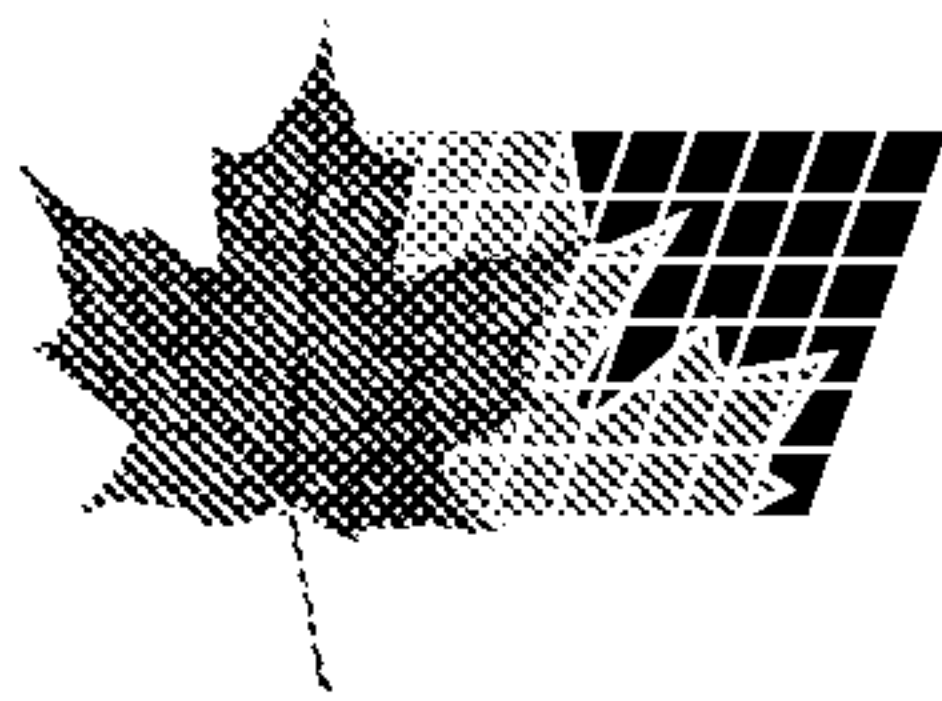




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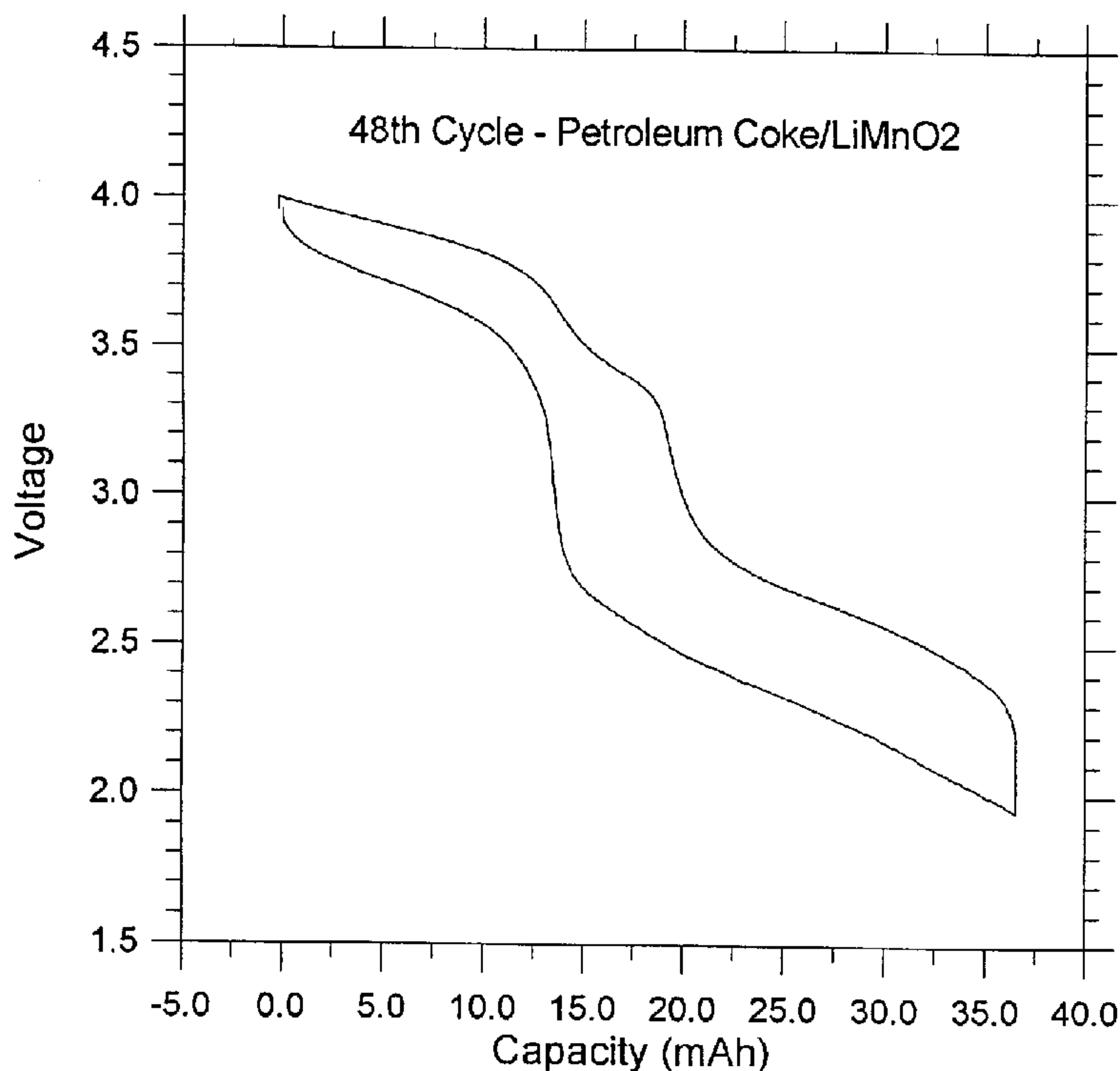
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(54) **UTILISATION D'UNE FORME STABLE DE LIMNO₂ COMME
CATHODE DANS UNE CELLULE AU LITHIUM**

(54) **USE OF A STABLE FORM OF LIMNO₂ AS CATHODE IN
LITHIUM CELL**



(57) The invention disclosed relates to a new method of forming spinel-related λ -Li_{2-x}Mn₂O₄, wherein $0 < x < 2$, solely by electrochemical means with air-stable orthorhombic LiMnO₂ as the starting material. This spinel-related material is hygroscopic, metastable and is typically made by chemical means, followed by electrochemical conversion of spinel-type LiMn₂O₄. Also disclosed are new secondary lithium ion electrochemical cells employing as initial active cathode material a compound of formula LiMnO₂, having a specific orthorhombic crystal structure.



Abstract of the Disclosure

The invention disclosed relates to a new method of forming spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$, wherein $0 \leq x \leq 2$, solely by electrochemical means with air-stable orthorhombic LiMnO_2 as the starting material. This spinel-related material is hygroscopic, metastable and is typically made by chemical means, followed by electrochemical conversion of spinel-type LiMn_2O_4 . Also disclosed are new secondary lithium ion electrochemical cells employing as initial active cathode material a compound of formula LiMnO_2 , having a specific orthorhombic crystal structure.

BACKGROUND OF THE INVENTION

This invention relates to a novel method of forming spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$, wherein $0 \leq x \leq 2$, in a secondary electrochemical cell, and to the use of a compound of
5 formula LiMnO_2 which has a specific orthorhombic crystal structure, as initial active cathode material in such cells.

The impetus for this invention was the recent, great
10 increase in demand for batteries having high energy density and low weight, such as had already been achieved with metallic lithium systems, but which are also rechargeable. Lithium electrodes do not meet this requirement over extended periods of time because even in an aprotic organic
15 solvent the cycling stability is severely limited, and problems with cell safety arise.

