

Factors that affect cycle-life and possible degradation mechanisms of a Li-ion cell based on LiCoO_2

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Abstract

An extensive test has been conducted on a lithium-ion (Li-ion) cell under a variety of cycling conditions in order to evaluate factors that affect its cycle-life. The study is performed on a 900-mAh wound prismatic cell with contains a LiCoO_2 positive electrode (cathode) and a synthetic graphite negative electrode (anode). Cycle-life is greatly influenced by the charge conditions, but is relatively insensitive to the discharge conditions. High charge cut-off voltages and a long float-charge period at 4.2 V or above have the most severe effects on cycle-life. Another damaging condition is high charge rates above the 1C rate, but reduction in the depth-of-discharge does not improve the cycle-life unlike the situation with other rechargeable batteries such as alkaline and lead–acid batteries. The dependence of the degradation rate on the charge voltage and the period of high charge voltage suggests that an electrochemical oxidation may be the cause.

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1. Introduction

Lithium-ion (Li-ion) batteries are becoming prime candidates for energy-storage systems of many electronic devices such as cellular phones, notebook computers, personal digital assistants (PDA), and camcorders. This is because of the high energy density and the high specific energy of the batteries that are not yet matched by other commercially available rechargeable batteries [1]. Naturally, understanding the service life capability of the batteries, i.e. the maximum exploitation and possible improvement of life, are a major interest of battery users as well as researchers and developers.

The objective of the present work is to elucidate the factors and mechanisms that affect the cycle-life of a Li-ion cell which contains LiCoO_2 -based material. This is the most popular positive electrode (cathode) material in commercially available cells. There are numerous possible factors, e.g. operation conditions such as temperature and cycle regimes, types of electrode active material, supporting structural material, cell design variables, and fabrication processes. $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ and LiMn_2O_4 are also used for the cathode material, but such cells command in a relatively small portion of the battery market. Despite significant advantages in cost, environ-

mental acceptability and safety, the main deterrent to using LiMn_2O_4 in commercial cells is a relatively short storage life at elevated temperature, e.g. near 55 °C [2,3]. The negative electrode (anode) is mostly made of graphitic material. The electrolyte is mostly a LiPF_6 solution in a mixed organic carbonate solvent which usually includes a combination of ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), diethyl carbonate (DEC), or ethylmethyl carbonate (EMC) with an optional additive.

1.1. Previous studies on storage life

There have been a considerable number of studies on the degradation rate of cell capacity [4–6] and power capability [7] of Li-ion cells during storage at various state-of-charge (SoC) or cell voltage in order to estimate the calendar life of the cell and understand the degradation mechanisms. Lim et al. [4] reported that a Li-ion cell (LiCoO_2 /petroleum coke; Sony 1994 vintage) stored at 30–60 °C at a constant voltage of 2.5, 3.7 or 4.2 V showed a linear decrease in capacity with storage time. The rate of capacity fade was indistinguishable between storage voltages of 2.5–3.7 V, whereas, the rate at 4.2 V was distinctively higher. The rate data at 3.7 V at various temperatures fit well to an Arrhenius equation:

$$k = A \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

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where k is the rate of degradation, E_a the activation energy of the reaction, R the gas constant; and A is a constant. The value of E_a from published data is approximately 11.7 kcal/(mol °C). Ratnakumar et al. [6] studied capacity degradation during storage at various temperatures (25, 40 and 55 °C) and SoC (50, 75, 100%) for Li-ion cells which contained a $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ cathode and a LiPF_6 electrolyte in various organic carbonate-based solvents. Data for the overall capacity degradation rate also fit the Arrhenius equation with an estimated slope of approximately 7.3 kcal/(mol °C).

