**Supporting Information**

**A dynamic analysis of reversible/irreversible capacity fading of Li-ion cells owing to low-temperature operation by differential capacity profile**†

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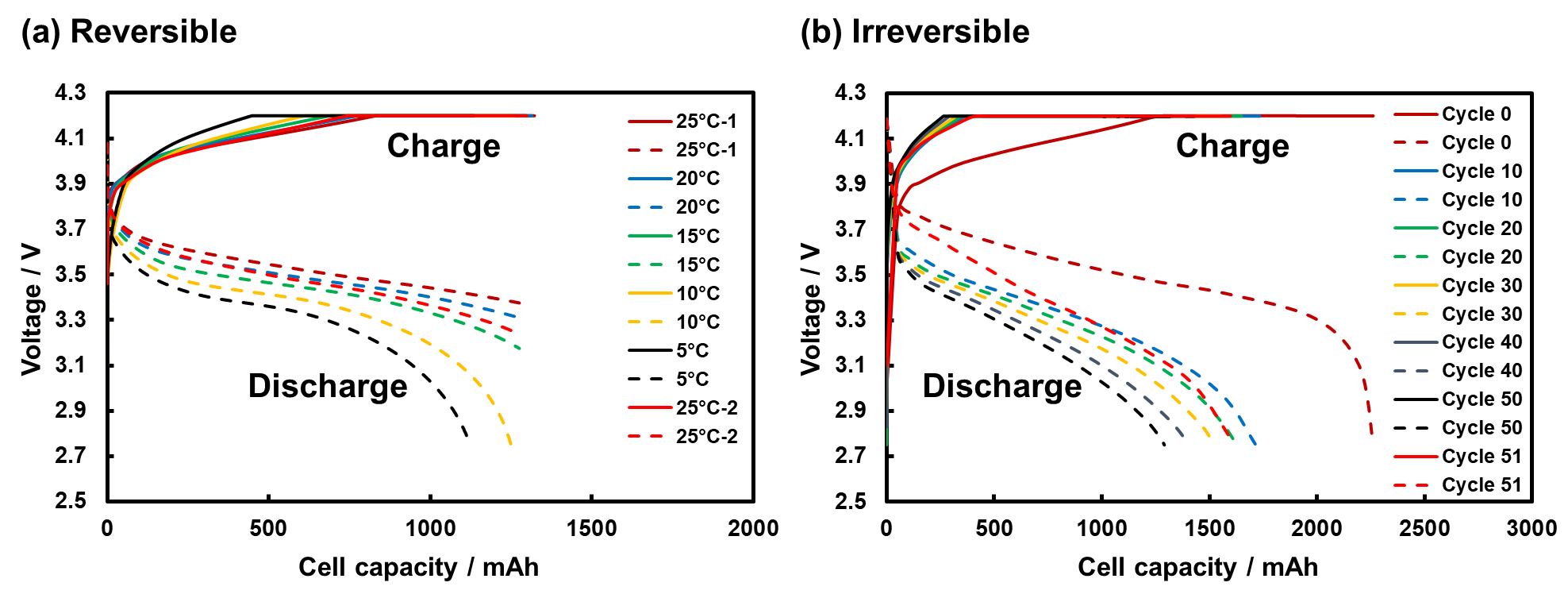
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Fig. S1. Voltage-capacity curves of 18650-type LCO cells for (a) reversible degradation, (b) irreversible degradation. Cycles 0 and 51 are surveyed at 25 °C to investigate the reversibility of cell capacity.

