

NON-AQUEOUS ELECTROLYTE SECONDARY BATTERY

FIELD OF THE INVENTION

The present invention relates to the improvement of the cycling performance of the non-aqueous electrolyte secondary battery.

BACKGROUND OF THE INVENTION

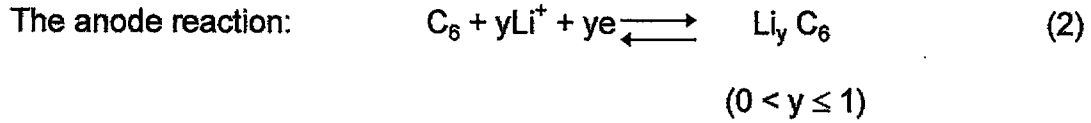
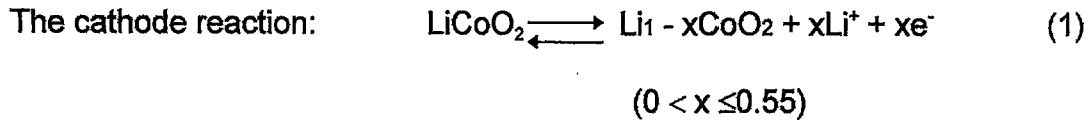
There has long been research into non-aqueous electrolyte secondary batteries with lithium metal as the anode in the search for high energy density secondary batteries. In non-aqueous electrolyte secondary batteries with lithium metal as the anode, although good cycling performance can be obtained when the depth of discharge (discharge capacity per cycle $\times$ 100 $\div$ battery full capacity) is small (20 - 30%). The cycling performance is extremely poor when the depth of discharge is large (80 - 100%). That is, in trying to obtain sufficient number of cycles of charging and discharging, only 20~30% of the energy stored in the battery can be used, making them meaningless as high energy density batteries.

In the cycling process of charging and discharging, the metallic lithium of the anode will go through repeated deposition and dissolution; the poor cycling performance, in such cases that the depth of discharge is large, is caused by the unsuitable state of metallic lithium deposition. When the lithium metal layer undergoes repeated deposition and dissolution across an extremely thin layer of just a few microns (when the depth of discharge is small), the

deposited metallic lithium is dense and is reactive as an active anode material. But when the lithium metal layer undergoes repeated deposition and dissolution across a thicker layer of several tens of microns (when the depth of discharge is large), the deposited metallic lithium gradually become powder-state and is not reactive as an active anode material.

By substituting lithium metal for carbon as the active anode material and adopting the anode reaction in which doping of lithium-ion into and de-doping of lithium-ion from the carbon take place, the new non-aqueous electrolyte secondary battery has been developed and finally brought into the stage of practical application. The non-aqueous electrolyte secondary battery concerned was successfully made into actual commercial product for the first time in the world by the inventor of the present invention and et al, and first introduced to the world in 1990 under the name of "lithium-ion secondary battery" (refer to Progress in Batteries and Solar Cells, Vol. 9, 1990, p. 209). It is currently recognised as the "next-generation secondary battery", and rapidly being adopted as energy sources for such equipment as mobile phones, video cameras, note-book computers, etc.

In the first lithium-ion secondary battery completed by the inventor of the present invention and et al, coke (which is quasi-graphite carbon) was used as the active anode material and LiCoO_2 as the active cathode material. The cathode reaction and anode reaction in equations (1) and (2) represent the battery reactions of this lithium-ion secondary battery, respectively.

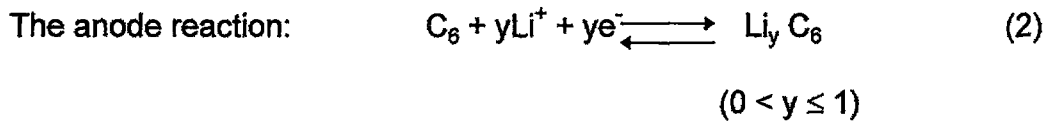
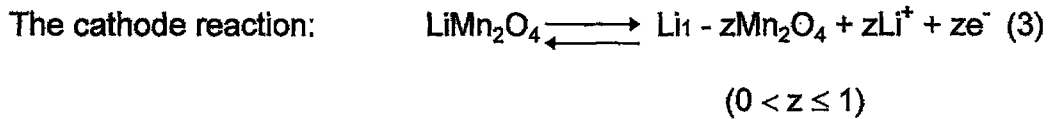


When the battery is under charging, both the cathode equation (1) and the anode equation (2) proceed to the right, with Li^+ being de-doped from LiCoO_2 at the cathode and Li^+ being doped into C_6 at the anode (lithium-ion is intercalated into the carbon). Conversely when the battery is under discharging, equations (1) and (2) proceed to the left, with Li^+ being de-doped from Li_yC_6 at the anode and Li^+ returning to the cathode.