Broussely et al. [5] also examined capacity degradation during storage at various temperatures (15–60 °C) and constant float voltages (3.6–4 V) for Li-ion cells which used LiCoO_2 , $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ or LiNiO_2 for the cathode material, electrolytes including an optional electrolyte additive of vinylene carbonate (VC), and a graphite-blend anode. Cells with LiCoO_2 or $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ cathodes show no dependence of the degradation rate on float voltages below 3.9 V, but a marginally increased rate at 4 V. Although the difference in capacity decreases in these cells is barely noticeable between 3.8 and 4.0 V, the amount of CO_2 gas evolution at 4.0 V is substantially larger than that at 3.8 V after storage for over 6 months at 60 °C. In contrast to these cells, those containing LiNiO_2 experience increased degradation rates as the float voltage is increased from 3.6 to 4 V. The cause of the voltage-dependent capacity degradation of LiNiO_2 cells is attributed to the growth of a thick passivation layer as a result of solvent oxidation at the cathode-active-material. The cause of CO_2 gas evolution as discussed previously has been attributed to this solvent oxidation. The cause of the voltage-independent capacity degradation of cells containing LiCoO_2 or $\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ is attributed to the growth of a thick passivation layer on the anode-active-material. It was also reported [5] that addition of VC in the electrolyte of a Li-ion cell ($\text{LiNi}_x\text{Co}_y\text{Al}_z\text{O}_2$ -cathode) substantially improves the storage life at 3.8 V. This observation is consistent with the suggestion that the voltage-independent capacity degradation below 3.9 V is due to the build up of a solid-state electrolyte interfacial (SEI) layer [8,9] on the carbon active material, since it has been suggested [10] that VC forms a good SEI layer.

Bloom et al. [7] studied the degradation of power capability of a Li-ion cell (18650-type cell with a $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode, a 1 M LiPF_6 EC-DEC electrolyte, and a graphite blend anode) during passive storage at various temperatures (40–70 °C) and SoC (40, 60, 80%). The SoC of 40, 60 and 80% corresponded to constant float voltages of 3.6, 3.75 and 3.92 V, respectively. Data for the power fade or increase of area specific impedance (ASI) of the cell fit well the following equation:

$$Q = A' \exp\left(-\frac{E_a}{RT}\right) t^q \quad (2)$$

where Q is the power or ASI, E_a the activation energy, A' and q are constants. The value of q for the storage test is approximately 0.5. The $t^{1/2}$ kinetics of the increase in

ASI have been suggested to be an indication of the growth of a passivation layer, probably an SEI [8,9]. The power fade of the cell containing the $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ material on storage increases (therefore, calendar life decreased) as the SoC is increased stepwise from 40 to 80% similar to the trend of the LiNiO_2 -cathode cell discussed earlier. The power fade and the impedance rise on storage has been attributed to the growth of a passivation layer with increasing charge-transfer resistance at the surface of the cathode-active-material [11,12]. The values of the activation energy of these cells containing $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ decreases as the storage voltage (or SoC) increases.

1.2. Previous studies on cycle-life

Bloom et al. [7] studied degradation on cycling of the power capability of a Li-ion cell ($\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ cathode, 1 M LiPF_6 EC-DEC electrolyte, graphite blend anode). The cycle regime was a typical one for a hybrid electric vehicle (HEV) [13]. It involved fast cycling at a very shallow depth-of-discharge (DoD) ($\Delta\text{SoC} = 3\%$ or 6%) at various temperatures (40–70 °C) and SoC of 40, 60 or 80%. The power fade or ASI data also fit well to Eq. (2). The value of q , however, depended strongly on the value of ΔSoC while its dependence on SoC (between 60 and 80%) is relatively small. For example, the value of q for ASI varied between 0.11 and 0.15 for a ΔSoC of 6%, while it was close to 0.5 for a ΔSoC of 3%. This indicates that the degradation mechanism for cycling at a ΔSoC of 6% may be quite different from that of the storage test. It has been suggested [11,12,14] that the cause of the power fade is predominantly the build up of a resistive layer on the cathode-active material.

