{\mathrm{m,Li^+}} = \frac{z_{\mathrm{Li^+}}^2 F^2 AD_{\mathrm{Li^+}}c_{\mathrm{Li^+}}}{RT}\frac{\partial\phi}{\partial x} \qquad (6)$$

$$I_{\mathrm{m,PF_6^-}} = \frac{z_{\mathrm{PF_6^-}}^2 F^2 AD_{\mathrm{PF_6^-}}c_{\mathrm{PF_6^-}}}{RT}\frac{\partial\phi}{\partial x} \qquad (7)$$

Since $\mathrm{PF_6^-}$ ions are not involved in the electrode reactions in Li-ion batteries, no net transport of $\mathrm{PF_6^-}$ ions takes place under steady state (dis)charging conditions, which leads to Equation (8).

$$I_{\mathrm{m,PF_6^-}} + I_{\mathrm{d,PF_6^-}} = 0 \qquad (8)$$

Consequently, Equation (3) can be simplified to Equation (9), which indicates that the total current, I, in the electrolyte is carried exclusively by the lithium ions.

$$I = I_{\mathrm{d,Li^+}} + I_{\mathrm{m,Li^+}} = z_{\mathrm{Li^+}}FAD_{\mathrm{Li^+}}\left[\frac{\partial c_{\mathrm{Li^+}}}{\partial x} + \frac{z_{\mathrm{Li^+}}Fc_{\mathrm{Li^+}}}{RT}\frac{\partial\phi}{\partial x}\right] \qquad (9)$$

The electroneutrality condition in the electrolyte states that $c_{\mathrm{Li^+}}$ is equal to $c_{\mathrm{PF_6^-}}$. Thus the concentration gradient for both ions must be identical, as given in Equation (10).

$$\frac{\partial c_{\mathrm{Li^+}}}{\partial x} = \frac{\partial c_{\mathrm{PF_6^-}}}{\partial x} \qquad (10)$$

Introducing Equations (5), (7) and (10) into Equation (8), and considering that $z_{\mathrm{Li^+}} = -z_{\mathrm{PF_6^-}}$ leads to Equation (11).

$$\frac{\partial \phi}{\partial x} = \frac{RT}{z_{\text{Li}^+} F c_{\text{Li}^+}} \frac{\partial c_{\text{Li}^+}}{\partial x} \tag{11}$$

Substitution of Equation (11) into Equation (9) after rearrangement ultimately yields Equation (12).

$$\frac{\partial c_{\text{Li}^+}}{\partial x} = \frac{I}{2 z_{\text{Li}^+} F A D_{\text{Li}^+}} \tag{12}$$

Since D_{Li^+} can be considered to be concentration-independent over a given concentration range and z_{Li^+} and F are constants, Equation (12) reveals that the concentration gradient of lithium ions in the electrolyte is a constant under galvanostatic steady-state conditions, indicating a linear concentration gradient in the electrolyte. Based on this linearity, it is possible to determine electrochemically the concentration gradient in the electrolyte.

Relation between the electric potential difference and concentration difference in the electrolyte: The presence of a concentration gradient and/or a potential gradient results in an electrochemical potential gradient. In the case of Li-ion batteries, the electrochemical potential of lithium ions in the electrolyte, $\bar{\mu}_{\text{Li}^+}$, is given by Equation (13),[17] in which $\mu^{\text{o}}_{\text{Li}^+}$ is the standard chemical potential (J mol^{-1}), a_{Li^+} and $a^{\text{ref}}_{\text{Li}^+}$ are the activities of lithium ions and their activity in the reference state (in mol m^{-3}), respectively, and ϕ is the Galvanic potential (in V).

$$\bar{\mu}_{\text{Li}^+} = \mu^{\text{o}}_{\text{Li}^+} + RT \ln \frac{a_{\text{Li}^+}}{a^{\text{ref}}_{\text{Li}^+}} + z_{\text{Li}^+} F \phi \tag{13}$$

The difference in electrochemical potential between two different locations in the electrolyte can then be expressed by Equation (14), in which the activities are replaced by concentrations of lithium ions for simplicity.

