Comparative Measurements of Side-Reaction Currents of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ Electrodes in Lithium-Ion Cells and Symmetric Cells

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Comparative Measurements of Side-Reaction Currents of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ Electrodes in Lithium-Ion Cells and Symmetric Cells

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Abstract

Lithium-ion batteries using $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LTO/LAMO) are very attractive for long-life and high-power applications. Capacity fading of the batteries mainly results from the deviation in the state of charges (SOCs) of LTO and LAMO electrodes caused by the difference in the side reaction currents of the electrodes. In this study, “real” and “intrinsic” side reaction currents are measured in LTO/LAMO cells and symmetric cells of LTO/LTO and LAMO/LAMO, respectively. An observed significant difference in the side reaction currents is affected by the coupled electrode. The real side reaction currents for both electrodes are a few times larger than the intrinsic side reaction currents at any temperature, which can be explained by taking into account the influence of oxidation (or reduction) products generated at the positive (or negative) electrode on the negative (or positive) electrode. A mechanism of the side reaction inside the cell is proposed to explain the above phenomenon. The mechanism indicates the importance for understanding the “secondary” effects of side reactions, which are influenced by decomposition products on the other electrode, in addition to “primary” effects of side reactions such as the formation of solid electrolyte interphase.

Keywords: lithium-ion battery, side reaction, calendar/cycle life, lithium titanium oxide

1. Introduction

Over the past two decades, lithium-ion batteries (LIBs) have been considerably developed in terms of energy and power densities as well as cycle life. Since LIBs are attractive for power sources of x-EVs such as hybrid electric vehicle (HEV), plug-in HEV (PHEV) and battery electric vehicle (BEV) which require more than 1000 cycles for 10-year service, cycle life of LIBs is one of the most important performance parameters for such applications. Lithium-ion batteries using lithium titanium oxide ($\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$; LTO) and lithium manganese oxides ($\text{Li}[\text{Li}_x\text{Mn}_{2-x}]\text{O}_4$; LMO) as electrode materials are one of the most attractive batteries for long-life and high-power applications¹⁻⁴, because LTO is a zero-strain insertion material^{5,6}, which is thought to have unlimited cycle life, and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO), one of the derivatives of LMO, shows excellent cyclability of more than 1000 cycles⁷.

Imbalance of the state of charges (SOCs) between positive and negative electrodes induces capacity fading in LIBs even when the electrode materials are not deteriorated⁸. Therefore, there has been considerable research to understand the reason for the deviation of SOC in order to extend the life time (cycle and calendar life) of LIBs. SOC imbalance induces capacity fading because side reactions at both electrodes result in lower current efficiency ($< 100\%$), defined by the net current for the lithium insertion reaction divided by the charge/discharge currents⁹⁻¹³. In our previous study¹², “intrinsic” side reaction currents of LTO and LAMO (Fig. 1a), which have no influence on the other electrode, have been successfully measured by using LTO/LTO and LAMO/LAMO symmetric cells. Capacity fading of an LTO/LAMO cell is due to the

difference in the rates of side reaction (side reaction currents, I_{SR}) between the LTO and LAMO electrodes, *i.e.*, $I_{SR,LTO} > I_{SR,LAMO}$. Based on the above results, we have proposed a method for extending the cycle/calendar life of LIBs by adjusting the rates of side reaction currents between positive and negative electrodes. If the side reaction currents on both electrodes are the same, *i.e.* $I_{SR,LAMO} = I_{SR,LTO}$, the deviation of SOC of the two electrodes would not occur even though coulombic and current efficiencies are below 100%.

However, recent studies on capacity fading due to side reactions in LIBs have proved that the side reaction current of an electrode is affected by the other electrode^{14–20}. When the positive and negative electrodes are combined, the amount of gas generation and increment of resistance at the positive electrode are different from those at the positive electrode alone^{14–16}. During aging of a LIB, the change in SOC of the negative electrode depends on the electrode potential of the positive electrode^{17,18}. To explain the above phenomena, oxidizing products generated at the positive electrode due to the side reaction are reduced at the negative electrode, resulting in “additional” side reaction currents (Fig. 1b). This indicates that the side reaction currents on the LIB electrodes, hereafter called “real” side reaction currents, are different from the corresponding “intrinsic” values measured by using a symmetric cell. In other words, the “real” side reaction currents of the positive and negative electrodes, not the “intrinsic” ones, must be adjusted for suppressing the deviation of SOC of the electrodes leading to extended life time of LIBs.