Accordingly, in designing said lithium-ion secondary battery the amount of lithium (X) which can actually be de-doped from LiCoO_2 at the cathode and the amount of lithium (Y) which can actually be doped into the active carbon (C_6) at the anode is kept balanced. As in normal designs $X \leq Y$, during normal charge the entire amount of lithium that is de-doped from the cathode can be doped into the active carbon (C_6). As such, there is no deposition of metallic lithium at the anode (except in the case of overcharging that there is deposition of metallic lithium at the anode), which can avoid the aforementioned flaw of the metallic lithium anode and thus can obtain stable cycling performance. However the high cost has become a significant drawback, for costly cobalt is used as the main active cathode material.

In order to realise a low cost lithium-ion secondary battery, it has been proposed to use spinel-structure lithium-containing manganese oxide (LiMn_2O_4)

as active cathode material which is much cheaper than LiCoO_2 . The battery reactions of said lithium-ion secondary battery with lithium-containing manganese oxide as its active cathode material are shown in the following equation (3) for the cathode, and the aforementioned equation (2) for the anode.



Up to now, in designing said lithium-ion secondary battery the amount of lithium (Z) that can be actually de-doped from the lithium-containing manganese oxide at the cathode and the amount of lithium (Y) that can actually be doped into the active carbon (C_6) at the anode is kept balanced, with $Z \leq Y$ in conventional designs. Since the entire amount of lithium de-doped from the cathode can be doped into the active carbon (C_6), there is no deposition of metallic lithium at the anode; and hence the aforementioned flaw of the metallic lithium anode is avoided.

However in comparison to lithium-ion secondary battery with LiCoO_2 as the active cathode material, cycling performance of the lithium-ion secondary battery with spinel-structure lithium-containing manganese oxide as the cathode active material is poorer, that is the capacity deterioration associated with cycling of charge and discharge is considerable. It is apparent that there is a new problem of cycling performance, which concerns more with the cathode

rather than the anode of the lithium-ion secondary battery with spinel-structure lithium-containing manganese oxide as the active cathode material. After repeated cycling tests and dismantling the conventional battery with spinel-crystal-structure lithium-manganese oxide and carbon material as the active cathode and anode material respectively, the results of analysis of the anode surface confirm the presence of a significant amount of manganese. It is thought that poorer cycling performance is due to the gradual dissolving out of manganese from the cathode and deposition of manganese at the anode during cycling. The dissolving out and deposition of manganese is an irreversible reaction; and it is thought that while the amount of manganese that dissolves out accumulates along with the cycling, the battery capacity reduces in proportion to the amount of manganese that dissolves out.

To improve said cycling performance, it has been proposed to adopt spinel-structure lithium-containing manganese oxide as represented in the general formula $\text{LiMn}_{2-y}\text{ByO}_4$ (B can be Li, Ni, Co, Fe, Cr, etc; $0 \leq y \leq 0.3$), in which a part of the Mn in LiMn_2O_4 is replaced with another element B. But this is still not sufficient enough to resolve the problem.

OBJECTS OF THE PRESENT INVENTION

It is therefore the object of the present invention to minimise capacity deterioration, accompanying charging and discharging of non-aqueous electrolyte secondary battery with spinel-structure lithium-containing manganese oxide as the main active cathode material, to a significantly low

level.

SUMMARY OF THE INVENTION

The inventor of the present invention has discovered that when the battery is under charging, there is a rapidly increasing amount of manganese dissolving out from spinel-crystal-structure lithium manganese oxide once its electrode potential exceeds 4.2 V (vsLi⁺/Li). Given this, the reason for the dissolving out of manganese from the cathode in the aforementioned battery is that even if the battery voltage is constantly maintained at no more than 4.2 V, the cathode potential may rise to more than 4.2 V (vsLi⁺/Li), causing the manganese to dissolve out at the cathode. Here, V (vsLi⁺/Li) is used as a unit for the electrode potential versus lithium metal electrode potential.