$$\bar{\mu}^1_{\text{Li}^+} - \bar{\mu}^2_{\text{Li}^+} = RT \ln \frac{c^1_{\text{Li}^+}}{c^2_{\text{Li}^+}} + z_{\text{Li}^+} F (\phi_1 - \phi_2) \tag{14}$$

Equation (11) can be rewritten as Equation (15).

$$\frac{\partial \phi}{\partial x} = \frac{RT}{z_{\text{Li}^+} F} \frac{1}{c_{\text{Li}^+}} \frac{\partial c_{\text{Li}^+}}{\partial x} = \frac{RT}{z_{\text{Li}^+} F} \frac{\partial \ln c_{\text{Li}^+}}{\partial x} \tag{15}$$

Equation (15) gives Equation (16) after integration with respect to x.

$$\phi_1 - \phi_2 = \frac{RT}{z_{\text{Li}^+} F} \ln \frac{c^1_{\text{Li}^+}}{c^2_{\text{Li}^+}} \tag{16}$$

Substitution of Equation (16) into Equation (14) then leads to Equation (17).

$$\bar{\mu}^1_{\text{Li}^+} - \bar{\mu}^2_{\text{Li}^+} = 2RT \ln \frac{c^1_{\text{Li}^+}}{c^2_{\text{Li}^+}} \tag{17}$$

The electrochemical potential is related to the measurable electric potential, E, by the relation $\bar{\mu} = zFE$.[18] As a result, Equation (18) is obtained.

$$E_1 - E_2 = \frac{\bar{\mu}^1_{\text{Li}^+} - \mu^2_{\text{Li}^+}}{z_{\text{Li}^+} F} = \frac{2RT}{z_{\text{Li}^+} F} \ln \frac{c^1_{\text{Li}^+}}{c^2_{\text{Li}^+}} \tag{18}$$

Measurement of the electric potential difference can be achieved by placing two microreference electrodes at different locations in the electrolyte. Since z_{Li^+}, R, T, and F are all known constants, it is then possible, according to Equation (18), to determine the concentration difference between two microreference electrodes in the electrolyte. If the distance between the two microreference electrodes is known, the concentration gradient in the electrolyte can be determined, as Equation (12) manifests a linear concentration gradient built up in the electrolyte under galvanostatic steady-state conditions.

Results and Discussion

To prove that linear concentration gradients are indeed experimentally established under steady-state conditions, the experiments performed with batteries containing three (see Figure 1) and four (see Figure 5, later) microreference electrodes will be described first. It will be shown that there is a close similarity of operation between a conventional Li-ion battery and one containing two microreference electrodes.
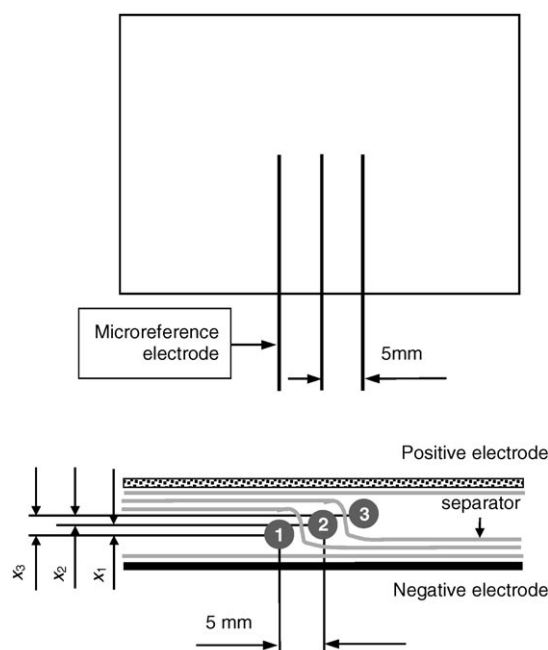

Figure 1. Schematic representation of a battery with three microreference electrodes: top view (top), side view (bottom). x is the distance between every two microreference electrodes, perpendicular to the electrode plane. It is assumed that $x_1 = x_2 = 30\ \mu\text{m}$.