An electrochemical cell in which both the anode and the cathode are lithium intercalation compounds is termed
20 a lithium ion cell. The intercalation compound serves as a host structure for lithium ions which are either stored or released depending on the polarity of an externally applied potential. During discharge, the electromotive force reverses the forced intercalation or de-intercalation
25 thereby producing current.

In a lithium ion cell, the positive electrode generally serves as the initial reservoir of lithium. The capacity of the cell will be limited by the amount of
30 lithium present in the positive electrode on cell assembly. In most cases, only a proportion of the lithium present, during fabrication of the positive electrode, can be reversibly removed (i.e. cycled).

35 LiMnO_2 is known to exist in several phases. Two phases, whose crystal structures have been well characterized, are a high temperature orthorhombic phase and a tetragonal

phase. Both structures involve cubic closest packing but they differ in the arrangement of the ordering of the lithium and manganese cations. The tetragonal form is normally written as

- 5 λ - $\text{Li}_2\text{Mn}_2\text{O}_4$. It has an atacamite-type structure which is often referred to as being spinel related. Another type of lithium manganate has a spinel structure of composition LiMn_2O_4 .

10 **DESCRIPTION OF THE PRIOR ART**

One approach to improving the reversibility of lithium electrodes involves the use of intercalation compounds.

- 15 Both LiMn_2O_4 and λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ have been used as cathodes in lithium ion cells [US Patents Nos. 5,135,732 and 5,110,696, and J. M. Tarascon and D. Guyomard, *J. Electrochem. Soc.*, 138 2864 (1991)]. λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ has twice the nominal capacity of LiMn_2O_4 but it is reported to be hygroscopic and
20 metastable [A. Mosbah, A. Verbaere and M. Tournoux, *Mat. Res. Bull.*, 18 1375 (1983)]. Specifically, spinel-related λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ is typically made by first heating lithium carbonate with manganese dioxide, to form spinel-type LiMn_2O_4 , followed by electrochemical or chemical conversion
25 to λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ in the presence of a lithium source. Neither process is very satisfactory. Moreover, lithium is pyrophoric and causes handling problems.

- In the reference [J. M. Tarascon and D. Guyomard, *J. Electrochem. Soc.*, 138, 2864 (1991)] it is reported that λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ slowly decomposes in ambient conditions to LiMn_2O_4 . λ - $\text{Li}_2\text{Mn}_2\text{O}_4$ converts to the high temperature orthorhombic form, LiMnO_2 , when heated in an argon atmosphere to 600 °C. It is prepared by electrochemically, or chemically, intercalating
35 lithium into the LiMn_2O_4 spinel structure, as described in the two preceding references.

The structure of the high temperature orthorhombic phase of LiMnO_2 was determined in detail by R. Hoppe, G. Brachtel and M. Jansen, [*J. Anorg. Allg. Chem.*, 417 1 (1975)]. This structure is described by the space group Pmmn and has unit cell dimensions $a = 4.572 \text{ \AA}$, $b = 5.757 \text{ \AA}$ and $c = 2.805 \text{ \AA}$. To our knowledge, the use of LiMnO_2 , having this structure, as the active material in the cathode of a reversible electrochemical cell has never been demonstrated. Recently, T. Ohzuku, A. Ueda and T. Hirai [Chemistry Express, 7 193 (1992)] have demonstrated the use of a low temperature form of orthorhombic LiMnO_2 as the active cathode material in a reversible lithium ion cell. The low temperature form of orthorhombic LiMnO_2 was prepared by heating an equimolar mixture of $\gamma\text{-MnOOH}$ and $\text{LiOH}\cdot\text{H}_2\text{O}$ to 450 °C. For the sake of simplicity, the high temperature form of orthorhombic LiMnO_2 with the structure described by Hoppe, Brachtel and Jansen will henceforth be referred to as orthorhombic LiMnO_2 .

20 SUMMARY OF THE INVENTION

It is an object of the present invention to provide a novel method of forming spinel-related $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$, wherein $0 \leq x \leq 2$, in the cathode of a secondary lithium ion electrochemical cell.