Recently, we have developed a method to measure “real” side reaction currents of

LTO and LiNiMO electrodes in LTO/LiNiMO cells²⁰, thus enabling the investigate of the nature of side reactions at the electrodes in LIBs. In this study, we measured the “real” side reaction currents in LTO/LAMO cells by the cumulative capacity plots, and compared them with the corresponding “intrinsic” side reaction currents of the LTO and LAMO electrodes measured by using symmetric cells. Both the LTO and LAMO electrodes are suitable for our purpose because they do not deteriorate to contribute to capacity fading. A mechanism is proposed to explain the difference between the “real” and “intrinsic” side reaction currents by introducing an “additional” side reaction current.

2. Experimental

2. 1 Electrode preparation and cell fabrication

Lithium titanium oxide $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ ⁶ (LTO; Ishihara Sangyo Kaisha Ltd. LT 855-17C) and lithium aluminum manganese oxide $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ ^{7,21,22} (LAMO, Tosoh Corp.) were used as electrode materials. Prior to cell performance examinations, the structural and electrochemical properties of LTO and LAMO were confirmed by XRD, SEM and electrochemical methods. Particle morphology of LTO and LAMO observed by SEM were shown in Fig. S1. The LTO and LAMO used in this study exhibited a reversible capacity of more than 90 % theoretical capacities with small polarization and no noticeable capacity fading during cycling. The active material and acetylene black as a conductive additive were mixed in an agate pot and mixed with polyvinylidene fluoride (PVdF) as a binder dissolved in N-methyl-2-pyrrolidone (NMP).

The mixture was stirred for 10 min to form a slurry. The composition of each electrode was set to 88 wt% of LTO or LAMO, 6 wt% of acetylene black, and 6 wt% of PVdF. An aluminum foil was used as the current collector; it was adhered onto a glass plate with acetone, and the obtained slurry was applied to obtain a certain thickness. The applied slurry was dried in vacuo at 80 °C for about 1 h and further vacuum-dried overnight at 150 °C. After drying, the electrode was punched out in 2-cm² areas. The weight was approximately 30 mg for both LTO and LAMO electrodes, and the corresponding thicknesses were 100 and 120 μm. Two sheets of Celgard 2500 were used as separators. The electrolyte employed herein was 1 M LiPF₆ containing a 3:7 mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (Kishida Chemical Co., Ltd., Japan).

2. 2 Measurements of "real" side reaction current by cumulative capacity plots

The side reaction currents of the electrodes in LTO/LAMO cells were measured by using a cumulative capacity plot obtained from continuous charge-discharge curves. We subjected an LTO/LAMO cell to a long-term (> 1200 h) charge-discharge test with a previously reported in-house-built high-current-precision battery cycler²⁰. The cell was placed in an incubator at 25 °C (< ±1 °C) and the battery cycler was operated at a constant temperature (25 ± 3 °C). The side reaction currents of the electrodes in a LTO/LAMO cell were influenced by the other electrode, viz. the “real” side reaction currents. The cumulative capacity plot was obtained by plotting the capacities at the end of charge and discharge (cumulative capacities (CQ_{Cha} and CQ_{Dis}, respectively)) as a function of cycling time. When the side reaction current of LTO is larger than that of

LAMO and the capacity of an LTO electrode is larger than that of a LAMO electrode, the cumulative capacities can be expressed as the following equations.

$$CQ_{\text{Cha}}(t) = Q_{\text{Cell}}(0) + \int I_{\text{SR, LAMO}} dt \quad (1)$$

$$CQ_{\text{Dis}}(t) = \int I_{\text{SR, LTO}} dt \quad (2)$$

where $Q_{\text{Cell}}(0)$ is the cell capacity before cycling, and t is the cycling time. The side reaction currents on the electrodes can be calculated as

$$I_{\text{SR, LAMO}} = d(CQ_{\text{Cha}})/dt \quad (3)$$

$$I_{\text{SR, LTO}} = d(CQ_{\text{Dis}})/dt \quad (4)$$

Thus, the side-reaction currents can be estimated either mathematically (by differentiation of the cumulative capacity with respect to cycling time) or graphically (from the slope of cumulative capacity vs. cycling time plots).