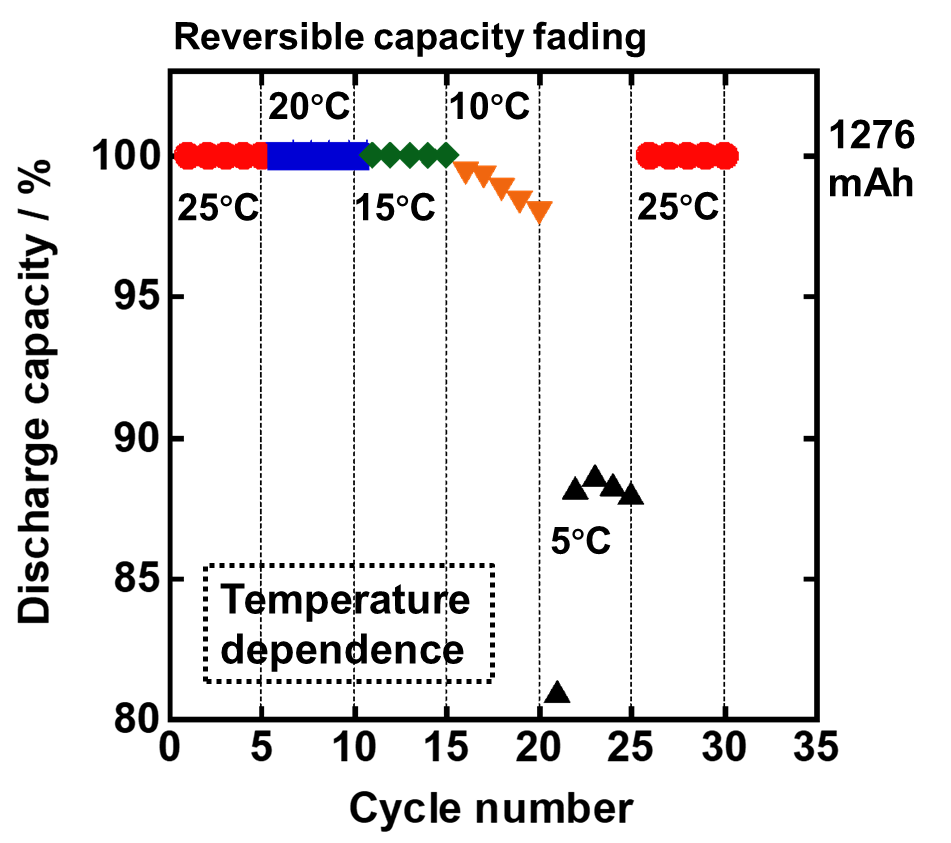
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Fig. S2. Discharge capacity of the 18650-type LiCoO2/graphite cell for 5 cycles at different temperatures following a constant current (CC)–constant voltage (CV) charge process at 1 C-rate for 35 min and CC discharge process at 1 C-rate for 30 min.

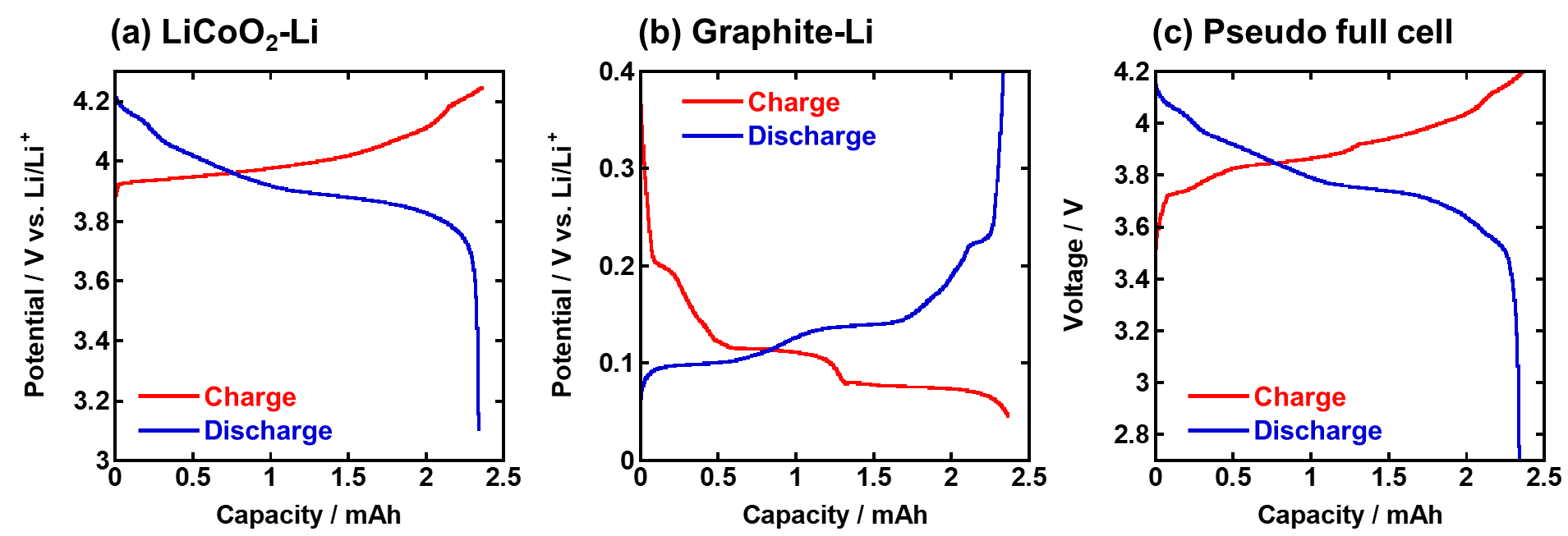
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Fig. S3. Charge/discharge curves of (a) LiCoO2-Li, (b) graphite-Li, and (c) pseudo full cell surveyed at 25 °C with a constant current of 0.05 C-rate.