It is another object of the present invention to provide a secondary electrochemical cell of high energy density, whose charge/discharge mechanism is based upon alternating intercalation and de-intercalation of Li^+ ions in the active materials of the positive and negative electrodes.

It is yet another object to provide good chemical resistance to the electrolyte and high cycling stability.

According to one aspect of the invention, a method of

forming spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$, wherein $0 \leq x \leq 2$, in the cathode of a secondary lithium ion cell is provided, which comprises

5 (a) providing a secondary lithium ion electrochemical cell, said cell comprising a lithium intercalation anode, a suitable non-aqueous electrolyte including a lithium salt, a cathode containing as initial active material orthorhombic LiMnO_2 characterized by the specific
10 orthorhombic crystal structure described by the space group Pmm and unit cell dimensions $a=4.572 \text{ \AA}$, $b=5.757 \text{ \AA}$ and $c=2.805 \text{ \AA}$, and a separator between the anode and cathode, and

15 (b) charging the cell to de-intercalate sufficient available lithium ions to convert the LiMnO_2 to spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$, and

(c) discharging the cell to intercalate sufficient
20 available lithium ions to convert the spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$ to spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $0 \leq x \leq 2$.

Preferably, the cell is charged to greater than 40-50%
25 of the nominal cathode capacity, and discharged to 30-40% of the nominal cathode capacity.

According to another aspect of the invention, the use of a compound of formula LiMnO_2 characterized by the
30 specific orthorhombic crystal structure, described by the space group Pmm and unit cell dimensions $a=4.572 \text{ \AA}$, $b=5.757 \text{ \AA}$ and $c=2.805 \text{ \AA}$, as initial active cathode material in secondary lithium ion electrochemical cells is also provided.

35

According to yet another aspect of the invention, a secondary lithium ion electrochemical cell comprising a

lithium intercalation anode, a suitable non-aqueous electrolyte including a lithium salt, a cathode containing as initial active material orthorhombic LiMnO_2 characterized by the specific orthorhombic crystal structure described by the space group Pmmn and unit cell dimensions $a=4.572$ Å, $b=5.757$ Å and $c=2.805$ Å, and a separator between the anode and cathode, is provided.

The orthorhombic LiMnO_2 is converted to spinel-type LiMn_2O_4 on the first charge and may be charged further to a lower lithium composition, and upon discharge spinel-related $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$ is formed. Spinel-related $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $0 \leq x \leq 2$ includes the true spinel composition LiMn_2O_4 , spinel-type compositions wherein $1 \leq x \leq 2$ and atacamite-type structures wherein $0 \leq x < 1$. Accordingly, the cell behaves the same way as a cell built with $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$ as the initial cathode material. However, LiMnO_2 is much simpler to prepare than $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$ which is not air-stable. See example 1 below.

20

The anode of the present invention serves as the recipient substance for Li^+ ions. The anode can be any intercalation compound which is capable of intercalating lithium and has an electrode potential sufficiently reducing to provide an adequate cell voltage over a range of lithium intercalation. Specific examples include transition metal oxides such as MoO_2 or WO_2 [Auborn and Barberio, *J. Electrochem. Soc.* **134** 638 (1987)], transition metal sulfides (see US 4,983,476) or carbon products obtained by the pyrolysis of organic compounds. As will be apparent hereinafter, various commercially available carbonaceous materials of predetermined structural characteristics have proven useful.

The non-aqueous electrolyte of the present invention

can be liquid, paste-like or solid. Preferably, the electrolyte includes a lithium salt with an organic solvent, and is in liquid form. Electrolyte salts useful
 5 for this purpose are LiAsF_6 , LiPF_6 , LiBF_4 , LiClO_4 , LiBr , LiAlCl_4 , LiCF_3SO_3 , $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, or mixtures thereof. As a water-free solvent for these salts, there can be used alone or in mixture with others an organic solvent of the group propylene carbonate, ethylene carbonate, 2-
 10 methyl tetrahydrofuran, tetrahydrofuran, dimethoxyethane, diethoxyethane, dimethyl carbonate, diethyl carbonate, methyl acetate, methylformate, γ -butyrolactone, 1,3-dioxolane, sulfolane, acetonitrile, butyronitrile, trimethylphosphate, dimethylformamide and other like
 15 organic solvents. The electrolyte solution can also contain additives such as Crown ethers e.g. 12-C-4, 15-C-5, and 18-C-6, or immobilizing agents such as polyethylene oxide or inorganic gel-forming compounds such as SiO_2 , or Al_2O_3 such as described in US Patent No: 5,169,736.