2. 3 Measurement of "intrinsic" side reaction current using symmetric cell

In contrast to the “real” side reaction currents generated by the effect of the counter electrode, “intrinsic” side reaction current of an electrode is independent of the counter electrode. "Intrinsic" side reaction currents of an electrode can be measured by using an LTO/LTO or LAMO/LAMO symmetric cell^{12,23}. The charge-discharge test of the symmetric cell was performed with a charge-discharge battery cycler (Battery Laboratory System, Keisokuki Center Co. Ltd., Japan). Since the symmetric cells consist of electrodes with the same weight, thickness, and electrode capacity, the side reaction currents of both the electrodes in the symmetric cell are the same. Therefore, the capacity of the symmetric cell fades during cycling according to the following

equation.

$$Q_{\text{Loss}} = 2 \int I_{\text{SR}} dt \quad (5)$$

The side reaction current of a single electrode can be obtained from the decrease in capacity of the symmetric cell as a function of cycling time, as follows.

$$I_{\text{SR}} = 1/2 (dQ_{\text{Loss}}/dt) \quad (6)$$

3 Results and discussion

3.1 Measurements of "real" side reaction currents of an LTO/LAMO cell

Long-term charge-discharge tests of LTO/LAMO cells were carried out using a high-precision battery cyclers to measure the "real" side reaction currents for both LTO and LAMO electrodes in the cell. Figure 2 shows the continuous charge-discharge curves of the LTO/LAMO cells cycled at 25, 40, and 55 °C at the current density of 0.25 mA cm⁻² in the voltage range from 1.5 to 3.1 V. The continuous charge-discharge curves were gradually shifted during cycling except for the early stage of the cycle. A large shift in the charge-discharge curves was observed, probably due to electrolysis of moisture and impurities in the cells. Cumulative capacity plots were depicted by plotting CQ_{Cha} and CQ_{Dis} as a function of cycling time (Figure 3). In the LTO/LAMO cells, charge and discharge capacities are limited by the LAMO positive and LTO negative electrodes, respectively^{7,12}. Therefore, the side reaction currents on the LAMO and LTO electrodes were estimated from the gradients of CQ_{Cha} and CQ_{Dis}, respectively, as a function of cycling time. With increasing cycling temperature, cumulative capacity rapidly increases, implying that the side reaction currents on both LAMO and LTO are

accelerated at high temperatures. The side reaction currents of the LTO electrode are larger than those of the LAMO electrode. The side reaction current of the LAMO electrode changed slightly with increasing temperature, while the corresponding change in the LTO electrode was large.

The plot of cumulative capacity against cycling time was slightly curved, and not a rigorous straight line. Straight lines can be obtained by plotting the cumulative capacities against the square root of cycling time (Figure 4). Since the cell capacity is equal to the difference between CQ_{Cha} and CQ_{Dis} , capacity of the LTO/LAMO cell fades as a function of square root of time, which agrees well with the previously reported relation of $Q \propto \sqrt{t}$ ^{4,7,24,25}. This indicates that capacity fading due to SOC imbalance is proportional to the square root of cycling time. Side reaction currents of LAMO and LTO electrodes can be calculated by the differentiation of CQ_{Cha} and CQ_{Dis} with respect to a cycling time, respectively.

$$I_{\text{SR, LAMO}} = dCQ_{\text{Cha}}/dt = k_{\text{LAMO}} \times t^{-0.5} \quad (7)$$

$$I_{\text{SR, LTO}} = dCQ_{\text{Dis}}/dt = k_{\text{LTO}} \times t^{-0.5} \quad (8)$$

