

Short communication

A fast formation process for lithium batteries

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Abstract

The formation process presently used in the manufacture of lithium-ion batteries includes the solid electrolyte interface (SEI) growth process and another process for lithium intercalation into carbon. The latter process is both time and energy consuming. This study proposes a new concepts that can shorten the formation time by narrowing the potential range and bypassing the intercalation step during formation. The optimum cut-off voltage is 3.7 V for industrial LiCoO₂/C cells, and the formation time is reduced to less than one half of that required in the conventional formation procedure. Cycle performance is not affected significantly because the desired SEI growth is mainly completed in the potential range. These results suggest that the new method is superior to conventional formation.

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1. Introduction

International efforts have been directed towards the development of improved lithium-ion batteries [1–3]. Conventionally, a transition metal oxide such as LiCoO₂ is used as the material for the positive electrode (cathode) and a carbonaceous material for the negative electrode (anode). Numerous types of material, including natural and artificial graphites, cokes, fibres, mesocarbons and others with selected additives, have been examined for higher capacity [4–6]. Theoretically, the maximum lithium content that can be intercalated into graphite is one lithium atom per six carbon atoms, i.e., LiC₆. This corresponds to a maximum specific capacity of 372 mAh g⁻¹.

Although the formation of LiC₆ appears to be quite reversible, the actual reactions are much more complex. The capacity loss is always accompanied by irreversible consumption of lithium and electrolyte to form a so-called solid electrolyte interface (SEI) layer. This is because the potential of LiC₆ is within 0.1 V of lithium metal, and a reaction between the electrolyte and the lithium atoms in LiC₆ is expected. Although it is generally believed that SEI formation

is almost complete in the first cycle, an irreversible reaction of electrolytes will proceed if the SEI is not sufficiently thick to prevent further electron tunneling [6]. Therefore, before being placed on the market, lithium-ion batteries must undergo one or more charge–discharge cycles, which is conventionally called the *formation process*, to make sure that the SEI layer has fully grown.

The life and discharge performance of a lithium cell are highly dependent on the SEI that is developed on the carbon electrode during the formation period. It is believed that low charge–discharge currents can produce a denser SEI layer that is beneficial for cycleability. There has been little research, however, on the effect of the cut-off potential of the formation process on SEI characteristics. Hence, in this study, an attempt is made to optimize the voltage range of formation process based on capacity fading and formation time. The impedance and capacity performance of the cells are also measured and compared with those displayed by existing technologies.

2. Experimental

The major materials used were mesocarbon microbeads (MCMB, Osaca Gas), LiCoO₂ (Nippon, Japan), LiClO₄ (Tomiyama, Japan), PVDF/HFP (Kureha), ethylene carbon-

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ate (EC) and diethyl carbonate (DEC) (Ferro Corp.). Carbon electrodes (about 86 μm in thickness with a copper) and LiCoO_2 electrodes (with a Al current-collector) were prepared. The carbon electrodes, which were 1.3 cm in diameter, contained 90 wt.% MCMB and 10 wt.% PVDF/HFP binder. The LiCoO_2 electrodes, which were 1.2 cm in diameter, contained 90 wt.% MCMB, 5 wt.% carbon black and 5 wt.% PVDF/HFP binder. The electrolyte was 1 M LiClO_4 dissolved in a mixture of EC and DEC (1:1, v/v).

Various formation conditions and the cycle performances were examined by means of a Maccor 2000 multichannel battery tester using $\text{Li|Cor LiCoO}_2|\text{C}$ coin cells with a PP/PE/PP (Celgard) separator (PP: polypropylene; PE: polyethylene). The coin cells were assembled in an argon-filled glove-box, in which the H_2O content was controlled to below 0.1 ppm. Since the most recent industrial formation process constitutes only one cycle, the method proposed here is also based on one cycle with a charge–discharge rate of 0.1 mA ($\sim C/30$). The cycle performance was evaluated between 1.5 and 0.002 V for Li|C half-cells and 2.7 and 4.2 V for $\text{LiCoO}_2|\text{C}$ full-cells at 0.6 mA ($\sim C/5$). All potentials and voltages are reported with respect to the Li|Li^+ electrode.

Commercial cylindrical-type 18650 Li-ion cells with rolled electrodes (Industrial Technology Research Institute, Taiwan) were employed in comparative studies. The major cathode and anode materials were LiCoO_2 and MCMB, respectively.

