Measurement of Side-Reaction Currents on Electrodes of Lithium-Ion Cells Using a Battery Cycler with a High-Precision Current Source

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ABSTRACT

Capacity fading mainly caused by state-of-charge deviations between the positive and negative electrodes of lithium-ion batteries (LIBs) can be accurately predicted if the rates of side reactions occurring on these electrodes are known. Herein, we show that the rates of side reactions on LIB electrodes can be determined using an in-house-built high-current-precision battery cycler comprising galvanostat, charge/discharge control, and current switching units. An \( \text{Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_{2/3}/\text{Li}[\text{Li}_{1/3}\text{Ti}_{2/3}]\text{O}_{2/3} \) (LTO/LTO) symmetric cell is used to verify that the battery cycler provides currents accurate enough to determine side-reaction rates, and the rates of side reactions on LTO (negative) and \( \text{LiNiMo} \) (positive) electrodes in an LTO/LiNiMO cell are compared with intrinsic values obtained for the symmetric cell.

Keywords : Lithium-ion Battery, Side Reaction, Calendar and Cycle Life, Battery Cycler

1. Introduction

Storage batteries have recently attracted much attention as power sources for automotive (e.g., electric vehicles) and stationary (e.g., sun- and wind-powered renewable energy plants) applications that require large capacity, high power, and long lifetime. Li-ion batteries (LIBs) satisfy the above criteria particularly well, exhibiting energy densities higher than those of other (e.g., Pb acid and Ni metal hydride) batteries.\(^{1-3}\) One of the most important LIB performance parameters is the lifetime or “cycle/calendar life,” since LIBs should sustain more than 3600 cycles and 70,000 h without marked capacity fading to achieve 10-year-long service.

LIB capacity fading is affected by a number of factors such as electrode material deterioration, increased polarization, and state-of-charge (SOC) imbalance between positive and negative electrodes. Since the commercialization of LIBs in the early 1990s, scientific and technological progress allowed their cyclability and calendar lifetime to be progressively improved, e.g., via the use doping/coating to enhance interfacial stability.\(^{4,5}\) These advances allowed capacity fading caused by electrode material deterioration to be significantly reduced. Hence, SOC imbalance–caused capacity fading, which occurs without any electrode material deterioration, remains the only major problem to be mitigated.

Numerical analysis of capacity fading has clarified how the effect of SOC imbalance on the rate of side reactions affects LIB longevity, and several methods of investigating this imbalance in terms of coulombic efficiency,\(^{11-13}\) self-discharge current,\(^{14}\) side-reaction rate,\(^{15}\) etc. have been described.\(^{11-18}\) Previously, we have reported that LIB capacity fading can be predicted based on the symmetric cell–determined rates of side reactions occurring on the electrodes.\(^{15}\) However, the side-reaction rate determined by a symmetric cell, i.e., the so-called intrinsic rate of a side reaction, does not account for the influence of the counter electrode, which cannot be neglected in LIBs.\(^{16-18}\)

Herein, we developed a battery cycler with a high-precision current source for measuring side-reaction currents of Li insertion electrodes in LIBs. In particular, side-reaction currents of positive and negative electrodes in a Li[Li\(_{1/3}\)Ti\(_{2/3}\)]O\(_{2/3}\)/Li[Li\(_{1/3}\)Ni\(_{2/3}\)]O\(_{2/3}\) (LTO/LiNiMO) cell were estimated using a cumulative capacity plot, since such plots are often used to determine side-reaction currents based on charge-discharge curves recorded during cycling.