The present invention is designed so that as long as the battery voltage is maintained at no more than 4.2 V, the cathode potential in the battery will always be no more than 4.2 V (vsLi⁺/Li). To be more specific, the anode of the battery of the present invention consists of two layers on the metallic current collector, one being a lithium-intercalated carbon layer and the other being a metallic lithium layer. Different from the concept of conventional lithium-ion secondary battery, the battery of the present invention is designed to maintain the relationship between the amount of lithium (Z) that can be de-doped from the cathode and the amount of lithium (Y) that can be doped into the active carbon (C₆) at the anode as $Y = 0.7 Z \sim 0.8 Z$. This means that when the battery is being charged, at the point when approximately 70 - 80% of the

lithium is de-doped from the cathode, the active carbon (C_6) at the anode has already been fully intercalated by lithium, then the metallic lithium starts to deposit at the anode. As such when the battery is at least 70 - 80% charged, the anode is formed from two layers, a lithium-intercalated carbon layer and a metallic lithium layer. Thus, the cathode potential of the battery will be no more than 4.2 V (vs Li^+/Li), provided that the battery voltage is not raised above 4.2 V. In this way, there is no dissolving out of manganese from the cathode, and therefore battery capacity deterioration, as a result of the charge-discharge cycling, can be minimised to a significantly low level.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig.1 illustrates the cycling performance of the battery (A) of the present invention and the conventional battery (B).

Fig.2 illustrates the cross-section of the anode of the present invention.

Fig.3 illustrates the cross-section of the anode of the conventional battery.

Fig.4-a and Fig.4-b illustrate the changes of terminal voltage, current and electrode potential of the battery of the present invention under charging.

Fig.5-a and Fig.5-b illustrate the changes of terminal voltage, current and electrode potential of the conventional battery under charging.

Fig.6-a, Fig.6-b, and Fig.6-c illustrate the cross-section of the battery of the present invention in each assembly process.

Fig.7-a, Fig.7-b, and Fig.7-c illustrate the cross-section of the battery of the present invention in each assembly process.

DETAILED DESCRIPTION OF THE INVENTION

In detail now and referring to the drawings, one embodiment of the present invention is to be introduced. Fig.4-a and Fig.4-b show the charging profile of the battery of the present invention (which has an outer diameter of 17.5 mm and a height of 65 mm) with charging current of 500 mA and the charging voltage set at 4.2 V. Fig. 4-a shows the changes of terminal voltage (BP) and charging current (C), while Fig. 4-b shows the changes of cathode potential (CP) and anode potential (AP). As is shown in Fig.4-a, the terminal voltage increases along with the charging time. After 2 hours and six minutes, the point when the battery is charged with $2.1 \text{ hours} \times 500 \text{ mA} = 1050 \text{ mAh}$ (which equates to approximately 80% of the full capability), the terminal voltage has reached the set charging voltage of 4.2 V. After that charging continues with the voltage maintained at 4.2 V. On the other hand, charging current continues to flow at 500 mA until the terminal voltage reaches the set charging voltage of 4.2 V, after which the current reduces and it becomes almost none at the end of the charging period, then charging is completed. The battery of the present invention as shown in Fig. 4, is designed so that the relationship between the amount of lithium (Z) that can actually be de-doped from the LiMn_2O_4 at the cathode and the amount of lithium (Y) that can actually be doped into the active carbon (C_6) at the anode is $Y \div 0.8 Z$. As such, at the

point when approximately 80% of the lithium has been de-doped from the cathode, namely when the terminal voltage has reached the set charging voltage of 4.2 V, the active carbon (C_6) at the anode has fully doped with lithium. Accordingly, once the terminal voltage has reached the set charging voltage of 4.2 V, the anode potential (AP) reaches the potential at which metallic lithium deposits, namely 0 V (vs Li^+/Li) as shown in Fig.4-b, and there is deposition of metallic lithium at the anode. In other words, when the battery is at least 80% charged, the anode is composed of a lithium-intercalated carbon layer and a metallic lithium layer. Moreover, the terminal voltage is the difference between the cathode potential and the anode potential ($BP = CP - AP$). Once the terminal voltage has reached the set charging voltage of 4.2 V, the anode potential becomes $AP < 0$ V (vs Li^+/Li). As such the cathode potential becomes $CP = BP + AP = 4.2$ V + $AP < 4.2$ V (vs Li^+/Li).

