Development of reliable lithium microreference electrodes for long-term in situ studies of lithium-based battery systems
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Rechargeable Li-ion batteries, using LiMnO$_2$ (where M = Co, Ni, Mn, and other combinations) as positive electrodes and certain types of carbon as negative electrodes, are attractive to supply portable electronic devices and (hybrid) electric vehicles with electrical energy due to their high energy density and power density. Because of the initial commercialization of Li-ion batteries by Sony, intense research and development efforts are continued to improve the performance of these batteries. For example, capacity fade and self-discharge during cycling and storage, respectively, has attracted a lot of attention. In addition, battery model is also of great importance to predict the performance of rechargeable batteries under a wide variety of operating conditions. In order to feed these models, the electrochemical performance of the individual electrodes should preferably be known. Measuring the overall performance across the terminals of the batteries is obviously not sufficient to interpret the electrochemical characteristics of the individual electrodes.

To measure the individual electrode contributions, some researchers adopted so-called half-cell measurements to investigate the positive and negative electrodes separately, while others managed to do this by dismantling the cycled batteries for making use of so-called T-shaped or symmetric cells. The evident shortcomings of these methods are that the measurements are carried out under deviating operating conditions. Moreover, disadvantageously, dismantling the batteries is a destructive method.

Some researchers implanted lithium-metal reference electrodes inside the batteries in order to study the individual electrode potentials. Such a conventional reference electrode can simply be a piece of lithium foil or can be made by attaching a piece of clean metallic lithium onto a copper wire, a copper grid, or a stainless steel sheet. However, the size of these conventional reference electrodes is always relatively big. As a consequence, the working circumstances inside the batteries are influenced, e.g., by locally disturbing the ionic pathway and shielding the electric field between the two battery electrodes. In addition, an inherent drawback of using conventional metallic lithium reference electrodes is that they have to be prepared and introduced inside the batteries in an inert-gas-filled glove box. In addition, such an electrode setup sometimes has to be operated in a glove box, creating a lot of inconvenience.

Several researchers suggested making microreference electrodes by means of electrochemical deposition of lithiumSn or lithium alloys onto nickel or copper wires. The advantage of this method is that the impact of the reference electrodes on the battery operation conditions is minimized because the wires have diameters in the micrometer range. The experiments can therefore be performed in situ. An additional advantage is that the battery electrodes with the substrate wires can be assembled in open air. However, some of the reported reference electrodes were based on Li-Sn alloys, whose potential deviates from that of the conventional Li/Li reference potential, which is most widely used in Li-based battery systems. The reported metallic lithium reference electrodes did not reveal stable potentials over a longer period of time, which is essential to study degradation effects induced by cycling and storage.

The aim of the present study is therefore to develop a reliable, in situ method to make stable lithium microreference electrodes. The factors that influence the stability of these electrodes are presented. The stability and reliability of the microreference electrode has been confirmed by means of three-electrode electrochemical impedance spectroscopy (EIS). Preliminary in situ electrode potential measurements obtained with microreference electrodes upon cycling are described.

**Experimental**

*Copper substrate processing.*—Copper wires, 40 μm diam, are chosen as the substrate material for the microreference electrodes. The Cu wires are entirely covered with an insulation layer that prevents copper from being exposed to the electrolyte. As a result, any possible mixed potential along the wire during electrochemical operation is avoided. Before being implanted into the batteries, the Cu wires were processed as follows: about 25 cm wires were cut from the roll. Approximately 15 cm was immersed into formic acid for 5 min. After being washed in vigorously stirred water, the wires were further processed in order to completely remove the partially dissolved insulation layers. Subsequently, the bare Cu wire was carefully coiled to make a mechanically solid connector outside the battery. This coil is to ensure a good electric contact between the reference electrode and the measurement equipment, as the Cu wire itself is too thin to guarantee this.