20

The cathode, having orthorhombic LiMnO_2 as the initial active material, has an electrochemical potential sufficiently positive of the negative electrode to produce a useful overall cell voltage. The greater the difference
 25 in potential, the greater the resulting energy density. In a lithium ion cell, the positive electrode generally serves as the initial reservoir of lithium. The capacity of the cell will be limited by the amount of lithium, available for de-intercalation, present in the positive electrode on
 30 cell assembly. In most cases, only a proportion of the lithium present, during fabrication of the positive electrode, can be reversibly deintercalated. The capacity of a lithium ion cell having a cathode of orthorhombic LiMnO_2 as initial active material increases after the first
 35 cycle in which the original structure is converted to spinel-related $\lambda\text{-Li}_{2-x}\text{Mn}_2\text{O}_4$.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is the trace of the X-ray diffraction pattern of orthorhombic LiMnO_2 , prepared as described in example 1. The JCPDF powder X-ray diffraction pattern for orthorhombic LiMnO_2 is included for comparison;

Figure 2 is the trace of the X-ray diffraction pattern, for the same sample as in figure 1, taken after 11 months of storage in ambient conditions;

Figure 3 shows a plot of a typical charge/discharge cycle for an electrochemical cell with a carbon coke anode and a cathode containing orthorhombic LiMnO_2 ;

Figures 4 and 5 are traces of diffraction patterns of cathodes from the two electrochemical cells described in example 3; and

Figure 6 shows the first five cycles of a coke// LiMnO_2 cell cycled to progressively higher voltage limits: first cycle (inverted triangles) to 3.0 v, second cycle (circles) to 3.5 v, third cycle (plus signs) to 3.8 v, and fourth (triangles) and fifth (diamonds) cycles to 4.0 v.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Orthorhombic LiMnO_2 has been found to be air-stable, and easily fabricated into cathodes for use in secondary lithium ion electrochemical cells of high reversible capacity.

The preferred negative electrode is based on a carbonaceous product. Petroleum coke is particularly preferred. Petroleum cokes are non-graphitic carbons which can intercalate up to approximately one lithium ion per

twelve carbon atoms.

Suitable anode carbonaceous materials include:

5

1) carbonaceous material with a d_{002} layer spacing of less than or equal to 3.70 Å with true density of greater than or equal to 1.70 g/cm³ prepared by carbonization of furan resins, as per US Patent No: 4,959,281.

10

2) the above doped with 2-5 % phosphorous and oxygenated petroleum or coal pitch carbonized and doped with 2-5 % phosphorous with the same d_{002} layer spacing and true density as per published European application No: 15 EP 0 418 514.

3) carbons formed by the thermal decomposition of gas phase hydrocarbons or hydrocarbon compounds with d_{002} from 3.37 to 3.55 Å as per US Patent No: 4,863,814.

20

4) carbon formed from mesophase microspheres with d_{002} layer spacing up to 3.45 Å as per US Patent No: 5,153,082.

25

5) commercial petroleum coke as per US Patent No: 4,943,497.

6) isotropic graphite composed of a mixture of graphite and carbonized pitch with a degree of 30 graphitization greater than or equal to 0.4 and heat treated fluid coke and commercial graphite whose first lithium electrochemical intercalation is performed at or above 50 °C, as per US Patent No: 5,028,500.

35

Typical electrodes in the present invention are fabricated from 80-94 weight percent of active material,

carbon coke or LiMnO_2 , 5 - 15 weight percent of a conductivity enhancer such as *Super S* carbon black, and 1-5 weight percent of a binder such as ethylene propylene diene monomer (EPDM). Other conductivity enhancers such as Shawinigan Acetylene Black, graphites or other conductive materials may be used. In addition, other binders such as Teflon®, poly(vinylidene difluoride), polyolefins or elastomers may be substituted for EPDM.