形状

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Fig. S4. Matching results for graphite peaks during charge and discharge, obtained by changing the charge cut-off voltage.

Table S1 The results of peak attribution in d*Q*/d*V* vs. *V* curves of a pseudo full cell

|  |  |  |
| --- | --- | --- |
| *Peaks of pseudo full cell* | *Attribution results* | *Corresponding reactions* |
| Charge |  |  |
| Peak 1 | Peak a (graphite) | Dilute stage-1 to stage-4 |
| Peak 2 | Peak b (graphite) | Stage-4 to stage-3 |
| Peak 3 | Peak c (graphite) | Stage-4 to stage-3 |
| Peak 4 (front half)  Peak 4 (back half) | Peak d (graphite)  Peak A (LiCoO2) | Stage-3 to stage-2  Hexagonal-I to hexagonal-I/II |
| Peak 5 (front half)  Peak 5 (back half) | Peak e (graphite)  Peak A (LiCoO2) | Stage-2 to stage-1  Hexagonal-I to hexagonal-I/II |
| Peak 6 | Peak B (LiCoO2) | Hexagonal-I/II to hexagonal-II |
| Peak 7 | Peak C (LiCoO2) | Hexagonal-II to monoclinic |
| Discharge |  |  |
| Peak 8 | Peak C' (LiCoO2) | Monoclinic to hexagonal-II |
| Peak 9 | Peak B' (LiCoO2) | Hexagonal-II to hexagonal-I/II |
| Peak 10 (front half)  Peak 10 (back half) | Peak A' (LiCoO2)  Peak d' (graphite) | Hexagonal-I/II to hexagonal-I  Stage-2 to stage-3 |
| Peak 11 | Peak c' (graphite) | Stage-3 to stage-4 |
| Peak 12 and 13 | Peak b' (graphite) | Stage-3 to stage-4 |
| Peak 14 (front half)  Peak 14 (back half) | Peak a' (graphite)  Peak A' (LiCoO2) | Stage-4 to dilute stage-1  Hexagonal-I/II to hexagonal-I |

***Differential capacity profiles of pseudo-three-electrode full cells with different*** ***electrode area ratios***

As described in *section 3.3.*, peak attribution of the d*Q*/d*V* vs. *V* curve was implemented using a pseudo-three-electrode full cell with an LiCoO2/graphite electrode area ratio of 1:1. To improve the reliability of peak attribution, pseudo-three-electrode full cells with LiCoO2/graphite electrode area ratios of 0.75:1 and 1:0.75 were used to validate the results. Fig. S5 shows the differential capacity profiles of the pseudo-three-electrode full cells with different LiCoO2/graphite electrode area ratios (d*Q*/d*V* vs. *V* curves, Fig. S5a) and LiCoO2-Li and graphite-Li half-cells with different electrode areas (d*Q*/d*E* vs. *E* curves, Figs. S5b and S5c, respectively).