The tip on the other end of the Cu wire was also immersed into formic acid. The same procedure as described previously was repeated to remove the insulation layer on the tip. The tip was then cut so that only about 0.5 mm was left uncovered for lithium deposition. Finally, the exposed tip was immersed in a polishing bath...
Battery construction.—The batteries tested in this work all have a nominal capacity of 700 mAh and consist of seven parallel-switched electrode stacks, 100 mAh each. The three-electrode batteries were assembled with Philips Lithylene technology, which has been described in detail elsewhere. \(^{18}\) The active components used in this study were LiCoO\(_2\) for the positive electrode and graphite as negative electrode material (both from SKC, South Korea) and battery-grade electrolyte LP70 [1 M LiPF\(_6\) in ethylene carbonate (EC):diethyl carbonate (DEC):dimethyl carbonate (DMC) = 2:1:2 w/w, Merck, Germany]. Celgard 2300 membranes were employed as separator. All the materials were used as-received. The processed copper wires were placed in-between two sheets of separator. The three-electrode batteries were finally sealed in airtight, Al-polymer bags. A schematic representation of one stack of such a three-electrode battery is shown in Fig. 1.

Electrochemical measurements.—An automatic cycling apparatus (Maccor 4000 lab unit, U.S.A.) was employed to activate and cycle the three-electrode batteries. The batteries were first activated during three cycles using a constant current, constant voltage (CCCV) regime. Charging was performed at 0.2 C rate until 4.2 V; the voltage was then kept constant until the current dropped to 0.05 C. After a resting period of 30 min, the batteries were discharged at 0.2 C until the cutoff voltage of 3 V was reached.

A similar regime was adopted to cycle the batteries. The batteries were, however, charged at a 0.5 C rate until 4.2 V. The voltage was subsequently kept constant at 4.2 V until the current dropped to 0.05 C rate. After a resting period of 30 min, the batteries were discharged at 0.5 C until the 3 V cutoff voltages were again reached. The potential plots of both the positive and negative electrode vs. micoreference electrodes were recorded during the long-term cycling experiments by means of the auxiliary inputs of the Maccor equipment.

An Autolab PGSTAT 20 (Ecochemie, Netherlands) was used to perform both the electrochemical measurements concerning the lithium deposition, to check the stability of the micoreference electrodes, and to carry out the EIS measurements.

Lithium was deposited \textit{in situ} onto the tip of the Cu wires under galvanostatic control after battery activation had taken place. Both the lithium layer thickness and the deposition current were varied. In order to check the stability of the micoreference electrodes, a second micoreference electrode was implemented at a distance of approximately 1 cm. The mutual voltage difference was regularly measured.

The EIS measurements were carried out under potentiostatic control using the frequency response analyzer (FRA) mode. The impedance spectra were obtained by applying a sine wave of 5 mV in amplitude in the frequency range of 10 kHz to 10 mHz.

\[ \frac{d}{F} = \frac{10^9 M i t}{n F \rho} \]  
\[ A = 2 \pi r l + \pi r^2 \]  

where \(M\) is the molecular weight of lithium (6.94 g/mol), \(n\), the number of electrons involved, is 1, \(F\) is the Faraday constant (96,500 C/mol), \(\rho\) is the density of metallic lithium (0.53 g/cm\(^3\)), and \(10^9\) is used to represent the thickness in micrometers.

For practical applications the absolute current \([I \ (A)]\) is important. Because the current is coupled to the current density via the exposed surface area \([A \ (cm^2)]\), \(A\) has to be calculated from

For a Cu wire that has an exposed tip 0.5 mm long, the amount of lithium required to form a 4 \(\mu\)m thick layer is only about 2
difference between Li-ion battery, it is to be expected that the potential differences during the two-step lithium deposition process. For a nominal capacity of the battery, this capacity loss is negligible with respect to 700 mAh, the voltage profile of the reference electrode the "loss" of the battery electrode capacities is only 5.4 \times 10^{-4} mAh. This capacity loss is negligible with respect to 700 mAh, the nominal capacity of the battery.

Figure 3 gives an example of the development of the potential differences during the two-step lithium deposition process. For a fully charged Li-ion battery, it is to be expected that the potential difference between Li,CoO₂ and the Li-reference electrode is above 4.2 V, while that of Li,C₆ and the Li reference electrode is above 0.08 V.\(^{20}\) Lithium deposition should therefore take place at these potentials with respect to the positive and the negative electrode, respectively. It can be seen in Fig. 3A that during the first deposition step, it took some time before the expected lithium deposition potential was reached. Charge consumed during this initial period is perhaps due to copper oxide reduction.\(^{15}\) This phenomenon is not observed when lithium was subsequently deposited from the negative electrode (Fig. 3B). Because no lithium deposition occurs when the potential is below the deposition potential, this initial period is not included in the calculation of time in Eq. 1. That is why the process of Fig. 3A took somewhat longer than that of Fig. 3B.