Measurements with three microreference electrodes: One of the characteristics of a linear concentration gradient is that given by Equation (19), in which $c_{Li^+}^1$, $c_{Li^+}^2$, and $c_{Li^+}^3$ are the concentrations at any three locations along this concentration gradient, and x_1 and x_2 are the distances between two locations.

$$\frac{c_{Li^+}^1 - c_{Li^+}^2}{x_1} = \frac{c_{Li^+}^2 - c_{Li^+}^3}{x_2} \qquad (19)$$

Figure 2 illustrates the linear concentration gradient generated when discharging the battery represented in Figure 1. In the special case when x_1 equals x_2 in Figure 2, Equation (19) reduces to Equation (20).
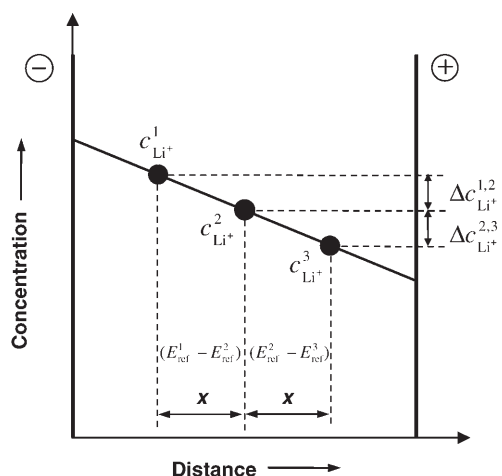
Figure 2. Illustration of a linear concentration gradient in the electrolyte. $c_{Li^+}^1$, $c_{Li^+}^2$, $c_{Li^+}^3$ are the concentrations of the electrolyte at three different locations. $\Delta c_{Li^+}^{1,2}$ and $\Delta c_{Li^+}^{2,3}$ are the concentration differences between two locations. x is the distance between two locations.

$$c_{Li^+}^1 - c_{Li^+}^2 = c_{Li^+}^2 - c_{Li^+}^3 \qquad (20)$$

From Figure 2 it is clear that $c_{Li^+}^1 = c_{Li^+}^2 + \Delta c_{Li^+}^{1,2}$ and $c_{Li^+}^3 = c_{Li^+}^2 - \Delta c_{Li^+}^{2,3}$. Introducing these concentrations into Equation (18) yields Equations (21) and (22), in which E_{ref} is the electric potential of the microreference electrode. Elegantly, $\left(\frac{\Delta c_{Li^+}^{1,2}}{c_{Li^+}^2}\right)$ and $\left(\frac{\Delta c_{Li^+}^{2,3}}{c_{Li^+}^2}\right)$ can be determined by measuring the potential differences $(E_{ref}^1 - E_{ref}^2)$ and $(E_{ref}^2 - E_{ref}^3)$, respectively.

$$E_{ref}^1 - E_{ref}^2 = \frac{2RT}{z_{Li^+}F} \ln \frac{c_{Li^+}^2 + \Delta c_{Li^+}^{1,2}}{c_{Li^+}^2} = \frac{2RT}{z_{Li^+}F} \ln\left(1 + \frac{\Delta c_{Li^+}^{1,2}}{c_{Li^+}^2}\right) \qquad (21)$$

$$E_{ref}^2 - E_{ref}^3 = \frac{2RT}{z_{Li^+}F} \ln \frac{c_{Li^+}^2}{c_{Li^+}^2 - \Delta c_{Li^+}^{2,3}} = -\frac{2RT}{z_{Li^+}F} \ln\left(1 - \frac{\Delta c_{Li^+}^{2,3}}{c_{Li^+}^2}\right) \qquad (22)$$

Figure 3 shows, as an example, a typical measurement of the potential difference between two microreference elec-
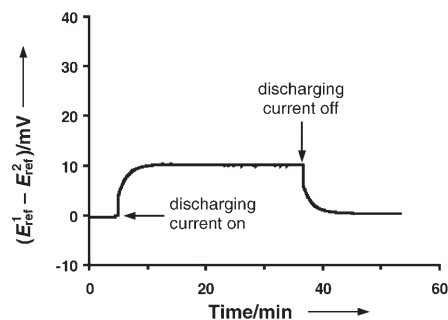

Figure 3. The potential difference between two microreference electrodes measured when discharging a 300 mAh battery at 0.12 A.

trodes when discharging a 300 mAh battery with a constant current of 0.12 A from its initial 50% state-of-charge (SoC). Before turning on the discharging current, there was no potential difference between these two microreference electrodes. When the current was switched on, a potential step, resulting from the electrolyte resistance, occurred instantly. After a short period of time, the potential difference entered a horizontal plateau, suggesting that the ionic current flowing through the electrolyte had reached its steady state. When the discharging current was switched off, a potential step was again observed and the potential difference subsequently started to decay, corresponding to the battery relaxation towards the new equilibrium state.