The ac impedance of cells was measured with an AUTO-LAB frequency response analyzer (Eco Chemie, Holland) after each charge or discharge step.

3. Results and discussion

A commonly used formation protocol for Li|C half-cells is discharging (intercalation) at constant current to a given voltage (usually 0.002 V) and then charging (de-intercalation) with the same current to 1.5 V. This voltage was varied to examine its effect on SEI formation and cycle-life. The various formation profiles for Li|C cells are shown in Fig. 1. The SC-1 curve is the result given by conventional formation with the potential controlled between 1.5 and 0.002 V. The process took 77 h to complete. By contrast, the total formation time of SC-2 (cut-off potential 0.2 V) and SC-3 (cut-off potential 0.3 V) was dramatically decreased to about 5 and 35 h, respectively.

The easiest way to verify that the SEI is properly produced is to check the cycle performance. Cycling data for different cut-off voltages are given in Fig. 2. Surprisingly, the capacity performance remains the same for all samples and is not affected by the reduction of process time. Although the capacity efficiencies in the first cycle of SC-2 and SC-3 are 0.98 and 0.97, respectively, which are slightly lower than that for SC-1 (0.99), all samples perform with perfect reversibility during prolonged cycling (cycle efficiency close to 1.0). Given these findings, it is concluded that the time required for a conventional formation process, such as SC-1, is much longer than necessary.

During the first discharge of a Li|graphite half-cell, a fraction of the lithium atoms that are intercalated in the carbon matrix will react irreversibly with the electrolyte. According to a previous study [7], this reaction between intercalated lithium atoms and electrolyte generally starts at 1.0 V

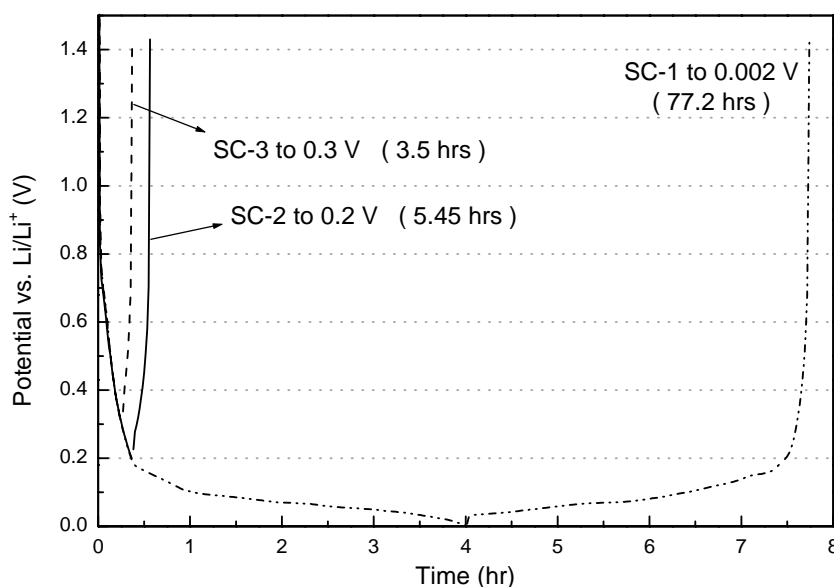


Fig. 1. Formation cycle of Li|MCMB with different potential periods: (---) SC-1, 1.5–0.002 V; (—) SC-2, 1.5–0.2 V; (---) SC-3, 1.5–0.3 V. Charge–discharge current is 0.1 mA. Electrolyte is 1 M $\text{LiClO}_4/\text{EC} + \text{DEC}$ (1:1).