图示

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Fig. S5. (a) Differential capacity profiles of the pseudo-three-electrode full cells with different LiCoO2/graphite electrode area ratios, (b) and (c) differential capacity profiles of LiCoO2-Li and graphite-Li half-cells with different electrode area ratios.

As shown in Fig. S5a for pseudo full cells, during charging the intensity of peak 5 of the pseudo full cell with a LiCoO2/graphite electrode area ratio of 1:1 decreased sharply when the LiCoO2 electrode area was reduced to 0.75 with the graphite electrode area unchanged, while peaks 6 and 7 showed an obvious shift to more positive voltage values when the graphite electrode area was reduced to 0.75 with the LiCoO2 electrode area unchanged. In addition, it can be seen that with a LiCoO2/graphite electrode area ratio of 1:0.75, peak 7 during charging became incomplete and peak 8 during discharging disappeared, compared with the results for the 1:1 ratio. Peak shifts in intensity and potential are known to represent changes in the reacting dose and reaction impedance, respectively.37–40 Thus, we conclude that reducing the LiCoO2 electrode area led to a decrease in the reacting dose of the reaction at peak 5, whereas reducing the graphite electrode area led not only to an increase in the reaction impedance of the reaction occurring at peaks 6 and 7, but also to a decrease in the reacting dose of the reaction occurring at peaks 7 and 8.

Meanwhile, comparing the results in Figs. S5b and S5c for the LiCoO2-Li and graphite-Li half-cells, it can be observed that some characteristic peaks of LiCoO2 and graphite also changed with changes in the electrode area ratio. With an LiCoO2/graphite electrode area ratio of 0.75:1, no obvious changes are seen in the three coupled characteristic peaks A/A', B/B', and C/C' of LiCoO2 during charge and discharge, but the charging peak e of graphite is obviously incomplete, compared with the results for the 1:1 ratio. This suggests that the structural change reaction of LiCoO2 between hexagonal-I and monoclinic occurred normally when the LiCoO2 electrode area was shrunk to 0.75 with the graphite electrode area unchanged; however, the final phase change reaction of graphite during charging, from stage-2 to stage-1, was incomplete because of the lack of intercalated lithium. Conversely, for a LiCoO2/graphite electrode area ratio of 1:0.75, the coupled characteristic peaks C/C' of LiCoO2 become smaller and even disappear, while the characteristic peaks a-e (including peaks a'–e') of graphite do not change significantly compared with the results for a 1:1 ratio. This suggests that the phase change reactions between dilute stage-1 and stage-1 of graphite occurred normally when the graphite electrode area shrank to 0.75 with the LiCoO2 electrode area unchanged, but the reacting dose in the structural change reaction of LiCoO2 between hexagonal-II and monoclinic decreased because of the limited graphite electrode area. Furthermore, a new graphite peak is observed at a potential below 0 V vs. Li/Li+ during the charging process (Fig. S5c, graphite with area ratio 0.75). It is considered that in the later stages of the charging process, a number of Li ions cannot intercalate into the graphite layers and are deposited on the surface of the graphite as metallic lithium because the layer space of graphite is limited by the relatively small area of the graphite electrode; thus, this peak is associated with the occurrence of lithium plating on the graphite electrode surface.7,25,29–36

In summary of Fig. S5, the intensity of peak 5 of the pseudo full cell with a LiCoO2/graphite electrode area ratio of 0.75:1 decreased compared with its intensity with a 1:1 ratio, while the peaks of LiCoO2 did not change significantly, but peak e of graphite became incomplete. Conversely, peaks 7 and 8 of the pseudo full cell became smaller and even disappeared when the LiCoO2/graphite electrode area ratio changed from 1:1 to 1:0.75, and identical changes were observed in the coupled characteristic peaks C/C' of LiCoO2. Thus, it is obvious that the reaction corresponding to peak 5 is related to the phase change reaction of graphite from stage-2 to stage-1 (peak e), and the reactions corresponding to peaks 7 and 8 are related to the structural change reaction of LiCoO2 between the hexagonal-II and monoclinic phases (peaks C/C').