Takei et al. [15] studied the capacity degradation of a Li-ion cell under a specially designed cycling regime which involved approximately 25% DoD and covered various SoCs (or cell voltages) to estimate effects of SoC on cycle-life. The test cell was a commercially available 18,650-size unit which contained LiCoO_2 and hard carbon. The results showed that the rate of capacity degradation was independent of either the SoC or the cell voltage when the charge voltage was 3.92 V or below or the SoC was 50% or lower, whereas the rate increased rapidly as the voltage increased over this voltage. This behaviour of the voltage effect is similar to that of the storage test of a LiCoO_2 cell discussed earlier [5]. The findings indicate that the degradation reaction of the cell may be controlled by two different mechanisms at voltages above and below 3.92 V, respectively. It has been suggested [5] that the voltage-independent reaction below 3.92 V is surface passivation (SEI) on the carbonaceous anode material, whereas the voltage-dependent reaction above 3.92 V is oxidation of the electrolyte to accumulate a resistive surface layer on the cathode-active-material. The same authors also studied the effect on cycle-life of alternate constant voltage (CV) float charging at 4.2 V after constant current (CC) charging at from C/10 to C/8 rates to 4.2 V using similar LiCoO_2 cells to those

described above. The performance in the cycling regime of CC and CV was 1700 cycles, whereas that in the regime of CC only was 2400 cycles. This suggests that the presence of the CV charging period accelerates the degradation of the cell. Without describing details of either the experimental conditions or the data analyses process, the authors concluded that charging at a high rate of 1C accelerated the degradation, while at low charge rates $<0.5C$ the degradation was independent of the charge rate. Finally, it was found that the effect of discharge rate on the degradation rate was small or negligible for from $C/10$ to 1C rates and DoDs between 70 and 100%. Majima et al. [16] reported the effect of charge–discharge current density ($0.4\text{--}1.6\text{ mA cm}^{-2}$) on the cycle-life of a laboratory $\text{LiCoO}_2/\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ test cell (in which the cycle-life is presumably limited by the LiCoO_2 electrode). The cycle-life reduced exponentially as the current density was increased (roughly by a factor of 8 when the current density was increased by 0.5 mA cm^{-2}).

Rubino et al. [17] studied the cycling performance of an AA-size cylindrical cell ($\text{LiCoO}_2/1\text{ M LiPF}_6\text{ EC-DMC}(3:7)/\text{MCMB2528}$) and a prismatic cell, both made of identical components except for the mechanical configuration. After 300 cycles between 4.1 and 2.75 V, the cylindrical and prismatic cells experienced a capacity fade of 16 and 24%, respectively. The capacity fade of the cylindrical cell has been attributed to a decay in the performance of the cathode. The capacity fade of the anode is much smaller than that of the cathode. By contrast, the capacity fade of the prismatic cell is dominated by the anode which swells with cycling. Much greater swelling of the anode is observed in the prismatic cell ($>15\%$) than in the cylindrical cell (approximately 7%). This effect was attributed to low stack compression in the prismatic cell. The swelling caused graphite particles to separate from each other and thus deteriorated the particle-to-particle electrical contacts in the anode. This interpretation has been supported by the fact that the capacity of the anode removed from the cycled cell improved significantly after re-compression of the electrode. Using impedance spectroscopy, Zhang et al. [18] studied the degradation of a Sony 18650-type Li-ion cell ($\text{LiCoO}_2/\text{LiPF}_6\text{ PC-DMC-EMC/coke}$), as well as individual electrodes from the cell, against a Li reference electrode before and after 800 cycles. The cell capacity dropped to 840 mAh from an initial value of 1250 mAh after 800 cycles between 4.2 and 2.5 V at 0.8C rate. The electrolyte resistance remained unchanged, but the impedance of the electrodes increased substantially after cycling, predominantly in the cathode. It was concluded that the decrease in cell capacity with cycling might be due to the growth of a resistive surface layer on the active material, predominantly in the cathode, which causes voltage drop and a slowdown in the electrode reaction rate. The conclusion is also consistent with the findings of other studies [14,17] that suggested that the deterioration in the capacity and the rate capability of a cylindrical Li-ion cell was due to the cathode rather than the anode.

