Short Communication

Effect of cathode/anode mass ratio in lithium-ion secondary cells

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Abstract

The effect of the cathode/anode mass ratio on the performance of lithium-ion secondary cells has been investigated systematically. The optimal ratio must be larger than that of the theoretical ratio and must make sure that no deposit of lithium metal appears on the surface of the anode.

Keywords: Lithium-ion cells; Cathodes; Anodes; Mass ratio

1. Introduction

The lithium-ion secondary battery (or so-called 'rocking chair' or 'swing' battery) is receiving increasing attention recent years because of its potential market. It has higher energy density compared with nickel/cadmium and nickel/metal hydride systems, and longer cycle life and greater safety than lithium batteries [1–7]. The Sony Company has used it in video cameras.

The lithium-ion battery employs carbon material as the anode and a lithiated intercalation compound as the cathode. The latter provides lithium ions. A lack of lithium ions will result in a small capacity while a surplus may cause the deposition of lithium metal on the anode. Therefore, finding an appropriate mass ratio of cathode to anode is very important in the design of the battery. This ratio can be calculated from the theoretical reaction equation of the battery but the value will be very different from that realized in practice due to the formation of a passivation film on the anode during the initial charging, which requires some of the lithium ions. Many authors have reported this phenomenon for lithium–carbon cells and it occurs in association with decomposition of the electrolyte solution [8,9]. Since the passivation reaction depends on the type of carbon and electrolyte, the required amount of lithium ions can only be determined by experiment. Taking into consideration the decomposition of the electrolyte used, the cathode/anode mass ratio has been

determined and reasons are given why an appropriate ratio must be taken.

2. Experimental

Treated graphite was used as the anode, and $LiNiO_2$ doped with cobalt as the cathode [10,11]. The electrolyte, 1 M $LiPF_6$ in ethylene carbonate (EC)–diethyl carbonate (DEC), was provided by Mitsubishi Petro-Chemical Ltd. The separator was Celgard 2400 from Hoechst. The cell holder was similar to that described in earlier work [12]. There was, however, a hole mid-way along the holder from which passed a lithium tip, to a place between the separator and electrodes that acted as a reference electrode. Three electrode cells with different cathode/anode mass ratios were constructed in a glove box filled with argon. Each cell was transferred to a glass bottle that was sealed with a lid that held the connectors for the three electrodes. The cells were charged galvanostatically to a certain cathode potential and then a voltage of 4.20 V was applied for 24 h. The cells were discharged at constant current. Some of the cells were cycled under this programme at room temperature.

3. Results and discussion

3.1. Theoretical mass ratio

In the experiments reported here, the electrode reaction was taken to be:

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$$6C + LiNiO_2 = Li_{0.6}C_6 + Li_{0.4}NiO_2 \qquad (1)$$
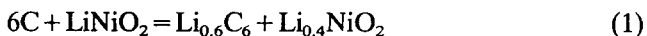
According to this equation, the anode/cathode mass ratio should be 1.35 for appropriate lithiation of the carbon material. Due to decomposition of the electrolyte, however, the actual mass ratio must be larger than the theoretical value.

3.2. Lack of lithium ions

For a mass ratio (r) of 1.23, a lack of lithium ions occurred in the cell. The potential–capacity relationship is given in Fig. 1. The anode potential is maintained at a high level at the end of charging and discharging. This means that the cell can only provide a small capacity. Given the poor performance, the cell was not investigated further. This result showed that a ratio that yields insufficient lithium ions is not desirable for constructing a practical lithium-ion battery.

3.3. Surplus of lithium ions

A cell with $r = 4.20$ provides a surplus of lithium ions. The potential–capacity dependence is given in Fig. 2. The anode potential is small and negative during charging. Thus, although the cell can give greater capacity, the negative potential may cause the deposition of lithium metal on the anode.