Stability of the microreference electrodes.—For a reference electrode to be meaningful, its potential must be stable for a long period of time. The stability of the microreference electrodes was checked by means of continuously monitoring the potential difference between two parallel oriented microreference electrodes in one battery at a distance of 1 cm. This method is based on the assumption that in case the two microreference electrodes are unstable, it is rather unlikely that any deviation from the expected reference voltage is of the same value for both electrodes. Hence, in the case of unstable reference electrodes the potential difference between the two changes as a function of time. Figure 4 shows a typical example of such a stability test. As can be seen, the potential difference between two reference electrodes was constant within 0.4 mV for more than 130 h, indicating that the two microreference electrodes had nearly identical potential within the accuracy of the voltage measurement.

\[ \text{Potential difference between two microreference electrodes during 130 h. Lithium layer thickness is 4 \mu m. Deposition current density is 0.2 mA/cm}^2. \]

\[ \times 10^{-8} \text{ mol. It can be calculated according to Faraday’s law that the “loss” of the battery electrode capacities is only 5.4 \times 10^{-4} mAh. This capacity loss is negligible with respect to 700 mAh, the nominal capacity of the battery.} \]

Influence of the Li-layer thickness on the reference electrode stability.—As discussed before, the formation of an SEI layer consumes the deposited lithium metal. When the deposited layer is not sufficiently thick, it might be all consumed by the SEI formation reaction. This ultimately results in an unstable and not well-defined reference electrode potential. Because it is a microreference electrode, the deposited lithium metal layer cannot be too thick with respect to the diameter of the Cu wire. In addition, despite the fact that the currents are low, all potential-measurement systems are, in principle, current driven, thereby slowly consuming the reference electrode in time.\(^{10}\) The input impedance of the reference electrode terminal of a potentiostat is usually larger than 10\(^{10}\) \Omega, which results in a measurement current lower than a few 100 pA. Such a low current leads to a small material consumption, i.e., of the order of 0.2 \mu Ah, which corresponds to about 10\(^{-8}\) mol of metallic lithium per month.\(^{10}\) In the case of microreference electrodes, this material consumption cannot be neglected on a longer term. Therefore, it cannot be expected that the as-prepared microreference electrodes are able to run continuously for more than several months. All together, it is worthwhile to study the influence of the layer thickness on the electrode stability and to find out the optimal deposition layer thickness.

In order to reduce the lithium consumption, the potential difference between two microreference electrodes was monitored for only 10 min each day. The results are shown in Fig. 5. The deposition current density was 0.2 mA/cm\(^2\) in all cases, while the lithium layer thickness of the microreference electrodes was 1, 2, and 4 \mu m in Fig. 5A-C, respectively. In Fig. 5A, the potential difference was 61 mV at the beginning and increased to 185 mV after only 1 day. This large and unstable potential difference indicates that 1 \mu m reference electrodes do not retain a stable potential. In contrast, the potential difference of 2 \mu m thick reference electrodes remained constant within 1 mV and started to fluctuate after some 470 h (Fig. 5B). The electrode using 4 \mu m lithium layers were found to be the most stable as is evidenced by Fig. 5C. This layer remains stable within 0.5 mV for more than 1500 h. It can be concluded that the thickness of deposited lithium layers plays a crucial role in the stability of microreference electrodes. A layer thickness of 4 \mu m is recommended to prepare long-term stable microreference electrodes.

Remarkably, the first data points in Fig. 5 all revealed a small deviation from the voltage measured after stabilization. This effect has been studied in more detail by continuously measuring the voltages during this stabilization period. Figure 6 shows a typical example of such an experiment. The stabilization effect can be ex-
The current density is 0.2 mA/cm². Stabilized reference electrode. Lithium layer thickness is 4 μm.