With respect to the factors that influence the cycle-life of a Li-ion battery, the influence of temperature is well established, as discussed previously. On the other hand, information available on the effects of cycling parameters such as charge–discharge voltages and rates and DoD appears to be insufficient to define such effects unequivocally. This is because the information is based on either an accelerated or a segmented partial cycling. Therefore, a further studies are required to confirm the effects. In the present paper, we report the effects of cycling parameters on a cycle-life of 500 cycles for a 900-mAh Li-ion cell.

2. Experimental

Test were conducted on a commercial design of wound prismatic Li-ion cell with a nominal capacity of 900 mAh. The cathode and anode were made of LiCoO_2 -based material and synthetic graphite coated on Al and Cu foil substrates, respectively, using a polyvinylidene fluoride (PVDF) binder. The electrolyte was a LiPF_6 solution in an organic carbonate-based solvent.

All cycling experiments were performed at room temperature, e.g. $\sim 25^\circ\text{C}$. Test cells were cycled by charging at a given constant current to the charge cut-off voltage, followed by an optional additional float charging at the cut-off voltage and then discharging at a given constant current to the discharge cut-off voltage. The charge and discharge cut-off voltages were 4.2 and 2.75 V, respectively, for the standard conditions. Float charging was either terminated after a total charging time of 2.5 h or when the float charging current reduced to a current cut-off value of 90 mA or 20 mA. All cycling tests were carried out with an open-circuit period of 10 min before and after discharging. Experimental data points are reported as average values for three–five test cells.

3. Results and discussion

The effects of various cycling regimes on the cycle-life of the 900-mAh prismatic Li-ion cells have been examined. The effects of a CV float charging period at various voltages of 4.2–4.35 V after a CC charging at the 1C rate for total of 2.5 h are shown in Fig. 1. The cell capacity increases slightly but its degradation accelerates rapidly as the float-charge voltage is increased above 4.2 V. The cycle-life performance of similar cells at various charge cut-off conditions which involve various periods for float charging at 4.2 V is shown in Fig. 2. The rate of capacity degradation accelerates as the period is increased, which indicates that an electrochemical reaction may be causing the degradation. The cycle-life performance is shown in Fig. 3 for charging at various charge rates that range from 1 to 1.4C to a constant cut-off voltage of 4.2 V, followed by float charging at this voltage for total period of 2.5 h. The cycle-life is reduced

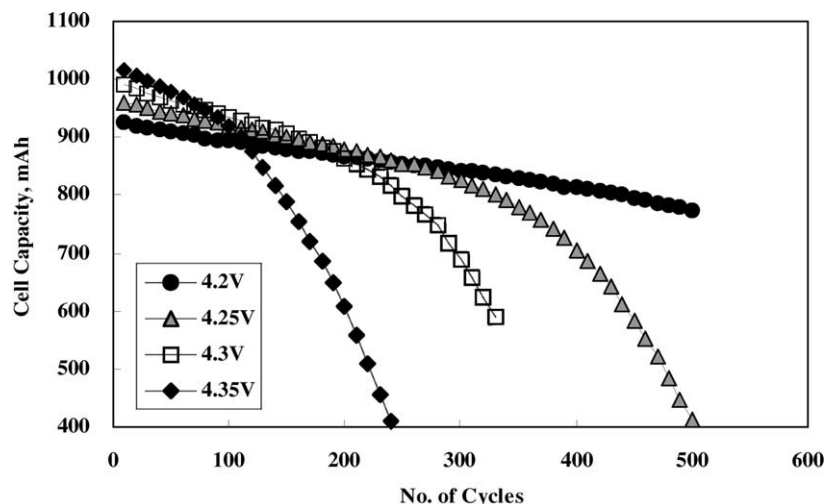


Fig. 1. Effect of CV charge voltage on cycle performance. Test cells charged at constant current at 1C rate to cut-off voltage followed by CV float charging at this voltage for 2.5 h and then discharged to 2.75 V at 1C rate.

substantially as the rate increase from 1 to 1.4C. The period for CV float charge at 4.2 V (100, 110 and 117 min for 1, 1.2 and 1.4C rates, respectively) also increases slightly. The anticipated effect of these relatively small increases in the period should be negligible in view of the observation that there is only a relatively small change in the degradation rate with a large change in the time period from 53 to 100 min, as shown in Fig. 2. Overall, the accelerated degradation rate as the charge rate is increased is due mainly to the increased charge rate itself rather than to the small increase in the time period of the CV charge.