As presented above, the characteristic of the battery of the present invention is that when the battery is charged 80% or more, the anode consists of a lithium-intercalated carbon layer and a metallic lithium layer. As such the anode potential is constantly the same as the electrode potential of the lithium metal layer, and the terminal voltage of the battery is the same as the cathode potential of the battery (vs Li^+/Li). Accordingly, as long as the battery voltage is maintained no more than 4.2 V, the cathode potential of the battery will be no more than 4.2 V (vs Li^+/Li).

Furthermore, in the battery of the present invention, approximately 20% of the capacity is lithium metal functioning as the active anode material. As the

deposition and dissolution of the lithium metal which occupies 20% of the capacity take place within a very thin layer of several microns, the deposition of the metallic lithium layer, which is extremely dense, does not cause the battery to degrade during the practical cycling of charging and discharging.

As a matter of interest, during the charging period the changes of terminal voltage, charging current, cathode potential and anode potential in the conventional battery (battery size: outer diameter = 17.5 mm; height - 65 mm) are as shown in Fig.5. As Fig.5-b shows that, at the point when the terminal voltage reaches the set up charging voltage of 4.2 V, since charging is not completed yet, lithium still can be doped into the carbon at the anode; the anode potential (AP) has not reached the potential (0 V) at which metallic lithium deposits, therefore $AP > 0 \text{ V}$. Accordingly, the cathode potential (CP) reaches more than 4.2 V (vs Li^+/Li) from some time just before or just after the time when the terminal voltage reaches the set up charging voltage of 4.2 V, and manganese dissolves out from the cathode.

Example 1

With reference to Fig.6 and Fig.7, a detailed process for making one embodiment of the present invention shall be described. Mixed 70 parts by weight of meso-carbon microbeads ($d_{002} = 3.36 \text{ \AA}$) which had been heat treated at 2800°C and 20 parts by weight of pitch coke. Then wet mixed with N-methyl-2-pyrrolidone, into which as a binding agent, 10 parts by weight of polyvinylidene fluoride (PVDF) had been dissolved, to create a slurry (a paste). Applied this slurry evenly to both sides of copper foil of 0.01 mm in thickness,

which is to be the anode current collector 21, dried it at a drying temperature of 110°C until all the solvent (N-methyl-2-pyrrolidone) was removed. Then a coated copper foil with a carbon layer on each of its surface was ready. After the coated copper foil was subjected to pressurised casting with a roll press and adjusted to have a width of 56 mm, a strip-shaped carbon electrode was formed. Weighed a piece of carbon electrode, which has certain area cut off from said strip-shaped carbon electrode, to measure the weight of the carbon layer. Paired the piece of carbon electrode up with metallic lithium to make a test cell, then measured the amount of lithium (Y) that can be doped into the carbon layer. The range of weight of the carbon layer was from 21.7 mg/cm² to 22.7 mg/cm², and the amount of lithium (Y) that could be doped into the carbon layer was approximately 6.25 mAh/cm².

Next, baked the manganese dioxide (MnO₂) available on the market for 19 hours at 400°C and then mixed with lithium carbonate (Li₂CO₃) in the proportion of 1.94 mol : 0.53 mol. Baked the mixture for 12 hours in air at a temperature of 860°C to synthesise the spinel-crystal-structure lithium manganese oxide (LiMn₂O₄) used for the present invention as the active cathode material. Crushed the lithium manganese oxide to powder with an average particle size of 0.015 mm in diameter. Wet mixed 88 parts by weight of said powder, 6 parts by weight of graphite and 6 parts by weight of polyvinylidene fluoride as a binding agent with the solvent of N-methyl-2-pyrrolidone to form a slurry (a paste). On both sides of the aluminium foil of 0.02 mm in thickness, which functions as the cathode current collector 22

evenly applied the slurry so that the coating weight in dry would be about 73 mg/cm². Then dried it at a drying temperature of 110°C until the solvent (N-methyl-2-pyrrolidone) was completely removed. Subjected it to pressurised casting with a roll press, adjusted the width to 55 mm, and created five strip-shaped cathodes with active cathode material layer which contains spinel-crystal-structure lithium manganese oxide (LiMn₂O₄) on both surfaces of the aluminium foil. Weighed a piece of cathode, which has certain area cut off from each said strip-shaped cathode, to measure the weight of the cathode active material layer. Paired up said piece of cathode with metallic lithium to make a test cell, and measured the amount of lithium (Z) which can be de-doped from the cathode active material layer of each cathode. The weight of the active cathode material layer ranged from 72 mg/cm² to 74 mg/cm², and the amount of lithium (Y) that can be de-doped from the active cathode material layer was at an average of 7.8 mAh/cm², completely in proportion to the weight of the active cathode material layer.