Figure 4 (top) shows the measured potential differences between the microreference electrodes obtained when discharging the battery with various constant currents. Note that all the potential differences presented in this paper are mean values of each horizontal plateau. In Figure 4a (top), two straight lines were observed. Considering Equation (18),
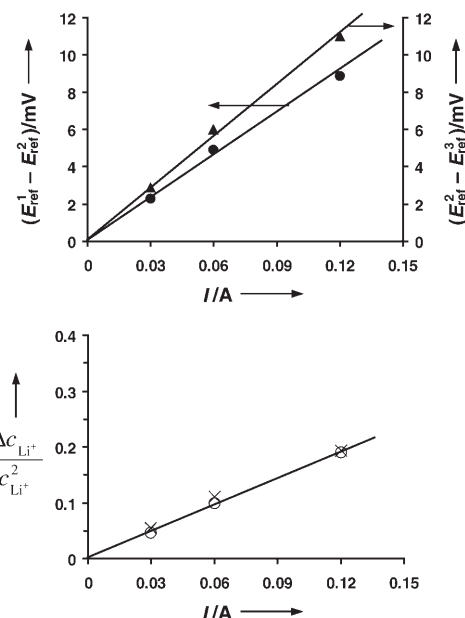

Figure 4. Measured potential differences (top) and calculated ratios (bottom) of concentrations ($\Delta c_{Li^+}^{1,2}/c_{Li^+}^2$, ○; $\Delta c_{Li^+}^{2,3}/c_{Li^+}^2$, ×) obtained when discharging a 300 mAh battery as shown in Figure 1 at different currents.

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it can easily be shown that linearity is expected for low concentration ratios ($\ln(1+x) \approx x$ when $x \to 0$). It was noticeable that $(E_{ref}^2 - E_{ref}^3)$ was always larger than $(E_{ref}^1 - E_{ref}^2)$ at all applied currents and the difference between $(E_{ref}^2 - E_{ref}^3)$ and $(E_{ref}^1 - E_{ref}^2)$ increased with the increasing currents. $\left(\dfrac{\Delta c_{Li^+}^{1,2}}{c_{Li^+}^2}\right)$ and $\left(\dfrac{\Delta c_{Li^+}^{2,3}}{c_{Li^+}^2}\right)$ are calculated according to Equations (21) and (22), respectively. The results are plotted in Figure 4 (bottom). $\left(\dfrac{\Delta c_{Li^+}^{1,2}}{c_{Li^+}^2}\right)$ and $\left(\dfrac{\Delta c_{Li^+}^{2,3}}{c_{Li^+}^2}\right)$ are found to be essentially equal at all currents, which proves that $(c_{Li^+}^1 - c_{Li^+}^2)$ is indeed equal to $(c_{Li^+}^2 - c_{Li^+}^3)$.