The coefficient k , corresponding to the slopes of the cumulative capacity plots, was calculated to be $k_{\text{LAMO}} = 0.46, 0.45, \text{ and } 0.57 \text{ mA h}^{0.5} \text{ g}^{-1}$, respectively, at 25, 40, and 55 °C and $k_{\text{LTO}} = 0.69, 1.26, \text{ and } 1.70 \text{ mA h}^{0.5} \text{ g}^{-1}$, respectively, at 25, 40, and 55 °C. The logarithmic value of k plotted against the reciprocal of absolute temperature, *i.e.* the Arrhenius plots are shown in Figure 5. Linear relations observed in the figure lead to the following equation, expressing k as a function of T .

$$k_{\text{LAMO or LTO}} = A \exp(E_a/RT) \quad (9)$$

The two straight lines shown in Figure 5 indicate activation energies of the side reactions of LTO and LAMO electrodes were calculated to be $E_{a,\text{LAMO}} = 6.15 \text{ kJ mol}^{-1}$ and $E_{a,\text{LTO}} = 24.8 \text{ kJ mol}^{-1}$, respectively. Therefore, side reaction current of LAMO and LTO at any temperature can be expressed by the following equation,

$$I_{\text{SR, LTO or LAMO}} = -A\sqrt{t} \times \exp(E_a/RT) \quad (10)$$

The activation energy of the side reactions at LTO and LAMO electrodes is of the same order of magnitude but slightly lower than that in LIBs containing graphite and layered materials ($\sim 40 \text{ kJ mol}^{-1}$) calculated from the capacity fading reported previously^{26–28}. This probably results from the difference in the electrode potentials of the negative electrodes, *i.e.* 1.55 V for LTO versus 0.1 V for graphite electrode. Therefore, the activation energy of side reactions at both electrodes can be measured by using the cumulative capacity plots.

3. 2 Measurements of “intrinsic” side reaction currents of LTO and LAMO electrodes by symmetric cells

As described in the previous section, the side reaction currents of LTO and LAMO electrodes calculated from the cumulative capacity plots are “real” values because they were measured in a lithium-ion cell in which side reaction currents of an electrode are affected by the other electrode. In contrast to “real” side reactions, “intrinsic” side reaction currents in the absence of the influence of a counter electrode can be measured

by using a symmetric cell because both electrode materials in the symmetric cell are the same. Constant-current charge-discharge tests of LAMO/LAMO symmetric cells were carried out at 25, 40, and 55 °C (Figure 6). The cells were cycled in the voltage range from -0.5 to 0.5 V at the current density of 0.5 mA cm^{-2} . In all the LAMO/LAMO symmetric cells, the capacity decreased with each cycle, and this capacity fading increased with increasing temperature. Figure 6b shows the cell capacities of the LAMO/LAMO symmetric cells as a function of cycling time. Cell capacities at all the temperatures decreased almost linearly, except for the early cycles, indicating that the “intrinsic” side reaction current of LAMO was constant during cycling in contrast to “real” side reaction currents that varied with cycling time. Capacity fading of the cells was faster with increasing temperature, meaning that the “intrinsic” side reaction current of the LAMO electrode increased with increasing temperature: 0.04 , 0.10 , and $0.25 \text{ } \mu\text{A}$ at 25, 40, and 55 °C, respectively. To measure the “intrinsic” side reaction current of an LTO electrode in the same way as the LAMO electrode, constant-current charge-discharge tests of an LTO/LTO symmetric cell were carried out at 25, 40, and 55 °C (Figure 7). Capacity fading of the LTO/LTO symmetric cells showed similar tendencies, i.e., cell capacities decreased almost linearly with cycling time and the fading rate was accelerated with increasing temperature. From the slope of the capacity plots (Figure 7b), the “intrinsic” side reaction currents of the LTO electrodes were calculated to be 0.21 , 0.29 , and $0.57 \text{ } \mu\text{A}$ at 25, 40, and 55 °C, respectively. The “intrinsic” side reaction currents of the LTO electrode were larger than those of the LAMO electrode at any temperature.