After inserting porous, polypropylene separator between the prepared anode and cathode, wound into a roll shape to create the battery element 20 with an average external diameter of 16.9 mm. Housed the battery element 20 in the battery casing 1, as shown in Fig. 6-a. Example 1 seeks to make a battery with the outer diameter (L2) of the battery casing of the finished battery to be A = 17.5 mm. The battery casing used here was a nickel-plated iron battery casing with an outer diameter of B = 18.0 mm at both the opening (L1) and at the central part (L2), and an height of 65 mm. The inner diameter of

said battery casing was 17.4 mm. As the outer diameter of the battery element is 0.5 mm smaller than the inner diameter of the casing, the battery element can be easily inserted into the battery casing. After housing the battery element 20 in the battery casing 1, reduced the outer diameter of the battery casing (apart from the immediate vicinity of the opening) to 17.5 mm, as shown in Fig.6-b.

After this, squeezed the battery casing at the point of 60.5 mm from the casing base (near the battery casing opening), as shown in Fig.6-c, and created striations 2 to support the gasket. Then followed the process shown from Fig.7-a to Fig.7-c to assemble the battery. Placed the gasket 3 at the opening of the battery casing, as shown in Fig.7-a. Welded the anode and cathode leads respectively to the casing bottom and the aluminium sealing cap 4, which functions as an anti-explosion valve. Then injected the electrolyte, housed the sealing cap 4 on the inner side of the gasket, laid the doughnut-shaped PTC (Positive Temperature Coefficient) element 5 on top of and in contact with the sealing cap, then laid the cathode external terminal 6 on top. Squeezed the outer diameter (L1) of the opening of the battery casing to the same size as the outer diameter (L2) of the central part of the battery casing (see Fig.7-b). Finally, adjusted the caulking machine so that the tightening pressure would not damage the functions of the PTC element, caulked and sealed the edge of the battery casing to produce five batteries (A) of 17.5 mm in outer diameter and 65 mm in height with a battery structure as shown in Fig.7-c.

Comparative Example 1

As a way of providing useful comparison between the present invention, battery (A), and a conventional battery (which will be referred to as battery (B)), a brief description of the process for producing the conventional battery shall be provided below.

Following the conventional design method the relationship between the amount of lithium (Z) that can be de-doped from the cathode and the amount of lithium (Y) that can be doped into the active carbon at the anode (C_6) is $Z \leq Y$.

Following the same procedure as described in Example 1, the anode, with the carbon layer ranging from 25.5 mg/cm^2 to 26.5 mg/cm^2 and the amount of approximately 6.95 mAh/cm^2 lithium (Y) to be doped into the carbon layer, was produced.

Five strip-shaped cathodes were made in exactly the same manner as presented in Example 1, except that the cathode was coated in such a way that the coating weight in dry was around 65 mg/cm^2 . After cutting off a piece of certain area, weighed the cathode to measure the weight of the cathode active material layer. Paired up the piece of cathode with metallic lithium to make test cells, and measured the actual amount of lithium (Z) that can be de-doped from the active cathode material layer of each cathode. The weight of the cathode active material layer ranged from 64 mg/cm^2 to 66 mg/cm^2 , and the amount of lithium (Y) that can be de-doped from the active cathode material layer was at an average of 6.93 mAh/cm^2 completely in proportion to the weight of the active cathode material layer.

With the prepared anode and cathode, battery elements 20 with average outer diameter of 16.9 mm were made in exactly the same manner as in Example 1. Five batteries (B) of 17.5 mm in outer diameter and 65 mm in height with a battery structure as shown in Fig.7-c, were produced.