10

Example 1

A sample of lithium manganese oxide of formula LiMnO_2 characterized by an orthorhombic crystal structure in accordance with the present invention was made by reacting Li_2CO_3 and $\beta\text{-MnO}_2$ in proportions such that the atomic ratio between lithium in Li_2CO_3 and the manganese in the $\beta\text{-MnO}_2$ was 1:1.

The Li_2CO_3 and $\beta\text{-MnO}_2$ were mixed using a mortar and pestle until the mixture was substantially homogenous. The resulting powder was formed into pellets in a 18 mm die, and then heated, in a flow of argon gas, at 600 °C for two hours followed by two intervals of three days each at 800 °C. The sample was ground again between the two firings. The product was examined by X-ray diffraction. Figure 1 shows the trace of the X-ray diffraction pattern of the product from the second firing and the reported diffraction pattern for orthorhombic LiMnO_2 , powder diffraction file card # 35-0749, from the JCPDS International Centre for Diffraction Data. Figure 2 shows the trace of an X-ray diffraction pattern of the same sample after 11 months of storage in ambient conditions. The second diffraction pattern is substantially identical to the first. Unlike $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$, the orthorhombic form of LiMnO_2 is air and moisture stable.

Example 2

An electrochemical cell was assembled with a cathode containing as the initial active material, orthorhombic LiMnO_2 formed by reacting stoichiometric amounts of Li_2CO_3 and $\beta\text{-MnO}_2$ in a manner similar to Example 1, except that reaction temperature was increased to 900 °C.

The cathode was prepared by drying a slurry made from orthorhombic LiMnO_2 with two weight percent of ethylene propylene diene monomer (EPDM) and 10 wt.% Super S carbon black in cyclohexane. The carbon anode was made from Asbury petroleum coke, with 2 wt.% of EPDM and 5 wt.% of Super S carbon black. Both the anode and cathode pellets were formed by pressing about 200 - 500 mg of the mixture of EPDM and carbon black coated material in a 17 mm die for 30 s with 3500 pounds of force applied by a hydraulic press. The diameter of the pellets was chosen to fit a commercial coin cell case of the type #2325. These coin cells have a diameter of 23 mm and a height of 2.5 mm, before crimping the seal. The cell stack consisted of a three layer sandwich of the cathode, a cell separator, and a carbon anode. The separator, a non-woven polypropylene felt, prevents the two electrodes from contacting directly. The separator also provides a reservoir for the electrolyte solution.

The electrolyte used was a 50/50 mixture by volume of propylene carbonate and dimethoxyethane containing 1 M $(\text{CF}_3\text{SO}_2)_2\text{NLi}^+$ from 3M company. The salt was dried under vacuum at 160 °C for 24 hours as recommended by the manufacturer. The propylene carbonate was vacuum distilled and the dimethoxyethane was distilled from lithium/naphthalide under helium. The water content of the electrolyte was under 30 ppm as determined by Karl-Fischer titration. The cell was assembled and crimped in a helium filled glove box to prevent the electrolyte solution from reacting with ambient moisture. The coin cell was charged

and discharged on custom built cyclers. The fully automated and fully programmable cyclers operate at a constant current anywhere from 0.1 μ A to 100 mA, with the current controlled to 0.1 μ A, or to 1 part in 4000 for higher currents. The current and voltage are measured every 30 s. The voltage can be resolved to 10 μ V over the range 0 to 12 V.

The anode had a thickness of 0.040" and a weight of 0.301 g, which corresponds to a capacity of 52.3 mAh to a composition of LiC_{12} . The cathode was 0.030" thick and weighed 0.312 g which corresponds to a theoretical capacity of 79.4 mAh if all the lithium ions in the cathode can be reversibly cycled. The cell completed 64 cycles at a current of 0.28 mA between voltage limits of 4.0 and 1.95 volts. On the 48th cycle the cell had a reversible capacity of 36 mAh (shown in figure 3). The capacity began to decrease significantly at about the 56th cycle and had diminished to 20 mAh by the 64th cycle. The voltage versus capacity plot for orthorhombic LiMnO_2 (figure 3) is very similar to that of $\lambda\text{-Li}_2\text{Mn}_2\text{O}_4$, shown in Figure 6 of Tarascon and Guyomard, [*J. Electrochem. Soc.*, 138 2864 (1991)].