Fig. 3 gives both the cathode and the anode potential at the end of charging as a function of cycle number for a cell with $r = 4.20$. The anode potential increases with cycling. This indicates that the reversibility of the lithium deposited on the anode is lowered. In other
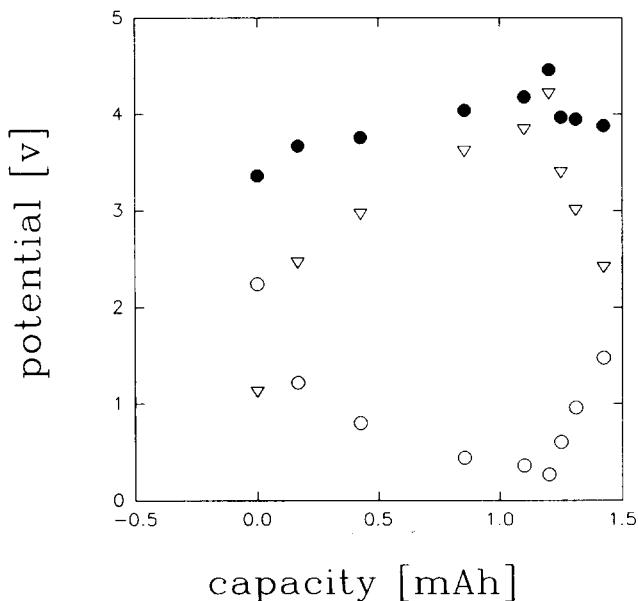

Fig. 2. Potential vs. capacity for cell with $r = 4.20$; charging at 0.2 mA/cm² and discharging at 0.3 mA/cm²: (O) anode potential; (●) cathode potential, and (▽) cell voltage.

Fig. 3. Cathode and anode potential at end of charging for cell with $r = 4.20$. Cutoff voltage from 4.2 to 3.0 V; charging at 0.2 mA/cm² and discharging at 0.3 mA/cm²: (●) anode potential, and (O) cathode potential.

words, the amount of lithium ions shuttling between the cathode and the anode is decreased. This, of course, results in a decay in cell capacity (Fig. 4). The relation between anode potential and cycle number at the end of discharge (3.0 V) is given in Fig. 5. For a cell with $r = 4.20$, the small value of the anode potential on the initial cycle shows that the lithium deposited on the anode provides capacity so that the cell has a higher capacity compared with one with $r = 2.73$ (Fig. 4). After the fifth cycle, the anode potential tends to increase

Fig. 1. Potential vs. capacity for cell with $r = 1.23$; charging and discharging at 0.2 mA/cm²: (O) anode potential; (●) cathode potential, and (▽) cell voltage.