2. Determination of Side-reaction Currents

Charge-discharge curves of a LIB comprising LTO\(^{19,20}\) and \( \text{Li}[\text{Li}_{1/3}\text{Al}_{1/3}\text{Mn}_{1/3}]\text{O}_{4} \) (LAMO)\(^{21}\) were simulated (Fig. 1) to show how the side-reaction current can be determined from charge-discharge curves. The simulation was performed under the following conditions: area-specific capacity of LAMO (positive) and LTO (negative) electrodes = 5 mAh cm\(^{-2}\), side-reaction current = \(-10 \mu\text{A cm}^{-2}\) (cathodic current for the LAMO electrode) or \(+25 \mu\text{A cm}^{-2}\) (anodic current for the LTO electrode). The side-reaction currents of both electrodes are assumed to be independent of operating voltages for simplicity. Charge-discharge curves in Fig. 1a are depicted continuously, thus, discharge/charge curves start from the end points of the previous charge/discharge curves with backward/forward directions, respectively. The side reactions taking place at both electrodes induce a continuous shift of charge-discharge curves toward the high-capacity (right-hand) side upon cycling, because the current efficiency is less than unity. Since the absolute values of side-reaction currents \( (I_{SR}) \) are not the same for LAMO and LTO electrodes, i.e., \( |I_{SR,LAMO}| < |I_{SR,LTO}| \), SOC deviations between these electrodes are observed upon cycling, and the charge capacity of the cell during cycling is therefore limited by that of the LAMO electrode, while cell discharge capacity is limited by that of the LTO electrode. The capacities at the end of charge and discharge (termed cumulative capacities \( (CQ_{Cha} \) and \( CQ_{Dis} \) respectively) can be expressed as

\[
CQ_{Cha}(t) = Q_{Cell}(0) + I_{SR,LAMO} \times t,
\]

\[
CQ_{Dis}(t) = I_{SR,LTO} \times t,
\]

where \( Q_{Cell}(0) \) is cell capacity before cycling, and \( t \) is cycling time. Combining the above equations with the condition mentioned earlier in the text, cell capacity after cycling time \( t \) \( (Q_{Cell}(t)) \) can be expressed as

\[
Q_{Cell}(t) = CQ_{Cha}(t) - CQ_{Dis}(t)
= Q_{Cell}(0) - (|I_{SR,LAMO}| - |I_{SR,LTO}|) \times t
\]
The above equation implies that cell capacity fading caused by SOC deviation between LAMO and LTO electrodes is proportional to the difference of electrode side-reaction currents. Based on the above, side-reaction currents on electrodes can be calculated as

\[ I_{SR,LAMO} = \frac{d(CQ_{Cha})}{dt} \]
\[ I_{SR,LTO} = \frac{d(CQ_{Dis})}{dt} \]

Thus, side-reaction currents can be estimated either mathematically (by differentiation of cumulative capacity with respect to cycling time) or graphically (from the slope of cumulative capacity vs. cycling time plots). The plots used in the latter case are denoted as cumulative capacity plots, and the corresponding plots obtained from simulated charge-discharge curves of the LTO/LAMO cell are shown in Fig. 1b. Notably, both cumulative capacities changed linearly with cycling time, because the side-reaction currents on both electrodes remained constant. During 200-h cycling, cumulative capacity on charge or discharge changed by 2.0 and 5.0 mAh, respectively, and the absolute values of side-reaction currents for LAMO and LTO electrodes were therefore determined as 10 and 25 µA, respectively. To our delight, these values equaled those determined by simulation, and the established technique was therefore concluded to be well suited for the calculation of side-reaction currents on both positive and negative LIB electrodes.

### 3. Battery Cycler Design

#### 3.1 Battery cycler specifications required to obtain cumulative capacity plots

The suitability of a battery cycler for cumulative capacity plot construction is largely determined by current precision during charge-discharge cycling, i.e., the estimation of side-reaction currents is difficult when the current actually flowing through the cell cannot be precisely determined.\(^{22,23}\) Figure 2 shows the effect of current precision on the construction of cumulative capacity plots assuming that the actually flowing current deviates from the set value. Despite the difference between pre-set values, almost no effect on plots was observed for the same values of actual charge and discharge currents, i.e., side-reaction currents determined from the slopes of the plots were virtually the same whenever actual charge and discharge currents were exactly equal. However, the deviation between charge and discharge currents had a noticeable effect on cumulative capacity plots, even when the actual current values were similar to the pre-set values, e.g., the accurate estimation of side-reaction currents was disturbed by an only 1% difference between actual and set currents. Thus, these results indicated that the accuracy of side-reaction current determination is strongly affected by the difference between charge and discharge currents rather than by that between actual and set currents.

Based on the above, a battery cycler with a high-precision current source is required to measure the side-reaction currents on positive and negative electrodes. As has already been reported in a previous paper,\(^{15}\) intrinsic side-reaction currents of LTO and LAMO measured in symmetric cells reached hundreds of nanoamperes, which correspond to tens of microamperes per unit weight of the active material. In the following section, we describe the design of a prototype battery cycler with the required current measurement precision.