Example 3

25

Another two cells were assembled, as described above, with cathodes containing orthorhombic LiMnO_2 , prepared as described in example 1. The first cell had a 0.045" thick anode weighing 0.354 g made with Conoco XP coke, and a cathode of 0.024" thickness, weighing 0.329 g. The cell completed 49 cycles between 1.8 and 4.0 volts at a current of 0.25 mA. The cell was stopped half way into the 50th charge. After a period of relaxation, the open circuit voltage of the cell was 3.04 volts. The cell was disassembled and the cathode pellet was examined by powder X-ray diffraction. The trace of the diffraction pattern, shown in figure 4, matches the JCPDF card file for LiMn_2O_4 .

The second cell had a 0.056" thick anode weighing 0.428 g and a cathode of 0.014" thickness and 0.190 g weight. A capacity of 33.7 mAh was required to charge the cell to 4.0 volts at 0.28 mA. This corresponds to a 70 %
 5 depth of charge of the cathode and to a composition of $\text{Li}_{0.3}\text{MnO}_2$ in the active material. This cell was cycled between 1.2 and 3.8 volts at 0.20 mA. The cell was stopped after completing the fifth charge. After a period of relaxation the open circuit voltage of the cell was 3.5
 10 volts. The cell was opened and the cathode was extracted for analysis by X-ray powder diffraction. The trace of the diffraction pattern is shown in figure 5. The peaks correspond to a cubic unit cell with $a = 8.143(3) \text{ \AA}$. The diffraction pattern matches that described for $\text{Li}_{0.6}\text{Mn}_2\text{O}_4$ [T. Ohzuku, M. Kitagawa and T. Hirai, *J. Electrochem. Soc.*, 137
 15 769 (1990)].

Example 4

20 Another sample of orthorhombic LiMnO_2 was made by reacting an intimate mixture of Li_2CO_3 and $\beta\text{-MnO}_2$, in proportions such that the atomic ratio between lithium and manganese was 1:1. The resulting mixture was formed into pellets, and then heated, in a flow of argon gas, at 650 °C
 25 for 3 hours followed by 3 days at 1000 °C. The product was examined by X-ray powder diffraction to confirm that it was a single-phase material having the crystal structure in accordance with the present invention. This sample of orthorhombic LiMnO_2 provided the active cathode material in
 30 a lithium ion cell prepared in the same way as in Example 2, except that the anode was made from Unocal needle coke with 7.5 wt. % Super S and 2 wt. % EPDM binder. The anode and cathode pellets weighed 0.402 and 0.350 g, respectively.

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This coke/ LiMnO_2 cell was cycled between 1.5 volts and a progressively increasing upper voltage limit. The first

two cycles, to voltage limits of 3.0 and 3.5 volts, respectively, showed very high irreversible capacities. As shown in figure 6, the second charge pushed the cathode to 40 % of its theoretical capacity. The third charge to a voltage limit of 3.8 volts, indicated by the plus symbols in figure 6, took the cathode to 46 % of its nominal capacity. The subsequent discharge, however, provided 12 % more capacity than the charge had consumed. The fourth and fifth cycles to 4.0 volts provided further small gains in discharge capacity relative to the prior charge. The first two discharges show no evidence of the higher voltage plateau (above 3.6 V) associated with lithium occupation of tetrahedral sites and indicative of the conversion to spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$. Although it is difficult to see on the figure, the third discharge shows a small amount of the high voltage plateau indicating that the conversion to spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$ began on the third charge. The coincidence of the phase conversion with increased reversible capacity suggests that it is important to the functioning of LiMnO_2 based cathodes.