The cycle-life performance of the cells at various discharge rates between 1 and 2C is shown in Fig. 4. The decrease in cell capacity with cycling accelerates as the discharge rate is increased. It is not clear, however, whether the greater decrease in capacity at high rate is due to genuine capacity degradation or to the effect of early cut-off (2.75 V)

of discharge by an increased iR drop as the current is increased. Since the capacity values for the standard discharge regime, e.g. 1C rate, are not available for these cells, an additional study that includes periodic monitoring of the change in capacity with cycling for the standard discharge regime may be needed to clarify the cause of capacity degradation at high rate. To estimate the DoD effect on cycle performance, change in capacity for a regime in which the discharge was cut-off at various voltages that ranged from 2.75 to 3.55 V after fully charging the cell at the 1C rate are shown in Fig. 5. No noticeable dependence of the rate of capacity decrease with cycling on the DoD is observed within 500 cycles.

The present results show that one of the most damaging conditions of cycling a Li-ion cell which uses LiCoO_2 as the cathode material is a high charge cut-off voltage (4.2 V or above) (Fig. 1) as well as float charging at the high voltage

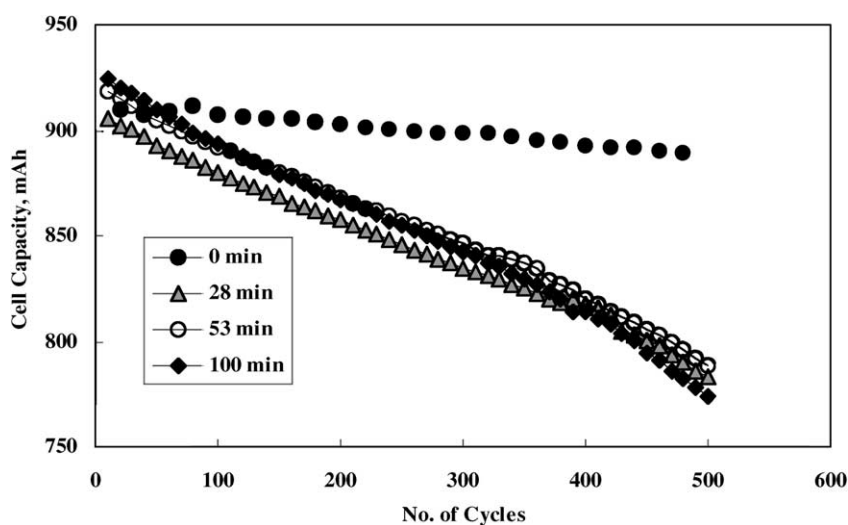


Fig. 2. Effect of CV charge period at 4.2 V on cycle performance. Test cells charged at constant current at 1C rate to 4.2 V followed by the CV float charging at this voltage for various periods and then discharged to 2.75 V at 1C rate.