#### 3.2 Electric circuitry of the high-current-precision battery cycler

Figure 3 shows a block diagram depicting the working principle of the battery cycler. In particular, the battery cycler comprised three functional units, namely (i) a galvanostat unit that applied a constant current flowing through the cell, (ii) a charge-discharge control unit that monitored cell voltage and output electrical signals to the current switching unit for controlling cell operation (charging or discharging), and (iii) a current switching unit that changed the current direction (positive to negative electrode on charge (red) and negative to positive electrode on discharge (blue)) using two relay circuits. If \( R \) is the resistance connected between the ground and inverting inputs of operational amplifiers (op-amps), and \( E_{cell} \) is the...
externally set voltage, the current flowing through the cell can be expressed as \( I = \frac{E_{\text{set}}}{R} \).

Figure 4 shows a circuit diagram of the galvanostat unit derived from an op-amp circuit (U1). The galvanostat unit was specifically designed for obtaining cumulative capacity plots, and the required current was therefore fairly low (<10 mA). The current required for charge and discharge could be set by changing the resistance (VR1) to vary \( E_{\text{set}} \). The accuracy and precision of the current flowing through the cell depended on the supplied voltage references. A shunt regulator (LM385) was used instead of the Zener diode to obtain a stable voltage reference, and reference voltage fluctuation was as low as 0.1 mV (0.004%) for a power supply voltage range of 8–12 V, which confirmed that this stability is sufficient for a setting \( E_{\text{set}} \) value.

The charge-discharge control unit (Fig. 5) was used to monitor battery voltage at high input resistance, check that the cell voltage reaches end-of-charge or end-of-discharge values, and output signals for switching the current direction. The voltage detection circuit comprised three op-amps (U2–U4) forming a so-called instrumentation amplifier particularly suitable for measuring cell voltage at high input impedance. Comparators (U5, U6) were used to check whether the cell voltage reached end-of-charge (\( E_U \)) or end-of-discharge (\( E_L \)) values. A flip-flop (U7) constructed from a pair of cross-linked NAND logic gates was used to store cell state information (charge or discharge). When the cell voltage was in the range between \( E_U \) and \( E_L \), SW1 and SW2 outputs remained in a constant state. The circuit controlled the cell state by outputting signals to the current switching unit.

The circuit diagram of the current switching unit is shown in Fig. 6. In this unit, the direction of the current flowing through the cell was controlled using a switching circuit based on the signal output from the flip-flop of the charge-discharge control unit. Two single-pole double-throw relays (RL1, RL2) were used to switch the direction of the current from the galvanostat, while transistors (Tr1, Tr2) amplified the received input signals to drive relays, and flyback diodes (D1, D2) connected across a relay were used to eliminate inductive current when the supply current was suddenly interrupted. Light-emitting diodes (LEDs; LED1, LED2) were used as an indicator of the cell state (green for charging and red for discharging).

4. Battery Cycler Verification Using a Symmetric Cell

The current precision of the battery cycler fabricated based on the circuitries shown in Figs. 4–6 was verified by applying the current
to a resistance and monitoring the IR drop with a high-precision voltmeter (Fig. 7). In this measurement, we observed a systematic voltmeter error due to an offset, and the IR drop was therefore measured at a positive value by reconnecting the voltmeter in a reversed direction. As seen in Fig. 7, the charge and discharge currents were almost equal (variation = ±0.01 µA). The statistical error of the 17-point-measurement during charging and discharging was similar to the above value, i.e., the standard deviations for charging and discharging currents equaled 6.4 and 6.1 nA, respectively. These results indicated that despite the low accuracy of the current value, the corresponding precision was high enough for measuring side-reaction currents.

To confirm the stability of current precision, we subjected an LTO/LTO symmetric cell to a long-term (1200-h) charge-discharge test. The cell was placed in an incubator at 25°C (< ±1°C) and the battery cycler was operated at constant temperature (25 ± 3°C). Since side-reaction currents on equivalent LTO electrodes in the symmetric cell are considered to be equal,26 current precision was verified by comparing side-reaction currents of two identical LTO electrodes determined from a cumulative capacity plot. Figure 8 shows the results of the above long-term test, demonstrating that continuous charge-discharge curves were symmetrically contracted inward and that the variations of CQCha and CQDis were almost equal. Based on the corresponding cumulative capacity plot (Fig. 8b), the side-reaction currents of the two equivalent LTO electrodes were calculated as 0.13 and 0.10 µA cm⁻², respectively. Digital multimeter VOAC7521H and 1 kΩ metal resistance are used to measure current of the battery cycler.