3. 3 “Real”, “intrinsic”, and “additional” side reaction currents of LTO and LAMO electrodes

To compare the “real” and “intrinsic” side reaction currents of the LTO and LAMO electrodes numerically, two kinds of side reaction currents after 500 h of cycling time were calculated: “real” side reaction current from the slopes of CQ_{Cha} and CQ_{Dis} of LTO/LAMO cells (Figure 4) and “intrinsic” side reaction current from the slopes of the capacity fading of the symmetric cells (Figures 6 and 7). Figure 8 shows the “real” and “intrinsic” side reaction currents of the LTO and LAMO electrodes at 25, 40 and 55 °C. The side reaction currents of the LTO electrode were larger than those of the LAMO electrode at any temperature. The “real” side reaction currents of both the electrodes were significantly larger than the corresponding “intrinsic” ones. These results indicate that the “real” side reaction current of one electrode was influenced by the other. By defining “additional” side reaction currents of the electrodes as the difference between the “real” and “intrinsic” ones, side reaction currents of the electrodes can be expressed by the following relation.

$$I_{\text{SR}}(\text{real}) = I_{\text{SR}}(\text{intrinsic}) + I_{\text{SR}}(\text{additional}) \quad (11)$$

The side reactions in the LTO/LAMO cell to explain the difference between the real and intrinsic side reaction currents of the electrodes were schematically shown in Fig. 1. In the absence of the influence of the counter electrode, only the “intrinsic” side reactions

take place at the electrode. However, in the LTO/LAMO cell, oxidation and reduction products were generated by the “intrinsic” side reactions at the LAMO positive electrode and the LTO negative electrode, respectively. These oxidation and reduction products are expected to be molecular species, such as H_2 , CO , CO_2 , hydrocarbons (CH_4 , C_2H_6 , etc.)^{3,29,30}, alkyl dicarbonates¹⁶, organophosphates³¹, dissolved metal ions¹⁸. When these chemical species, which can easily migrate through the micropores of separators, arrive at the other electrode due to diffusion or migration in the cell, “additional” side reactions occur at the other electrode. The oxidized products generated at the LAMO positive electrode are reduced at the LTO negative electrode and vice versa. Consequently, “real” side reaction currents of the electrodes are the sums of the corresponding “intrinsic” and “additional” side reaction currents. The chemical species produced by the side reactions accumulate in the electrolyte, producing different trends in the “real” and “intrinsic” side reaction currents as a function of cycling time; “intrinsic” side reaction current is proportional to cycling time, while “real” side reaction current is proportional to the square root of cycling time. Figure 1 shows that in order to extend battery life, “additional” side reactions due to the chemical species generated by “intrinsic” side reactions must be considered (secondary effects of side reaction) in addition to the influence of “intrinsic” side reactions on the deterioration of battery performances (primary effects of side reactions), such as solid-electrolyte interphase (SEI) formation.

4. Conclusion

We have measured and compared “real” and “intrinsic” side reaction currents (I_{SR}) of $\text{Li}[\text{Li}_{1/3}\text{Ti}_{5/3}]\text{O}_4$ (LTO) and $\text{Li}[\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8}]\text{O}_4$ (LAMO) electrodes, measured by using the cumulative capacity plots of LTO/LAMO cells and by using the LAMO/LAMO and LTO/LTO symmetric cells, respectively. At both LTO and LAMO electrodes, the “real” side reaction currents were significantly larger than the corresponding “intrinsic” values at any temperature. Both real and intrinsic side reaction currents at LAMO electrodes were larger than those at LTO electrodes at any temperature. Real and intrinsic show different trends side reaction current against cycling time; intrinsic side reaction current is proportional to cycling time, while real one is proportional to the square root of cycling time.