Figure 6. Potential change of a freshly deposited reference electrode vs. a stabilized reference electrode. Lithium layer thickness is 4 μm. Deposition current density is 0.2 mA/cm².

explained by the SEI formation onto the deposited lithium. As a matter of fact, the two microreference electrodes were not deposited with lithium simultaneously but consecutively. When the second microreference electrode was being deposited, the first reference electrode already started to build-up an SEI layer, inducing the potential to equilibrate. If the potential difference between the two microreference electrodes is measured directly after the lithium deposition at the second electrode was completed, the potential difference between the passivated and freshly deposited reference electrodes was significant, which is clearly shown by the first data point in Fig. 5C. This difference decreases once the SEI layer formation starts to saturate at the second electrode until its potential reaches a steady-state value. The result of Fig. 6 reveals that the SEI layer formation takes about 1 h under the present conditions.

Influence of deposition current density on the stability of reference electrodes.—The potential stability of the microreference electrodes is apparently based on the stability of the deposited lithium layer, which depends not only on the deposit thickness but also on the adhesion of the deposit. A crucial factor that affects the quality of a deposit and its adhesion is the current density. It is known that an increase in current density may bring about the formation of a more spongy deposit, the adhesion of which is less than that of a dense deposit. Furthermore, high current densities may also result in the formation of nonuniform deposits, e.g., lithium dendrites. For a microreference electrode, the thinnest spot of the nonuniform lithium layer might be quickly consumed due to the reaction with the electrolyte, which exposes the Cu wire to the electrolyte. A mixed potential is subsequently induced and thus, the potential of the microreferences is not stable anymore. Small current densities frequently may generate the formation of a dense electrodeposit. However, this dense electrodeposit can result in the development of internal stresses that may have an adverse effect on the adhesion, leading, in extreme cases, to spontaneous flaking of the deposit from the substrate. It is therefore interesting to investigate the influence of the current density on the electrode stability.

The current density was varied in the range 0.2-1 mA/cm². The results are shown in Fig. 7. The lithium layer thickness was 4 μm in all cases. All microreference electrodes are stable over a long period of time. However, the microreference electrodes produced at 1 mA/cm² (Fig. 7A) became unstable after 800 h. In contrast, Fig. 7B and C reveals good stability for electrodes produced at 0.5 and 0.2 mA/cm², respectively. Both are stable for more than 1500 h. Therefore, a layer thickness of 4 μm deposited at a current density of 0.2 mA/cm² are concluded to be the most favorable preparation conditions.

Validity of the microreference electrodes in EIS measurements.—EIS is well known as a powerful technique which can generate much useful information. For instance, in Li-ion batteries, the resistance of electrolyte ($R_{el}$), diffusion/migration through the SEI layer ($R_{diff}$), charge transfer ($R_{ct}$), and host diffusion ($R_{host}$) can be determined by EIS measurements, which is useful for understanding the complex electrochemical processes occurring inside Li-ion batteries.

In order to perform three-electrode EIS measurements, the validity of the reference electrodes in EIS measurements needs to be examined. The simplest experimental validity test of the three-electrode measurements is to conduct the EIS measurements and compare the sum of the two three-electrode measurements (positive vs. reference + negative vs. reference) with the result of two-electrode measurements (positive vs. negative). These results are shown in Fig. 8. The EIS spectra of the positive and the negative electrodes measured vs. the reference electrode are shown in Fig. 8A, curve (a) and (b), respectively. The sum of curves (a) and (b) in Fig. 8A is represented by the circles in curve (a) in Fig. 8B, while the measured EIS spectrum of the battery is presented as spectrum in Fig. 8B. Less than 1% difference was found between the sum of the three-electrode impedance results and the two-electrode measurement in both the real part ($Z_r$) and the imaginary region ($\sim Z_{im}$) of the spectrum, except at high frequencies (about the first five points whose differences were less than 5%), indicating that the measure-
ment setup is appropriate. Thus, the validity of the measurements with the microreference electrodes is confirmed. More EIS measurements, concerning, for example, impedance changes as a function of state-of-charge (SOC) and cycle numbers, are in progress.

Electrode potentials monitored during cycling.—One interesting application of the microreference electrodes is to monitor the electrode potentials during cycling. Figure 9 shows, as an example, the results for one cycle. The potential change of the positive electrode and the battery is presented in Fig. 9A, while that of the negative electrode is shown in Fig. 9B. In addition, the current is also indicated in both figures on the right side axis. From Fig. 9 it can be seen that the positive electrode mainly contributes to the potential change of the battery during both charge and discharge. The positive electrode reveals a potential change of some 0.5 V during charge and 1.1 V during discharge. In contrast, the potential change of the negative electrode is only about 0.2 and 0.1 V during charge and discharge, respectively.