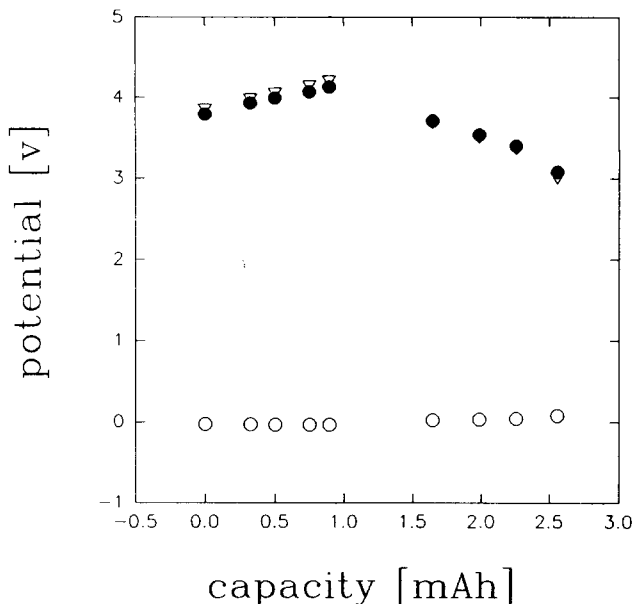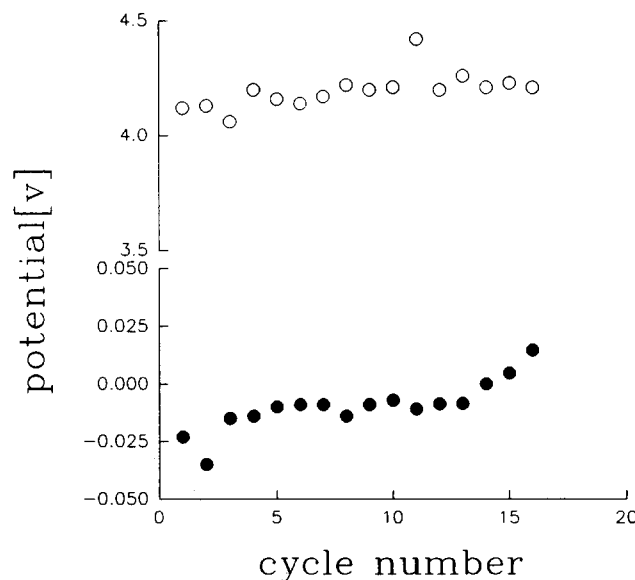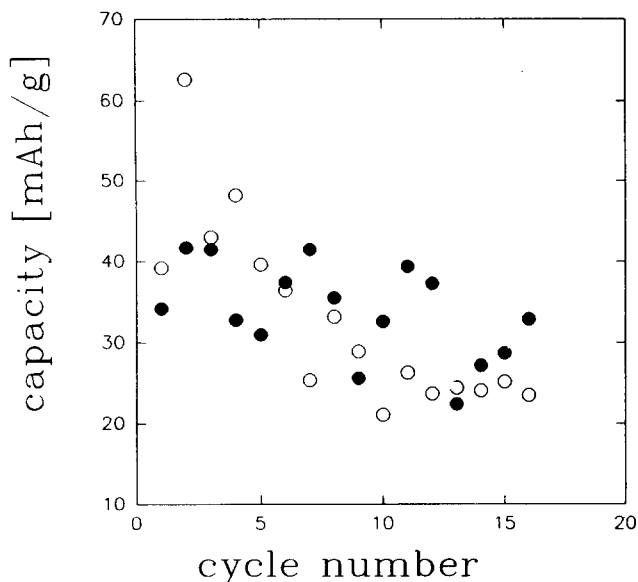Fig. 4. Discharge capacity of cells with (O) r=4.20 and (●) r=2.73. Cycle conditions as given in Figs. 2, 3 and 6.

Fig. 6. Potential vs. capacity for cell with r=2.73; charging at 0.3 mA/cm² and discharging at 0.4 mA/cm²: (O) anode potential; (●) cathode potential, and (∇) cell voltage.
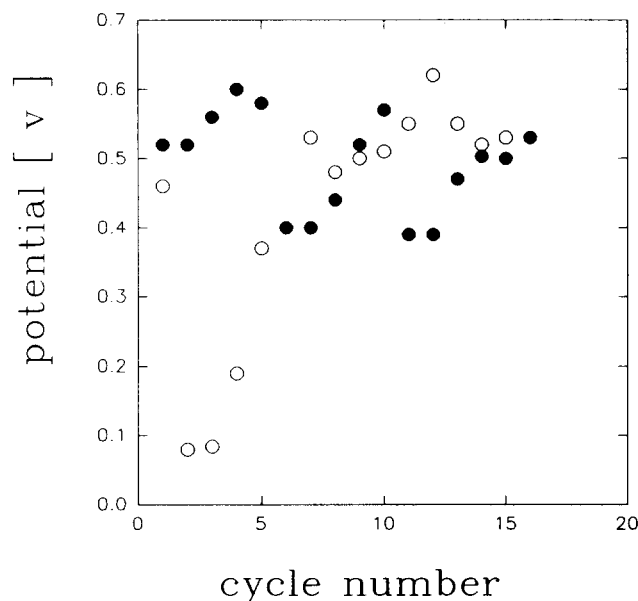

Fig. 5. Anode potential at end of discharge for cells with (O) r=4.20, and (●) r=2.73.