Figure 7. Current precision of the in-house built battery cycler. Red and blue circles show charge and discharge currents, respectively. Digital multi-meter VOAC7521H and 1 kΩ metal resistance are used to measure current of the battery cycler.

Figure 8. (a) Continuous charge and discharge curves of an LTO/LTO symmetrical cell operated at 0.25 mA cm⁻² in voltage ranging from −0.5 to 0.5 V at 50°C. Both LTO electrodes consist of 88 wt% active materials, 6 wt% acetylene black, and 6 wt% of PVdf. One electrode is 30.1 mg with 109 µm thick and the another is 30.2 mg and 114 µm thick. (b) Cumulative capacity plots of the LTO/LTO symmetrical cell. The side reaction currents on LTO positive and negative electrodes are 0.261 µA and 0.206 µA, respectively.

5. Measuring the Rate of Side Reactions at LTO (Negative) and LiNiMO (Positive) Electrodes in an LTO/LiNiMO Cell

Long-term cycling (~1000 h) of an LTO/Li[Li₁₂₋₂Mn₁₂]O₄ (LiNiMO)²⁷ cell was carried out using the battery cycler to measure the side-reaction currents of LTO (negative) and LiNiMO (positive) electrodes. The cell was operated at 0.25 mA cm⁻² in the voltage range of 1.5–3.8 V at 25°C, and the obtained continuous charge-discharge curves are shown in Fig. 9a. During cycling, no significant change in voltage profiles was observed, and the presence of a voltage plateau at ~3.2 V indicated that the extent of cell polarization did not increase upon cycling. Therefore, the capacity fading of the LTO/LiNiMO cell was caused only by the SOC imbalance between LTO and LiNiMO resulting from the difference in the corresponding side-reaction currents. As seen in Fig. 9, charge-discharge curves were shifted toward the high capacity (right-hand) side, and the above shift was faster for CQDis than for CQCha, which resulted in capacity fading of the LTO/LiNiMO cell. Side-reaction currents on LTO and LiNiMO electrodes were calculated based on the corresponding cumulative capacity plot (Fig. 9b). The SOCs and capacities of both electrodes were confirmed by refabricating these electrodes in lithium cells after cycling. At the end of the LTO/LiNiMO cell discharge after cycling, the LiNiMO electrode retained some capacity, while the LTO electrode was fully discharged (oxidized). Reversible capacities of both LTO and LiNiMO electrodes were virtually the same before and after cycling. Thus, the capacity of the LTO/LiNiMO cell was limited by those of the LiNiMO or LTO electrodes at the end of charge or discharge, respectively. Therefore, Isr,LiNiMO and Isr,LTO corresponded to the slopes of plots of CQCha and CQDis versus time, respectively. The side-reaction currents of both electrodes should be constant, because both materials have flat operating voltage over the entire capacity region. The side-reaction currents of the LTO/LiNiMO cell were calculated as −1.8 µA (cathodic current for the LiNiMO electrode) and +2.2 µA (anodic current for the LTO electrode). The difference in the absolute value of these currents equaled 2.2 – 1.8 = 0.4 µA, which corresponded to the rate of capacity fading, QΔcap = 0.4 × t (µAh). Battery life can be predicted using the value calculated from the side-reaction currents. Notably, the side-reaction current of the LTO electrode in the LTO/LiNiMO cell was larger than the intrinsic Isr in the symmetric cell by an order

Electrochemistry, 87(3), 188–192 (2019)
of magnitude, which indicated that side reactions of the above electrode were accelerated in the presence of the LiNiMO counter electrode. Thus, the side-reaction current of a given LIB electrode is influenced by its counter electrode. This finding not only contributes to a deeper understanding of mass balance inside the cell but also allows one to predict capacity fading caused by SOC imbalance between positive and negative LIB electrodes. Factors affecting the side-reaction currents, such as temperature, electrode potential, charge-discharge current density, those are of importance for predicting lifetime of LIB. Such experiments are beyond the scope of the current paper. The important point is that our results demonstrate that the side-reaction current of a given electrode is influenced by the counter electrode in LIBs.