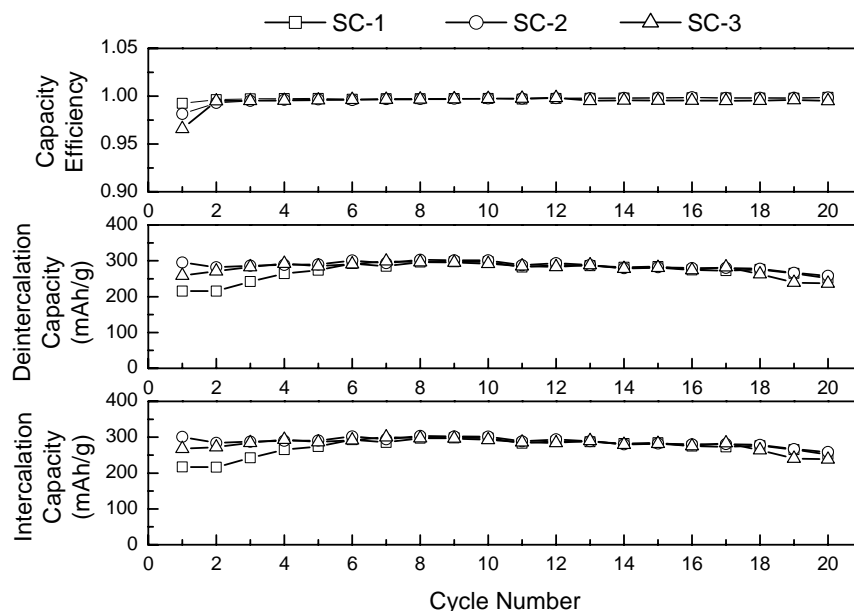


Fig. 2. Cycle performance of Li|MCMB after formation: (□) SC-1, 1.5–0.002 V; (○) SC-2, 1.5–0.2 V; (△) SC-3, 1.5–0.3 V. Capacity efficiency = deintercalation capacity/intercalation capacity. Charge–discharge current is 0.6 mA. Electrolyte is 1 M LiClO₄/EC + DEC (1:1).

and continues to form the SEI even below 0.3 V. Nevertheless, SEI formation mainly occurs before lithium intercalation into graphite (about 0.3 V). This means that the desired SEI formation actually takes place during only a very short period in the first discharge (for a Li|C cell). When the discharge potential is below 0.3 V, the intercalation of lithium into the carbon matrix becomes the dominant reaction, although SEI formation may still continue, as shown in Fig. 3. This may account for the lower capacity efficiency in the

first cycle of SC-2 and SC-3. It does not, however, lead to significant capacity loss (0.02 loss for SC-2 and 0.03 for SC-3), and has no effect on cycle performance. Under prolonged cycling, the intercalation of de-intercalation capacity of SC-1, SC-2 and SC-3 is almost identical ($\sim 300 \text{ mAh g}^{-1}$), although it decreases slightly after the 18th cycle in the case of SC-3. Hence, cycle performance is crucially affected by the SEI formed in the early stage (before 0.3 V), rather than by that in the later stage. This is why the cycling results of

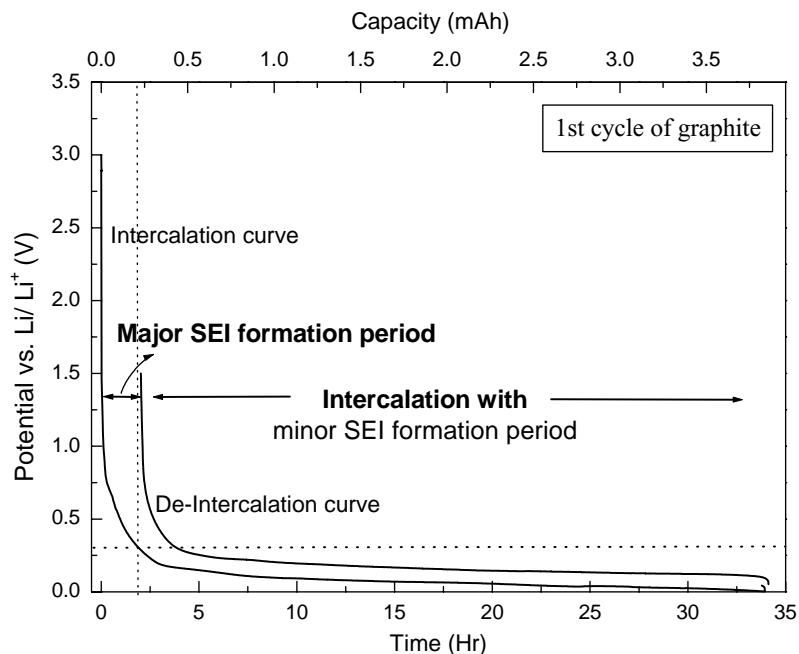


Fig. 3. Illustration of first charge–discharge cycle of graphite.