(Fig. 5). This is also an indicator of a lower reversibility for the lithium ions.

3.4. Appropriate lithium ions

A cell with r=2.73 provides the appropriate amount of lithium ions. The relation between potential and capacity is presented in Fig. 6. The apparent characteristics of the anode potential are very small but positive. This means that the cell can provide a larger capacity than the others discussed above. The anode potential at the end of charging varied around 0 V
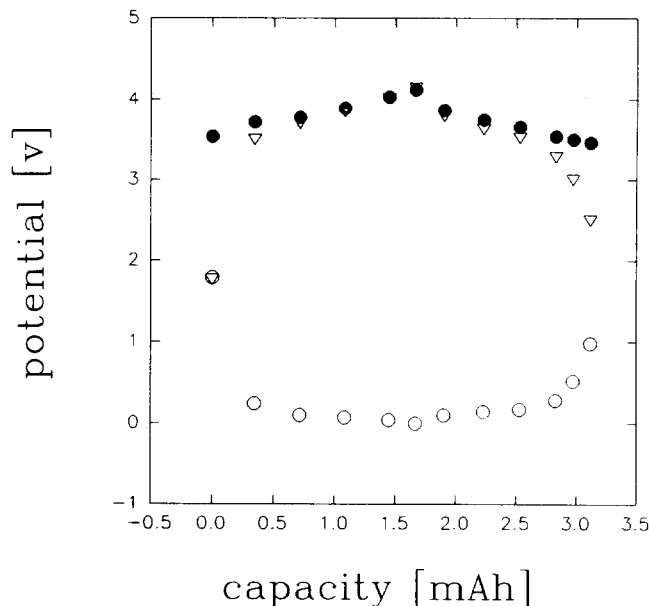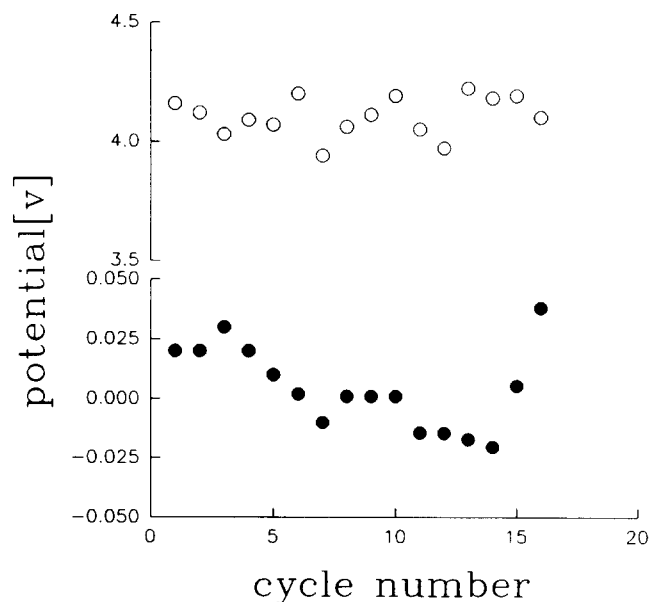

Fig. 7. Cathode and anode potential at end of charging for cell with r=2.73. Cutoff voltage from 4.20 to 3.0 V; charging at 0.3 mA/cm² and discharging at 0.4 mA/cm²: (●) anode potential, and (O) cathode potential.

with cycling (Fig. 7) while that at the end of discharging was around 0.5 V (Fig. 5). These results indicate a better cell cycle life. The capacity was around 35 mAh/g (Fig. 4). The fluctuation of capacity with cycle number corresponded with that observed for the electrode potential. The reason for this requires further study.

4. Conclusions

Finding an optimal cathode/anode mass ratio for lithium-ion secondary batteries is very important for obtaining good performance. An appropriate mass ratio is able to provide higher capacity and better cycle life. The optimum mass ratio can be determined by experiment through using a three-electrode cell. In this study, the value was found to be 2.73.

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