The “additional” side reaction currents, in which oxidation products generated due to side reactions at the positive electrode are reduced at the negative electrode, are introduced to explain the difference between the “real” and “intrinsic” side reaction currents. To suppress capacity fading of LIBs due to SOC imbalance between positive and negative electrodes, it is necessary to adjust real side reaction current, not the intrinsic one, between the positive and negative electrodes. The presence of an additional side reaction in LIBs, as evidenced by comparing the real and intrinsic side reaction currents, demonstrates that in addition to the “primary” effects of electrolyte decomposition on electrodes, *e.g.*, formation of solid-electrolyte interphase, “secondary” effects of side reactions, *i.e.* the influence of decomposition products on the other electrode, should be considered for extending the life-time of LIBs and for

understanding the complex nature of side reactions in LIBs resulting from the influence of oxidation/reduction products produced by side reaction at the other electrodes. Qualitative analysis of the chemical species, which are the source of additional side reaction current, would provide useful information to understand the accumulation and circulation of the chemical species between the electrodes in LIBs, thus qualitative analysis of chemical species should be addressed in near future.

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Figure 1. Schematic of side reactions in (a) the LTO/LTO symmetric cell and (b) the LTO/LAMO cell to explain the difference between real and intrinsic I_{SR} of the electrodes; (red) intrinsic, (green) additional, and (blue) real side reaction currents. The real side reaction currents, $I_{SR}(\text{real}) = I_{SR}(\text{intrinsic}) + I_{SR}(\text{additional})$.

Figure 2. Charge-discharge curves of LTO/LAMO cells operated at 0.25 mA cm^{-2} in the voltage range from 1.5 to 3.8 V at (a) 25, (b) 40, and (c) 55 °C. The LTO electrodes are (a) 30.1 mg with 108 μm , (b) 31.0 mg with 113 μm , and (c) 34.8 mg with 125 μm , while the LAMO electrodes are (a) 32.3 mg with 92 μm , (b) 32.5 mg with 92 μm , and (c) 31.7 mg with 93 μm .

Figure 3. Cumulative capacity plots of LTO/LAMO cells cycled at (a, d) 25, (b, e) 40, and (c, f) 55 °C, calculated from the continuous charge-discharge curves shown in Fig. 1. The cumulative capacities (a, b, and c) at the end of charge, CQ_{Cha} , and (d, e, and f) at the end of discharge, CQ_{Dis} .

Figure 4. The cumulative capacities (a, b, and c) at the end of charge, CQ_{Cha} , and (d, e, and f) at the end of discharge, CQ_{Dis} at (a, d) 25, (b, e) 40, and (c, f) 55 °C as a function of the square root of cycling time.

Figure 5. Plots of the slopes of cumulative capacities [(a) CQ_{Dis} and (b) CQ_{Cha}] calculated from Fig. 3 against the reciprocal of the absolute temperature. The slopes of (a) CQ_{Dis} and (b) CQ_{Cha} correspond to “real” side reaction currents in the LTO-negative and LAMO-positive electrodes, respectively. Thus, the side reaction currents of LAMO and LTO electrodes can be expressed in the general form of $I_{\text{SR, LTO or LMAO}} = -A\sqrt{t} \times \exp(E_a/RT)$.

Figure 6. (a) Charge-discharge curves of LAMO/LAMO symmetric cells operated at 0.5 mA cm^{-2} in the voltage range from -0.5 to 0.5 V at 25, 40, and 55 °C. (b) Capacities of LAMO/LAMO symmetric cells as a function of cycling time. The LAMO electrodes were $32 \pm 2 \text{ mg}$ with $100 \pm 10 \text{ }\mu\text{m}$.

Figure 7. (a) Charge-discharge curves of LTO/LTO symmetric cells operated at 0.5 mA cm^{-2} in the voltage range from -0.5 to 0.5 V at 25, 40 and 55 °C. (b) Capacities of LTO/LTO symmetric cells as a function of cycling time. The LTO electrodes were 33 ± 3 mg with 120 ± 5 μm .

Figure 8. Open circles (a, c) and squares (b, d) indicate “real” and “intrinsic” side reaction currents, respectively. The blue (a, b) and red (c, d) symbols indicate side reaction currents of the LTO and LAMO electrodes, respectively.