Measurements with four microreference electrodes: The effect of the distance between two microreference electrodes on the measured potential differences was also examined. A battery with four microreference electrodes was constructed, as shown in Figure 5. These four microreference electrodes were divided into two groups and located between different positive and negative electrodes. Microreference electrodes 1 and 2 were separated with four separators, while 3 and 4 were separated with one. The thickness of the single separator was measured after battery assembly and it was found that it remained 30 µm. In contrast, the total thickness of four separators was 105 µm. Therefore these are the values used for the distances in the calculations.
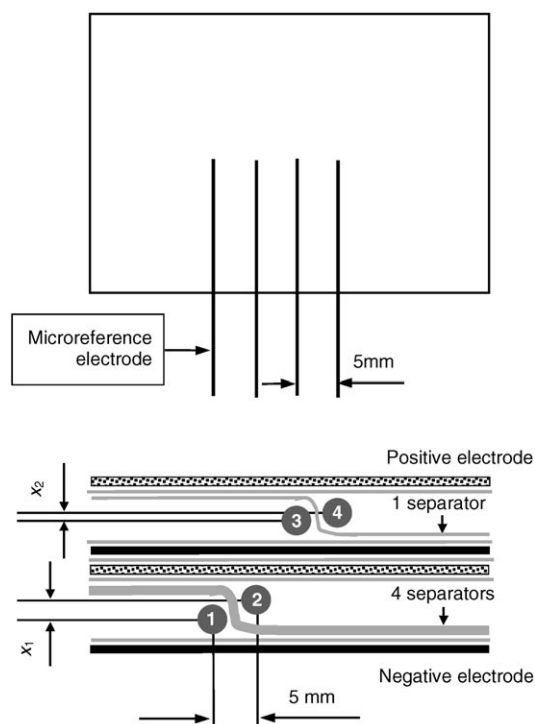

Figure 5. Schematic representation of a battery with four microreference electrodes: top view (top), side view (bottom). x is the distance between two microreference electrodes, perpendicular to the electrode plane. The measured distances are $x_1 = 105$ µm, $x_2 = 30$ µm. The gray and black bars represent the positive and negative electrodes, respectively.

The potential differences between two microreference electrodes, $(E_{ref}^1 - E_{ref}^2)$ and $(E_{ref}^3 - E_{ref}^4)$, were measured under steady state conditions when discharging the battery with different currents. The results are summarized in Figure 6
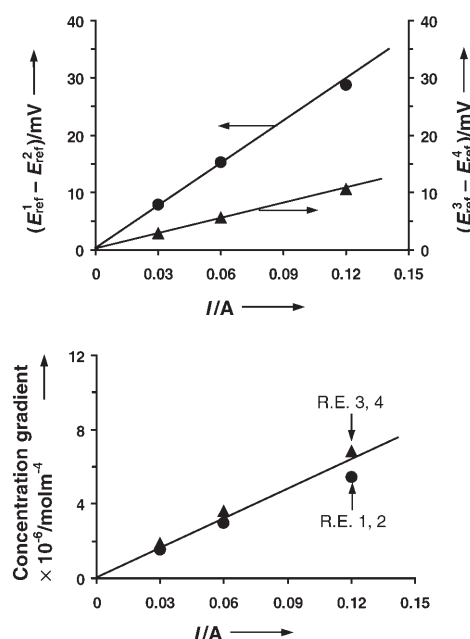

Figure 6. Measured potential differences (top) and calculated concentration gradients (bottom) obtained when discharging a 300 mAh battery as shown in Figure 5. R.E. stands for reference electrode.

(top) and clearly show that for all currents, $(E_{ref}^1 - E_{ref}^2)$, the potential difference between microreference electrodes one and two, was larger than $(E_{ref}^3 - E_{ref}^4)$, the potential difference between microreference electrodes three and four. Moreover, the difference between $(E_{ref}^1 - E_{ref}^2)$ and $(E_{ref}^3 - E_{ref}^4)$ increases with increasing current.

Figure 6 (bottom) shows the calculated concentration gradients corresponding to Figure 6 (top). In contrast to the significant differences observed between $(E_{ref}^1 - E_{ref}^2)$ and $(E_{ref}^3 - E_{ref}^4)$, the concentration gradients calculated from $(E_{ref}^1 - E_{ref}^2)$ and $(E_{ref}^3 - E_{ref}^4)$ are almost the same, especially at small currents. According to Equation (18), for a linear concentration gradient as shown in Figure 2, the larger the distance between two microreference electrodes, the larger the measured potential difference is while the calculated concentration gradient remains the same. This prediction is in agreement with the data in Figure 6, proving that the concentration gradient in the electrolyte is linear.