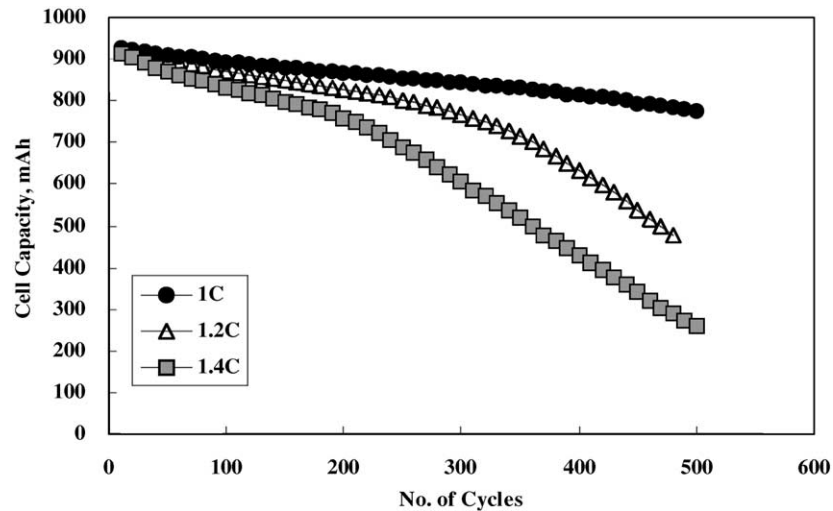


Fig. 3. Effect of charge rate on cycle performance. Test cells charged at constant current at various rates to 4.2 V followed by CV float charging at 4.2 V for 2.5 h and then discharged to 2.75 V at 1C rate. Periods of CV float charging for 1, 1.2 and 1.4C rates are 100, 110 and 117 min, respectively.

(Fig. 2). The present results for a cell of typical commercial design agree well with an earlier accelerated test result [15] that showed that charging at high voltages >3.92 V accelerated cell degradation. Our results clearly suggest that an extended period of float charging at high voltage is an especially dominant damaging condition, and becomes increasingly more damaging as the voltage is increased. This behaviour is probably due to an oxidation of the electrolyte at the surface of the charged cathode material ($\text{Li}_{1-x}\text{CoO}_2$ where x is approximately 0.5) at voltages >3.9 V to build up a resistive surface layer [5,11,12,16] as a predominant, but not an exclusive, mechanism of cell degradation as discussed later. Such an oxidation might occur at lower voltages (<3.9 V) but without exerting major effect on the life of the cell. In the cells containing $\text{LiNi}_x\text{Co}_y\text{O}_2$ [7,11,12] and $\text{LiNi}_{1-x}\text{Co}_x\text{O}_2$ [5], however, such an

oxidation may become the dominant cause on the life even at voltages below 3.9 V. There is no indication of degradation of cathode ($\text{LiNi}_{0.81}\text{Co}_{0.09}\text{O}_2$) or anode material itself after a storage test in the charged state (presumably at 4 V or below) at 60°C for a year [5]. The anode material recovered from the storage-tested cell shows identical performance characteristics, while the corresponding cathode material has an identical X-ray structure to the corresponding virgin material. These results appear to be consistent with the suggested mechanisms of a resistive interface build-up as discussed earlier, rather than the degradation of the bulk material at a mild charge voltage, perhaps, 4.2 V or below. At higher voltages (e.g. 4.35 V), however, degradation of LiCoO_2 material itself may also occur. A wide range of physical damage on the surface of a LiCoO_2 particle after cycling between the cut-off voltages of 2.5 and 4.35 V for 50 cycles