In addition, by converting the voltage values on the horizontal axis in Fig. S5a to the amount of charge in coulombs, the results for pseudo full cells with electrode area ratios could be overlapped, as shown in Fig. S6. By comparing the results for pseudo full cells with various electrode area ratios, an obvious peak shift can be found in the back half of peaks 4 and 5 when the LiCoO2 electrode area was shrunk to 0.75 with the graphite electrode area unchanged, whereas an obvious peak shift can be found in the front half of peaks 4 and 5 when the graphite electrode area was shrunk to 0.75 with the LiCoO2 electrode area unchanged. It can be concluded that the reactions corresponding to the back half of peaks 4 and 5 are related to the electrode reactions of LiCoO2, and the reactions corresponding to the front half of peaks 4 and 5 are related to the electrode reactions of graphite.

Some peaks (peaks 4,5,7,and 8) of the pseudo full cell were attributed to specific electrode reactions by measuring and comparing the differential capacity profiles of pseudo-three-electrode full cells with different electrode area ratios. The peak attribution results in Figs. S5 and S6 are consistent with the results shown in Table S1, and we are therefore confident that the peak attribution results in Table S1 are reliable.

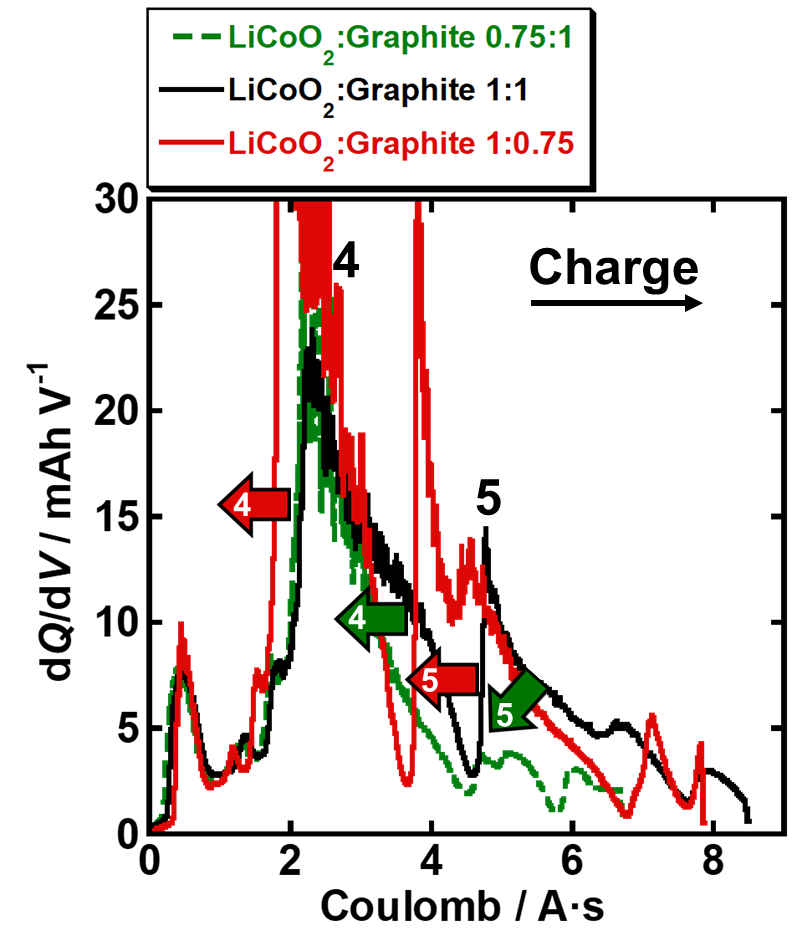


Fig. S6. Overlap of the curves in Fig. S5a obtained by converting the voltage values shown in the horizontal axis to the amount of charge during the charge process.