To make a charge-discharge cycling comparison between the batteries (A) of the present invention and conventional batteries (B), stabilised the inside of both the batteries (A) and batteries (B) made as per Example 1 and Comparative Example 1, set the charging voltage at 4.1 V, charged the batteries for 8 hours at a current of 500 mA, and then at a current of 500 mA discharged them to cut-off voltage of 2.5 V. Next, set up the charging voltage at 4.2 V, charged the batteries for 4 hours at a current of 500 mA, and then discharged them to a cut-off voltage of 2.5 V at 500 mA. In the same way, repeated charge and discharge for 300 times, with the results shown in Fig.1.

As is shown in Fig.1, even in the 300th cycle of discharging, the discharge capacity of the batteries (A) of the present invention is maintained at no less than 80% of initial capacity (the discharge capacity of the tenth cycle). In contrast to this, in the 300th cycle of discharging, the discharge capacity of the batteries (B) made in Comparative Example 1 has fallen to 67% of the initial capacity (the discharge capacity of the tenth cycle). Thus, this invention has greatly improved charge-discharge cycling performance, as these results indicate.

To make an observation of the anodes of the batteries of the present invention and that of the conventional batteries, the process below was

followed. After having finished 10 cycles of charge-discharge, two of each batteries (A) in Example 1 and batteries (B) in Comparative Example 1, were charged with a setting charging voltage at 4.2 V and a charging current of 500 mA for 2.5 hours. When the batteries were charged for 2.5 hours, charge capacity (mAh) was 88% of full capacity of batteries (A), and was 90% of full capacity for batteries (B), with neither battery achieving full charging. After that dismantled the batteries to observe the surface of the anode.

In addition, charged another battery (B) for 4 hours at a current of 500 mA and the charging voltage set at 4.2 V, then dismantled it in the same way as described above to observe the surface of the anode. When this battery (B) was charged for 4 hours, charged capacity (mAh) was 100% of full capacity of battery (B).

The surface of the anodes removed from the batteries (A) were in silver-white colour; scraped it away, revealed a gold colour layer underneath. The thin, silver-white layer is a layer of metallic lithium, and the layer in gold colour is lithium-intercalated carbon. It is evident that even when the batteries are only charged to 88% of full capacity, the anodes removed from batteries (A) have the cross-section structure as shown in Fig. 2, indicating that there were two layers on the metallic current collector 30, a lithium-intercalated carbon layer 31 and a metallic lithium layer 32.

On the other hand, the surfaces of anodes removed from batteries (B) were in gold colour, but did not have the silver-white surface layer that was observed on the anodes removed from batteries (A). The anodes removed

from batteries (B) which were charged to 90% of full capacity, and anode removed from the battery (B) which was charged to 100% of capacity, had the cross-section structure as shown in Fig. 3, which indicated that they were anodes with only one layer of lithium-intercalated carbon on the metallic current collector 30.

From the results of the above observation, the improvement in charge-discharge cycling performance through the present invention can be attributed to the followings.

Fig.4-a and Fig.4-b show the batteries (A) of the present invention, with an outer diameter of 17.5 mm and a height of 65 mm, being charged at a current of 500 mA and the voltage set at 4.2 V. The change of terminal voltage (BP) and the change of charging current (C) are shown in Fig.4-a, while the change of cathode potential (CP) and the change of anode potential (AP) are shown in Fig.4-b. As Fig.4-a shows that, the battery terminal voltage reaches 4.2 V after 2.1 hours of charging (approximately 1050 mAh; this equates to approximately 80% of full charge capacity), and after that charging continues with the voltage maintained at 4.2 V. On the other hand, the charging current continues to flow at 500 mA until the terminal voltage reaches the set up charging voltage of 4.2 V. Then it reduces after the terminal voltage has reached the set charging voltage of 4.2 V. At the end of charging period almost no current flows, and charging is over.