Measurements with two microreference electrodes: Figure 7 depicts a battery with two microreference electrodes positioned at equal distances from the center. As the concentration of the electrolyte used in this work is 1 mol L^{-1}, it is easy to prove by symmetry that the concentration at the midpoint of a linear concentration gradient is 1 mol L^{-1}. Therefore, as illustrated in Figure 7, it is known that the
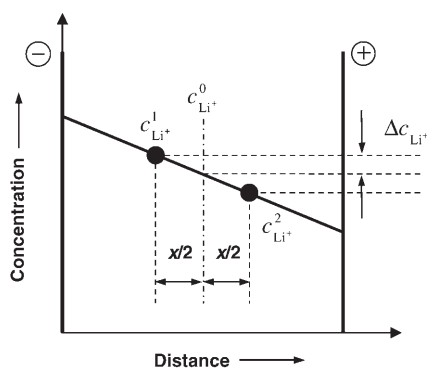
Figure 7. Illustration of a linear concentration gradient in the electrolyte when discharging a battery. The dash-dotted line in the center gives the $c_{Li^+}^0$ concentration in the electrolyte at the midpoint, which is $1\,\mathrm{mol\,L^{-1}}$ in this work. Two microreference electrodes (solid dots) are placed at equal distance from the center.

concentration of the electrolyte where the two microreference electrodes are located can be expressed by Equations (23) and (24).

$$c_{Li^+}^1 = 1 + \Delta c_{Li^+} \tag{23}$$

$$c_{Li^+}^2 = 1 - \Delta c_{Li^+} \tag{24}$$

The value of Δc_{Li^+} can be obtained by substituting Equations (23) and (24) into Equation (18), through using the measured potential difference between these two microreference electrodes. Because the distance between the two microreference electrodes is known to be 30 μm, the concentration gradient, as well as $c_{Li^+}^1$ and $c_{Li^+}^2$, can be calculated.

Figure 8 (top) shows the measured potential differences under steady-state conditions between two microreference electrodes for both charging and discharging the battery at various currents. The sign of the measured potential differences is an indication of the direction of the concentration gradient. The curves of charging and discharging were symmetric with respect to the zero voltage level. This result was expected, as the concentration gradients of lithium ions in the electrolyte must have the same value but different directions for charging and discharging.

The calculated concentration gradients corresponding to Figure 8 (top) are plotted in Figure 8 (bottom). A clear linear relation between the concentration gradient and applied current is observed for both charging and discharging, which is consistent with Equation (12), showing that the concentration gradient is proportional to the applied current. The charging and discharging curves are symmetric with respect to the zero concentration gradient level, emphasizing the reliability of the measurements.

Diffusion coefficient of lithium ions and diffusion overpotential: Once the concentration gradient is known, the diffusion coefficient of lithium ions in the electrolyte can be obtained from Equation (12). The calculated diffusion coefficients using the discharging data presented in Figure 8 are
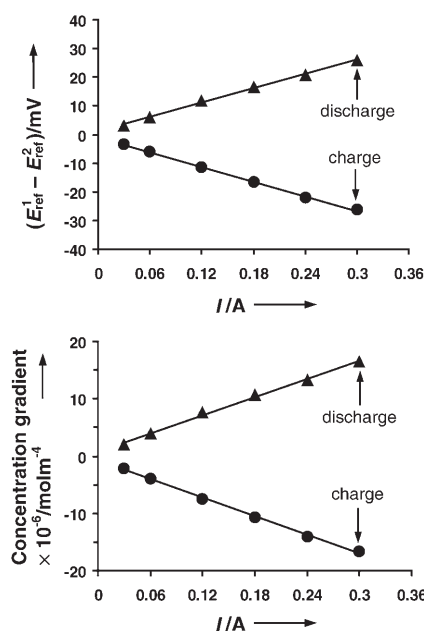

Figure 8. Top: Measured potential differences between two microreference electrodes when (dis)charging a 300 mAh battery at different currents. Bottom: The correspondingly calculated concentration gradients. The geometric surface area of this battery is $8.9 \times 10^{-3}\,\mathrm{m^2}$.

listed in Table 1. It can be seen that the diffusion coefficient was almost constant over the current range from 0.03 to 0.30 A, showing only small fluctuations, and giving values very close to those reported in the literature.[7]

Table 1. Diffusion coefficient of lithium ions in the electrolyte and the diffusion overpotential for the individual electrode calculated with the discharging data in Figure 8. T is 298 K.