Table 1
Comparison of formation time for LiCoO₂|C full-cells cycled between 2.8 V and different cut-off voltages with 0.1 mA

No.	Cut-off voltage (V)	Formation time (h)		
		Charge step	Discharge step	Total time
SFC-0	4.2	39.48	32.71	72.19
SFC-1	3.8	16.17	12.97	29.14
SFC-2	3.7	6.53	3.97	10.50
SFC-3	3.6	3.59	1.56	5.15

SC-2 and SC-3 are as good as those of SC-1. Consequently, an improved formation method is proposed by narrowing the potential range and, thereby, results in a much reduced process time.

Similar tests have been made on LiCoO₂|C full-cells to see the effect of potential on SEI formation. The formation times for cells cycled to various cut-off voltages are given in Table 1. SFC-1 represents the normal process with a formation potential from 2.8 to 4.2 V. In order to determine the optimum potential range, the cells have been cycled at a constant current of 0.1 mA ($\sim C/30$) to different end voltages. The results in Table 1 show that the charge step is longer than the discharge step by about 3 h for most samples, except SFC-0 and SFC-3. This 3 h difference is due mainly to formation on the carbon electrode. By contrast, SFC-0 takes almost 7 h to complete the SEI formation process. As mentioned before, most of the time and energy are consumed in the plateau region for lithium intercalation into carbon.

The difference between charge and discharge for SFC-3 is about 2 h, and it is suspected that this process produces an incomplete SEI layer. Accordingly, cycle performance and impedance measurements have been carried out to clarify these phenomena.

The cycling performance in this study includes discharge and charge capacities and capacity efficiency (discharge-capacity/charge-capacity). The capacity efficiency of all sample is close to 100%, except for the first cycle. SFC-0, SFC-1 and SFC-2 exhibit a very similar cycling performance in spite of having different voltage-regulations. This means that the formation of the SEI is mostly completed before 3.7 V, so that the change of cut-off voltage does not significantly affect the cycling performance. As for the first cycle of SFC-3, the fairly low capacity efficiency (85%) indicates that SEI cannot form completely when the formation cycle is between 2.8 and 3.6 V. This is consistent with the insufficient time difference between charge and discharge of SFC-3 for SEI formation, see Table 1. A closer look at the results shows that there are some slight differences of discharge and charge capacity between the samples. It is considered that this is due to slight differences in the amount of active materials in various samples due to the manual preparation (Fig. 4).

Variations in the impedance of SFC-0, SFC-2 and SFC-3 at 3.2 V after the formation process are shown in Fig. 5. The spectrum of SFC-3 has a smaller semicircle than that of SFC-2 or SFC-0, which again suggests that SEI cannot be completely formed by the SFC-3 procedure (cut-off voltage at 3.6 V). On the other hand, SFC-2 has similar