Accordingly, at the point when battery (A) has been charged for 2.5 hours, the terminal voltage reaches 4.2 V; the anode potential (AP) reaches 0 V

(vsLi⁺/Li) or lower, as shown in Fig.4-b; and deposition of metallic lithium starts at the anode. The battery of the present invention is designed in such a way that the relationship between the amount of lithium (Z) which can actually be de-doped from the LiMn₂O₄ at the cathode and the amount of lithium (Y) which can actually be doped into the active carbon (C₆) at the anode is $Y \div 0.8Z$. So when approximately 80% of the lithium has been de-doped from the cathode, the doping of lithium into the active carbon (C₆) has completed at the anode. Therefore, after the batteries (A) are charged for 2.5 hours (charged to at least 80% of capacity) consequently deposition of metallic lithium starts at the anodes. By dismantling the batteries and observing the anodes, the results are apparent that the anodes removed from the batteries (A) after 2.5 hours of charging have the cross-section structure as shown in Fig. 2, with two layers, a lithium-intercalated carbon layer 31 and a metallic lithium layer 32 on the metallic current collector 30. After the charging voltage has reached 4.2 V, the anode potential maintains at the potential at which lithium metal deposits (0 VvsLi⁺/Li or lower), and the cathode potential in the battery is constantly at no more than 4.2 V (vsLi⁺/Li). Thus, there is no dissolving out of manganese from the cathode, and the capacity deterioration, which accompanies the charge-discharge cycling, is minimised to a significantly low level.

As for the conventional the battery (B), the cathode potential reaches higher than 4.2 V (vsLi⁺/Li) at the last period of charging. Fig.5 shows the battery (B) being charged at a current of 500 mA with the charging voltage set at 4.2 V. Fig.5-a shows the change of terminal voltage (BP) and the change of

charging current (C), while the Fig.5-b shows the change of cathode potential (CP) and the change of anode potential (AP).

As shown in Fig.5-a, the terminal voltage rises in line with the length of charging time, reaching the set up charging voltage of 4.2 V after approximately 1.9 hours, and remaining at that level of 4.2 V. The charging current continues to flow at 500 mA until the terminal voltage reaches the set up charging voltage of 4.2 V. After that, it reduces and at finally there is almost no current flowing, when charging is over. Looking solely at changes of terminal voltage (BP) and the changes of charging current (C), those of the batteries (B) are almost the same as those of the batteries (A) shown in Fig.4. However, as the terminal voltage is the difference between the cathode potential and the anode potential ($BP = CP - AP$), when the terminal voltage has reached 4.2V if the anode potential is $AP > 0 \text{ V (vsLi}^+/\text{Li)}$, the cathode potential could be $CP = BP + AP = 4.2 \text{ V} + AP > 4.2 \text{ V (vsLi}^+/\text{Li)}$. Because in the conventional battery the relationship between the amount of lithium (Z) that can be de-doped from the cathode and the amount of lithium that can be doped into the active carbon (C_6) at the anode is $Z \leq Y$, in reality (as shown in Fig.5-b) when the terminal voltage has reached the set charging voltage of 4.2 V, charging has not completed and lithium still can be doped into the carbon at the anode. The anode potential (AP) has not reached the potential (0 V) at which lithium deposits, thus $AP > 0 \text{ V}$. Accordingly, the cathode potential (CP) goes up to more than 4.2 V (vsLi^+/Li) from the time just before or just after the terminal voltage reaches the set charging voltage of 4.2 V, and manganese dissolves out from the cathode.

Due to this, capacity deterioration accompanying the charge-discharge cycling occurs in proportion to the amount of manganese dissolved out.

As the battery of the present invention adopts spinel-structure lithium-containing manganese oxide as the main active cathode material, material cost for Li-ion battery can be kept lower. In addition, the anode has two layers on the metallic current collector (a layer of lithium-intercalated carbon and a layer of metallic lithium) the cathode potential in the battery does not reach more than 4.2 V (vsLi⁺/Li). Accordingly, there is no dissolving out of manganese from the cathode and capacity deterioration, which accompanies the charge-discharge cycling, is minimised to a significantly low level.

The present invention, which can create a low-cost lithium-ion secondary battery with good cycling performance, is of great industrial value.

The present invention may be embodied in other specific forms without departing from the spirit or essential characteristics thereof.

The presently disclosed embodiments are, therefore, to be considered in all respects as illustrative and not restrictive, the scope of the invention being indicated by the appended claims and all changes which come within the meaning and range of equivalency of the claims are, therefore, to be embraced therein.

CLAIMS

1. A non-aqueous electrolyte secondary battery comprising an anode, a cathode, separator and non-aqueous electrolyte, wherein said cathode has spinel-frame manganese oxide as the main active cathode material and which is characterised by that said anode consists of two layers on the metallic current collector, namely a lithium intercalated carbon layer and a metallic lithium layer, even when said battery is no more than 90% charged.