6. Conclusion

We developed a battery cycler with a high-precision current source for measuring side-reaction currents on positive and negative LIB electrodes based on cumulative capacity plots. The battery cycler enables to predict LIB capacity fading caused by an imbalance in SOCs between positive and negative electrodes. High current precision of the battery cycler was verified by subjecting a symmetric LTO/LTO cell to long-term cycling despite featuring a relatively low current accuracy. The side-reaction current of the LTO (negative) electrode in the LTO/LiNiMO cell exceeded the intrinsic side-reaction current in the LTO/LTO symmetric cell, which revealed that the side-reaction current of a given electrode is influenced by the counter electrode in LIBs.

References

1. J.-M. Tarascon and M. Armand, Nature, 414, 359 (2001).
2. M. Winter and R. J. Brodd, Chem. Rev., 104, 4245 (2004).
3. P. Atora, R. E. White, and M. Doyle, J. Electrochem. Soc., 145, 3647 (1998).
4. J. W. Fergus, J. Power Sources, 195, 939 (2010).
5. J. Wang and X. Sun, Energy Environ. Sci., 5, 5163 (2012).
6. W. Liu, P. Oh, X. Liu, M.-J. Lee, W. Cho, S. Chae, Y. Kim, and J. Cho, Angew. Chem., Int. Ed., 54, 4440 (2015).
7. B. Zhao, R. Ran, M. Liu, and Z. Shao, Mater. Sci. Eng. R Rep., 989, 1 (2015).
8. W. Li, B. Song, and A. Manthiram, Chem. Soc. Rev., 46, 3006 (2017).
9. J. Christensen and J. Newman, J. Electrochem. Soc., 150, A1416 (2003).
10. J. Christensen and J. Newman, J. Electrochem. Soc., 152, A818 (2005).
11. A. J. Smith, J. C. Burns, D. Xiong, and J. R. Dahn, J. Electrochem. Soc., 158, A1136 (2011).
12. J. C. Burns, A. Kassam, N. N. Sinha, L. E. Downie, L. Solnickova, B. M. Way, and J. R. Dahn, J. Electrochem. Soc., 160, A1451 (2013).
13. J. Xia, L. Ma, and J. R. Dahn, J. Power Sources, 287, 377 (2015).
14. N. R. Vadivel, S. Ha, M. He, D. Dees, S. Trusk, B. Polzin, and K. G. Gallagher, J. Electrochem. Soc., 164, A508 (2017).
15. K. Nakura, Y. Ohsugi, M. Imazaki, K. Ariyoshi, and T. Ohzuku, J. Electrochem. Soc., 158, A1243 (2011).
16. S. R. Li, C. H. Chen, X. Xia, and J. R. Dahn, J. Electrochem. Soc., 160, A1524 (2013).
17. M. D. Levi, V. Dargel, Y. Shilina, V. Borgel, D. Aurbach, and I. C. Halalay, J. Power Sources, 278, 599 (2015).
18. J. A. Gilbert, I. A. Shkrob, and D. P. Abraham, J. Electrochem. Soc., 164, A389 (2017).
19. T. Ohzuku, A. Ueda, and N. Yamamoto, J. Electrochem. Soc., 142, 1431 (1995).
20. K. Ariyoshi, R. Yamato, and T. Ohzuku, Electrochem. Acta, 51, 1125 (2005).
21. K. Ariyoshi, E. Iwata, M. Kuniyoshi, H. Wakabayashi, and T. Ohzuku, J. Electrochem. Solid-State Lett., 9, A557 (2006).
22. A. J. Smith, J. C. Burns, S. Trussler, and J. R. Dahn, J. Electrochem. Soc., 157, A196 (2010).
23. T. M. Bond, J. C. Burns, D. A. Stevens, H. M. Dahn, and J. R. Dahn, J. Electrochem. Soc., 160, A521 (2013).
24. A. I. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, 2nd ed., John Wiley & Sons, New York (2001).
25. T. Ohzuku and K. Sawai, Denki Kagaku (presently Electrochemistry), 64, 1060 (1996).
26. T. Ohzuku, R. Yamato, T. Kawai, and K. Ariyoshi, J. Solid State Electrochem., 12, 979 (2008).
27. K. Ariyoshi, Y. Ikawoshi, N. Nakayama, and T. Ohzuku, J. Electrochem. Soc., 151, A296 (2004).