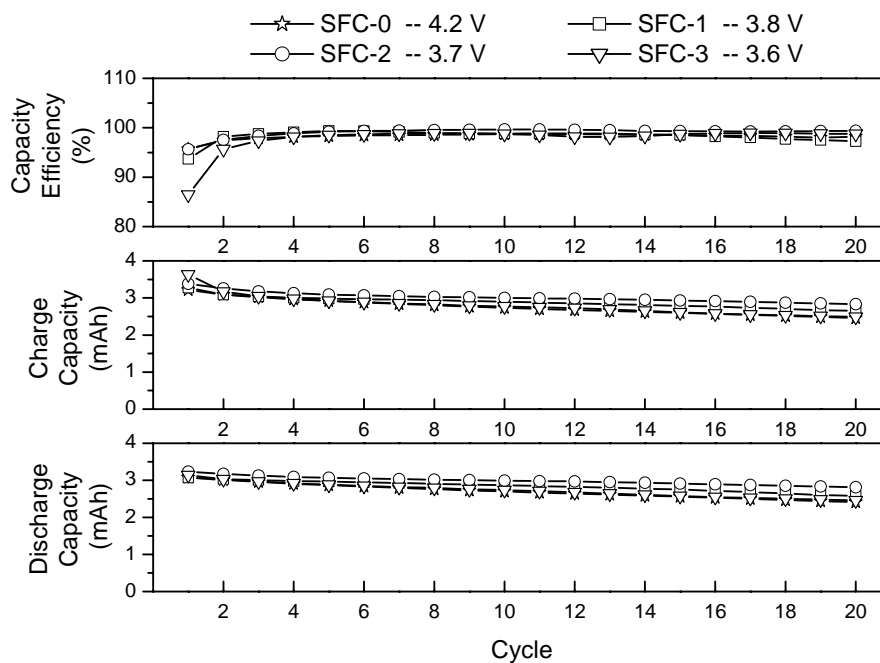


Fig. 4. Cycle performance of LiCoO₂|MCMB cells after various formation conditions: formation with 0.1 mA in potential range of (☆) SFC-0, 2.8–4.2 V; (□) SFC-1, 2.8–3.8 V; (○) SFC-2, 2.8–3.7 V; (▽) SFC-3, 2.7–3.6 V. Cycling current is 0.6 mA. Electrolyte is 1 M LiPF₆/EC + PC + DEC (3:2:5).

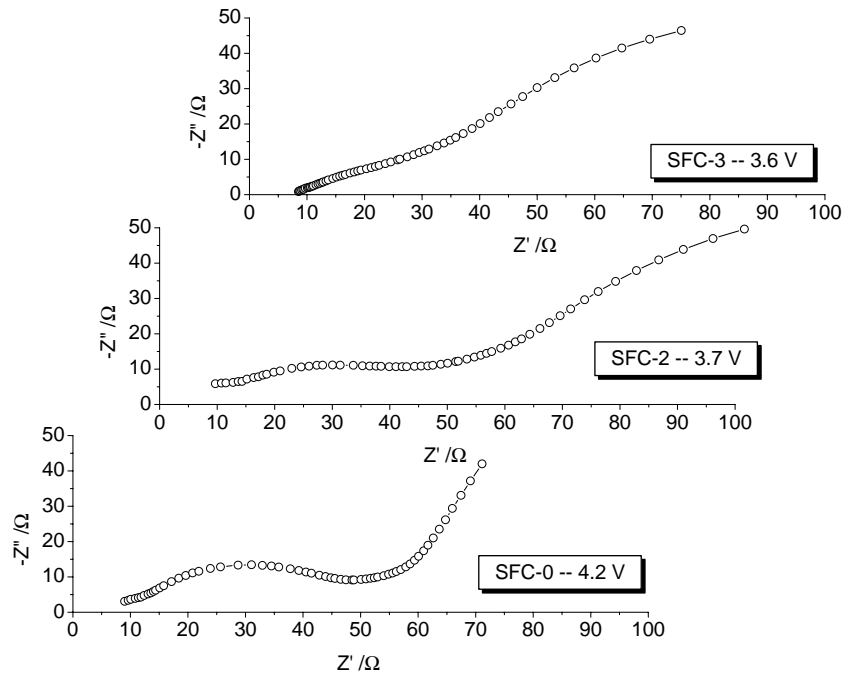


Fig. 5. Nyquist plot of LiCoO₂/MCMB coin cells at 3.2 V after various formation conditions: charge with 0.1 mA to cut-off potential 4.2 V for SFC-0; 3.7 V for SFC-2; and 3.6 V for SFC-3, and then discharge to 3.2 V with 0.1 mA. Impedance spectra are measured at their cut-off potentials. Electrolyte is 1 M LiPF₆/EC + PC + DEC (3:2:5).

SEI impedance as that indicated in the semicircle part of SFC-0 [8]. This means, for SFC-2, that the formation time is shortened to only 10.5 h with a cut-off voltage at 3.7 V, and the desired SEI has been produced to meet performance requirements. Thus, SFC-2 is attractive for industrial applications.

The final criterion is whether the cells made by the proposed formation method are capable of good cycling according to industrial standards. Hence, extended tests on commercially available 18650-type cells were run, with the relevant parameters listed in Table 2. It is found

Table 2

Comparison of formation time for 18650-type full-cells cycled between 2.8 V and different cut-off voltages at *C*/5 rate, except SLC-4 which is cycled at *C*/30 rate

No.	Cut-off voltage	Formation time (h)			
		Charge time		Discharge time	Total time
		CC ^a	CV ^b		
SLC-0	4.15	5.51	2.64	5.02	13.17
SLC-1	3.8	1.21	6.29	1.68	9.18
SLC-2	3.7	0.69	3.02	0.42	4.13
SLC-3	3.6	0.52	1.31	0.23	2.06
SLC-4	3.7 ^c	5.02 ^c	–	2.52 ^c	7.54

^a Constant current.