Furthermore, as can be seen in Fig. 9A, when charging starts, the potential of the positive electrode shows an abrupt increase of about 0.25 V and the voltage then increased slowly until the end of charg-
to increase because the overpotential decreases. This overpotential can also be seen during the rest period when charging has been interrupted. A small current, 0.05 C, was reached at the end of charge. However, a slow potential relaxation of some 0.02 V was still observed. When discharge started, the negative electrode showed a nearly vertical potential increase of some 0.03 V, followed with a small potential peak. The potential of the negative electrode increased slowly until the end of discharge. A small potential drop for the negative electrode was again observed after current interruption, indicating small overpotential. Wang et al.\textsuperscript{25} reported that the process of Li-ion extraction from the graphite has a larger diffusion coefficient than that of Li-ion intercalation into graphite, which is in agreement with the observed potential behavior of the negative electrode in this work.

In addition, by making use of the long-term stability of the microreference electrodes, it is also possible to monitor the electrode potentials during prolonged cycling. Figure 10 shows the preliminary results for ten cycles. A good reproducibility of the potential plots for the positive and negative electrode was observed, again proving the stability and reliability of the microreference electrodes.

It has been shown here that for the negative electrode, Li-ion deintercalation attains better diffusion properties than intercalation. More efforts in an attempt to understand the kinetics and diffusion properties of Li-ion intercalation/deintercalation in detail with the positive and the negative electrodes are being carried out in our laboratory.

Stability of the redeposited microreference electrodes.—As the deposited lithium may be consumed during the electrochemical measurements, the microreference electrode potential will eventually degrade after a long period of time and is no longer suitable for proper electrochemical measurements. However, this degradation does not necessarily mean that the reference electrodes can no longer be used. One advantage of the microreference electrodes is that it can be easily “revived” by redepositing lithium. Figure 11 shows the potential difference as a function of time between a redeposited and a freshly deposited microreference electrode, which amounted to not more than 0.46 mV, indicating that the redeposited microreference electrode has the same potential as the freshly deposited electrode. In addition, the fluctuation of this potential difference was within 0.1 mV for more than 300 h, which proves that the redeposited microreference electrode also attains a stable potential. Therefore, the redeposited microreference electrode is reliable to be employed in long-term, \textit{in situ} electrochemical measurements.

Conclusions

\textit{An in situ} method to make microreference electrodes was developed. A lithium reference electrode was made by electrochemically depositing lithium from both the positive and negative electrodes onto a copper wire placed in-between the positive and negative electrodes of Li-based battery systems. Both the depositing current density and the layer thickness were found to have a profound influence on the stability of the microreference electrodes. A current density of 0.2 mA/cm\textsuperscript{2} and lithium layer thickness of 4 \textmu m is shown to be the favorable lithium deposition condition. Deposition of lithium from both electrodes indeed results in uniform lithium layers. Advantageously, the potential of the redeposited microreference electrode is also stable and has the same value as the freshly deposited electrodes.

Figure 9. Potential plots measured with one microreference electrode during one cycle: (A) one cycle for the battery and positive electrode and (B) one cycle for the negative electrode. Room temperature and C/2 rate for both charge and discharge.

Figure 10. Potential plots of the positive and the negative electrode measured with one microreference electrode for ten cycles at room temperature and C/2 rate for both charge and discharge.

Figure 11. Potential difference between a redeposited and a freshly deposited microreference electrode. Lithium layer thickness is 4 \textmu m. Deposition current density is 0.2 mA/cm\textsuperscript{2}.
The validity of the microreference electrodes was confirmed by conducting both two-electrode and three-electrode EIS measurements and comparing the sum of the three-electrode impedance results and the two-electrode measurement in both the real part ($Z'$) and the imaginary region ($-Z''$) of the spectrum. The perfect agreement proves that microreference electrodes are reliable to perform complex electrochemical measurement, like EIS.

The microreference electrodes were employed to monitor the potential change of the positive electrodes and the negative electrodes during cycling. By comparing the potential plot of the negative electrodes and the microreference electrodes during charge and discharge, it has been found that Li-ion deintercalation in graphite has better diffusion properties than intercalation.

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