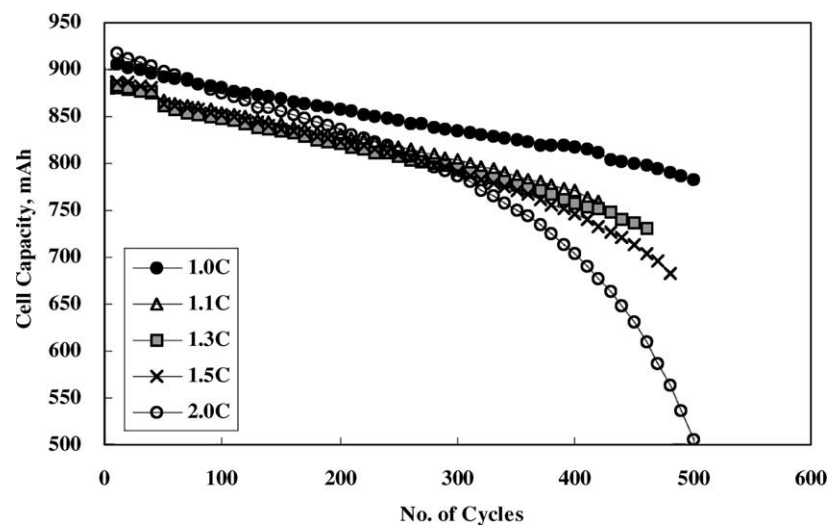


Fig. 4. Effect of discharge rate on cycle performance. Test cells charged at constant current at 1C rate to 4.2 V followed by CV float charging at 4.2 V to 90 mA current cut-off and then discharged at various specified rates to 2.75 V.

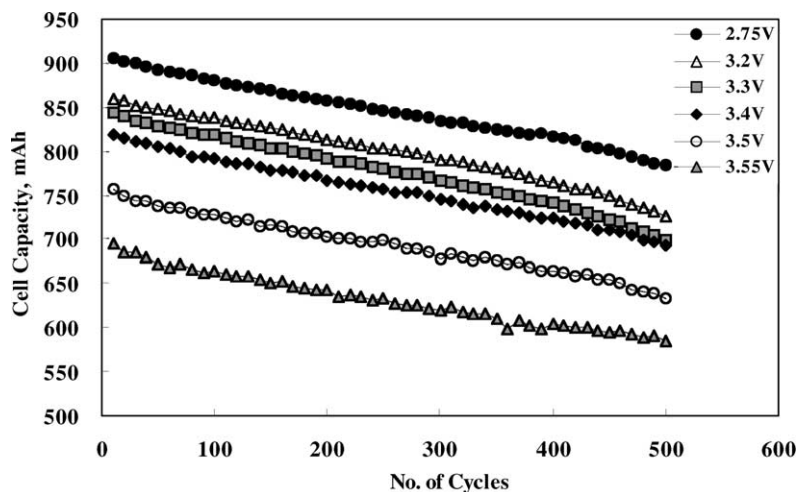


Fig. 5. Effect of discharge cut-off voltage (essentially depth-of-discharge) on cycle performance. Test cells charged by constant current at 1C rate to 4.2 V followed by CV float charging at 4.2 V to 90 mA current cut-off and then discharged to specified discharge cut-off voltage.

has been observed by transmission electron microscopy (TEM) [19]. Cycling appeared to have induced severe strain, high defect densities, and occasional fracture in the particles of the active material. These features were also detectable by a conventional bulk characterization technique such as X-ray diffraction spectroscopy.

Another damaging condition is cycling at a high charging current, especially $>1C$ rate for the present design of cell (Fig. 3). This finding is an extension of earlier tests (up to 1C rate) that showed the capacity degradation rate to be independent or insignificantly dependent on the charge rate up to 0.5C rate but to accelerate significantly at the 1C rate [15]. These results also appear to be consistent with those of another report [16] which found that an increased current density for both charge and discharge accelerates the degradation, although the individual effects of charge and discharge rates were not separated. Our study demonstrates that cycle-life is independent of the DoD, which is in agreement with an early report [15]. This behaviour contrasts with that of other batteries, e.g. alkaline secondary cells such as Ni–Cd, Ni–MH, Ni–Zn and Ni–H₂ [20,21] or lead–acid cells [20], whose cycle-life is strongly dependent on the DoD.

4. Conclusions

Cycling tests of a Li-ion cell at ambient temperature reveal that cycle-life is influenced mainly by the charge conditions, but is relatively insensitive to the discharge conditions. High charge cut-off voltages above 4.2 V and a long float-charge period at 4.2 V or above are the most severe conditions for cycle-life. Another damaging condition is a high charge rate, i.e. $>1C$, but reduction in the depth-of-discharge does not improve the cycle-life unlike for other rechargeable batteries such as alkaline and lead–acid batteries. The dependence of degradation rate on charge voltage and period of high charge voltage suggests

that an electrochemical oxidation may be the cause of the degradation.

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