^b Constant voltage.

^c Current rate is *C*/30.

that formation with a *C*/30 current and a 3.7 V cut-off voltage (SFC-2) are the optimum conditions. Hence, the SLC-4 condition was chosen to duplicate that of SFC-2. The charge step of other formation processes complies with the industrial standard, i.e., constant current followed by constant voltage charging. Hence, SLC-2 follows this pattern with 3.7 V as the cut-off voltage. The other two processes, namely, SLC-1 and SLC-3, have higher and lower cut-off voltages, respectively, and SLC-0 is the typical commercial condition for comparison. The data in Table 2 show that the formation time of SLC-2 and SLC-4 is much reduced, i.e., to below one-third (4.13 h) and one half (7.54 h) of that for SLC-0 (13.17 h), respectively.

The capacity retention of these cells during 200 cycles is shown in Fig. 6. The SLC-2 and SLC-4 samples have exactly the same cycle performance profile as the SLC-0 sample. The profile of SLC-1 decays slightly faster than those of SLC-0, SLC-2 or SLC-4. The capacity retention of SLC-3, however, quickly reduces to less than 80% after 100 cycles. The poor cycle performance of SLC-3 probably results from insufficient SEI layer formation because the cut-off voltage is as low as 3.6 V. Based on the results so far obtained, 3.7 V appears to be the best cut-off voltage, whatever the formation process, when cycled at low current (SLC-4) or high current followed by a constant-voltage step (SLC-2). This is because their cycle performances are as good as that given by the conventional formation process (SLC-0).

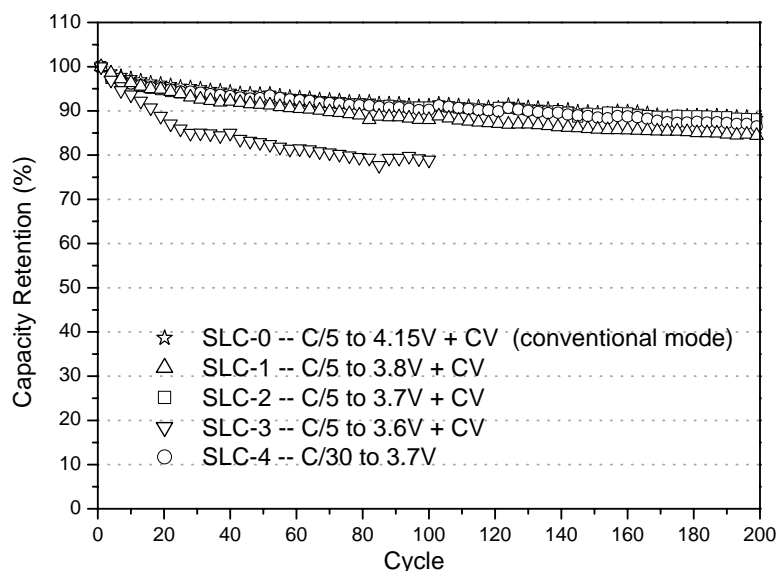


Fig. 6. Cycle performance of 18650-type cells after various formation conditions: constant current $C/5$ to: (\star) SLC-0, 4.15 V; (\triangle) SLC-1, 3.8 V; (\square) SLC-2, 3.7 V; (∇) SFC-3, 3.6 V followed by holding the potential, and then discharging to 2.8 V with $C/5$; (\circ) SLC-4, formation with $C/30$ in potential range of 2.8–3.7 V.

4. Conclusions

The formation process consumes considerable time and energy because it takes an excessively long time for lithium intercalation after the growth of the SEI, which is the major purpose for formation. Accordingly, a new formation procedure is proposed, in which the intercalation period is eliminated and the formation time can be markedly reduced. The results indicate that this new formation method is suitable for LiCoO_2/C cells, including large 18650 commercial cells. The novel feature of this method is to raise the cut-off voltage of the carbon electrode so that the formation process can be completed in a period that is less than one-half of that for the conventional process, without affecting the cycle efficiency or cycle-life of batteries. It is found that a cut-off voltage of 3.7 V is the optimum value for a LiCoO_2/C cell.

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