I [A]	$D_{Li^+} \times 10^{12}$ [m²s⁻¹]	$c_{Li^+}^{neg}$ [mol L⁻¹]	$c_{Li^+}^{pos}$ [mol L⁻¹]	$\lvert \eta_d^{neg} \rvert$ [mV]	$\lvert \eta_d^{pos} \rvert$ [mV]
0.03	9.0	1.03	0.97	0.7	0.8
0.06	8.8	1.06	0.94	1.5	1.6
0.12	9.2	1.11	0.89	2.8	3.1
0.18	9.8	1.16	0.84	3.8	4.5
0.24	10.6	1.20	0.80	4.6	5.7
0.30	10.6	1.25	0.75	5.7	7.3

Figure 9 schematically represents a conventional Li-ion battery without microreference electrodes under steady state discharging conditions. $c_{Li^+}^{neg}$ and $c_{Li^+}^{pos}$ are the electrolyte concentrations at the surface of the negative and positive electrode, respectively. The distance between the positive and negative electrode is the same as that between two microreference electrodes, for which the distance was assumed to be determined by the thickness of the separator. Considering the results described above it can be concluded that the concentration gradient obtained with two microreference electrodes is exactly the same as that between the positive and negative electrode as long as the current is the
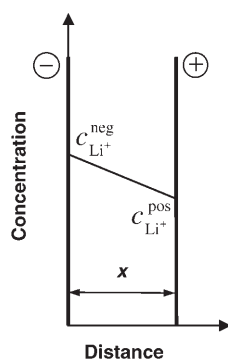
Figure 9. A concentration gradient between the positive and negative electrode. This concentration gradient is the same as that shown in Figure 7.

same. Therefore, by comparison, $c_{Li^+}^{neg}$ and $c_{Li^+}^{pos}$ in Figure 9 are known to be equal to $c_{Li^+}^1$ and $c_{Li^+}^2$, respectively, in Figure 7 at the same current. Since $c_{Li^+}^1$ and $c_{Li^+}^2$ can be resolved from Equations (23) and (24), $c_{Li^+}^{neg}$ and $c_{Li^+}^{pos}$ are consequently also known.

According to Vetter,[10] the diffusion overpotential, η_d, is defined by Equation (25) in which E^{eq} is the equilibrium potential in the absence of current flow and $E^{eq'}$ is the quasi equilibrium potential which forms during current flow as a result of the changed concentrations of the species j directly adjacent to the electrode surface, in accordance with the Nernst equation.

$$\eta_d = E^{eq'} - E^{eq} \tag{25}$$

Hence, using Equation (25) and the Nernst equation, the diffusion overpotential is given by Equation (26), in which $c_{Li^+}^0$ is 1 mol L^{-1} in this work, and c_{Li+} is either $c_{Li^+}^{neg}$ or $c_{Li^+}^{pos}$.

$$\eta_d = \frac{RT}{z_{Li+}F} \ln \frac{c_{Li^+}}{c_{Li^+}^0} \tag{26}$$

The calculated values for $c_{Li^+}^{neg}$, $c_{Li^+}^{pos}$ and the diffusion overpotential are also summarized in Table 1. The diffusion overpotential for the negative electrode was always smaller than that for the positive electrode throughout the current range, which can be seen easily from Equation (26). At the lowest current, both the value for the diffusion overpotential and the difference between η_d^{pos} and η_d^{neg} is negligibly small. Gradually, both the diffusion overpotential and the difference between η_d^{pos} and η_d^{neg} increase with increasing current. At 0.3 A, the diffusion overpotential becomes appreciable, especially for the positive electrode.

Limiting current: A battery attains its limiting current when the electrolyte concentration at the surface of one electrode reaches zero. The concentration of the electrolyte used in this work is 1 mol L^{-1}. When the concentration of the electrolyte at the surface of, for instance, the negative electrode approaches zero, the concentration of the electrolyte at the surface of the positive electrode is 2 mol L^{-1}, due to the mass balance of lithium ions in the electrolyte and the linearity of the concentration gradient. Therefore, the maximum concentration gradient in this Li-ion battery is given by Equation (27), with a distance between the positive and negative electrode of 3.0×10^{-5} m.

$$\frac{\Delta c_{Li^+}}{\Delta x} = \frac{2000}{3.0 \times 10^{-5}} = 6.7 \times 10^7 \text{ mol m}^{-4} \tag{27}$$

Thus, the limiting current for a 300 mA h battery with a geometric surface area of 8.9×10^{-3} m^2 is calculated, according to Equation (12), to be 1.1 A, with the data listed in Table 2. This limiting current corresponds to a C-rate of 3.7

Table 2. Value of z, the Faraday constant, the diffusion coefficient and the concentration gradient.

z	F [C mol^{-1}]	D_{Li+} [m^2 s^{-1}]	$\frac{\Delta c_{Li^+}}{\Delta x}$ [mol m^{-4}]
1	96485	$9.7 \times 10^{-12[a]}$	6.7×10^7

[a] Mean value of the diffusion coefficient from Table 1.

for the Li-ion batteries studied in this work.

It is known that a large overpotential, and consequently a large increase in battery voltage, arises if the applied current is beyond the limiting current. We indeed observed experimentally that a fully discharged Li-ion battery reached 4.2 V instantaneously when being charged at 1.17 A (C-rate of 3.9).

Conclusion

It has been proven theoretically that the concentration gradients in the electrolyte of sealed Li-ion batteries are linear under galvanostatic steady-state conditions. Based on this finding, an in situ electrochemical method has been developed to determine quantitatively the concentration gradients in the electrolyte by measuring the potential difference between two microreference electrodes placed between the positive and negative electrodes. The experimental results confirmed the linearity of the concentration gradients and proved the concentration gradient to be proportional to the applied current under galvanostatic steady-state conditions. Subsequently, the diffusion coefficient of lithium ions in the electrolyte was determined and was found to be almost constant at different currents. Moreover, the diffusion overpotential related to the concentration gradient was calculated to be substantial at high charging/discharging currents. Based on the values obtained, the limiting current of the batteries studied in this work was estimated to be 1.1 A, corresponding to a C-rate of 3.7.

In principle, with appropriate modification, this method should also be applicable to other battery systems.

Experimental Section

All batteries investigated in this work had a nominal capacity of 300 mA h and were assembled with the Philips Lithylene technology reported elsewhere.[19] These 300 mA h batteries consisted of three stacks, each stack including one positive and one negative electrode. The active components were LiCoO$_2$ for the positive electrode and graphite as the negative electrode material (both from SKC, South Korea) and battery-grade electrolyte LP70 (1 M LiPF$_6$ in ethylene carbonate/diethyl carbonate/dimethyl carbonate = 2:1:2 w/w) from Merck (Germany). A Celgard 2300 membrane with a thickness of 30 μm was employed as separa-

tor. All materials were used as received. The microreference electrode was prepared following the previously published procedure.[20] The substrate material for the microreference electrode was a copper wire 80 μm in diameter and covered with an insulation layer. The insulation layer on the tip of the copper wire was removed in order to deposit lithium metal onto it electrochemically from both the positive and negative electrodes.[20] Finally the batteries were sealed in airtight, Al-polymer bags and filled with electrolyte.

The construction of a battery with three microreference electrodes is represented schematically in Figure 1. Note that only the stack in which the microreference electrodes were placed is depicted. These three microreference electrodes, with their tips located in the central area of the battery, were positioned at constant intervals of 5 mm. The microreference electrodes were separated from each other with separators. The distance between two microreference electrodes was assumed to be the thickness of the separator(s) in between them. For example, x_1, the distance between microreference electrodes 1 and 2, was 30 μm, while x_3, the distance between microreference electrodes 1 and 3, was 60 μm (see Figure 1). Thus, the microreference electrodes had different distances measured perpendicularly to the electrode surface. Batteries with two or four microreference electrodes were also made for different purposes.

The batteries were formed before testing using a Maccor 4000 battery test system (U.S.A.). The formation regime has been described previously.[20] For the measurements of the potential difference between the microreference electrodes, the batteries were charged or discharged galvanostatically with a 2300 Keithley (USA). Simultaneously, the mutual potential differences between the microreference electrodes were recorded with an Autolab PGSTAT 20 (Ecochemie, The Netherlands).

Acknowledgements

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