CLAIMS:

1. A method of forming spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$, wherein $0 \leq x \leq 2$, in the cathode of a secondary lithium ion electrochemical cell, which comprises

(a) providing a secondary lithium ion electrochemical cell, said cell comprising a lithium intercalation anode, a non-aqueous electrolyte including a lithium salt, a cathode containing as initial active material, orthorhombic LiMnO_2 characterized by the specific orthorhombic crystal structure described by the space group Pmm and unit cell dimensions $a=4.572$ Å, $b=5.757$ Å and $c=2.805$ Å,

(b) charging the cell to de-intercalate sufficient available lithium ions to convert the LiMnO_2 to spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$, and

(c) discharging the cell to intercalate sufficient available lithium ions to convert the spinel-type λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $1 \leq x \leq 2$ to spinel-related λ - $\text{Li}_{2-x}\text{Mn}_2\text{O}_4$ wherein $0 \leq x \leq 2$.

2. A method according to Claim 1, wherein the cell is charged to greater than 40% of the nominal cathode capacity.

3. A method according to Claim 2, wherein the cell is discharged to at least 30% of the nominal cathode capacity.

4. A method according to Claim 1, wherein the anode comprises a material selected from the group consisting of transition metal oxides, transition metal sulfides and carbonaceous materials, and wherein the electrolyte is in liquid form and includes an organic solvent.

5. A method according to Claim 4, wherein the lithium salt is selected from the group consisting of LiAsF_6 , LiPF_6 ,

LiBF₄, LiClO₄, LiBr, LiAlCl₄, LiCF₃SO₃, LiC(CF₃SO₂)₃,
LiN(CF₃SO₂)₂ and mixtures thereof, and wherein the organic
solvent is selected from the group consisting of propylene
carbonate, ethylene carbonate, 2-methyl tetrahydrofuran,
5 tetrahydrofuran, dimethoxyethane, diethoxyethane, dimethyl
carbonate, diethyl carbonate, methyl acetate, methyl
formate, γ -butyrolactone, 1,3-dioxolane, sulfolane,
acetonitrile, butyronitrile, trimethylphosphate,
dimethylformamide, and mixtures thereof.

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6. A method according to Claim 5, wherein the anode
comprises a carbonaceous material.

7. A method according to Claim 6, wherein the anode
15 comprises petroleum coke.

8. A method according to Claim 7, wherein the electrolyte
comprises 1M LiN(CF₃SO₂)₂ in a 50/50 mixture by volume of
propylene carbonate and dimethoxyethane.

20

9. A secondary lithium ion electrochemical cell,
comprising a lithium intercalation anode, a non-aqueous
electrolyte including a lithium salt, a cathode and a
separator between the anode and cathode, wherein the cathode
25 comprises as initial active material, a single phase
compound of formula LiMnO₂ characterized by the specific
orthorhombic crystal structure described by the space group
Pmmn and unit cell dimensions $a=4.572 \text{ \AA}$, $b=5.757 \text{ \AA}$ and
 $c=2.805 \text{ \AA}$ and by the x-ray diffraction pattern shown in
30 figures 1 and 2.

10. An electrochemical cell according to Claim 9, wherein
the initial cathode material comprises 80-94%/w of active
material, 5-15%/w of a conductivity enhancer, and 1-5%/w of

a binder.

11. An electrochemical cell according to Claim 10, wherein the conductivity enhancer is selected from the group
5 consisting of carbon black and graphite.

12. An electrochemical cell according to Claim 11, wherein the binder is selected from the group consisting of polyvinylidene difluoride and polytetrafluoroethylene.

10

13. An electrochemical cell according to Claim 9, wherein the anode comprises a material selected from the group consisting of transition metal oxides, transition metal sulfides and carbonaceous materials, and wherein the
15 electrolyte is in liquid form and includes an organic solvent.

14. An electrochemical cell according to Claim 13, wherein the lithium salt is selected from the group consisting of
20 LiAsF_6 , LiPF_6 , LiBF_4 , LiClO_4 , LiBr , LiAlCl_4 , LiCF_3SO_3 , $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{CF}_3\text{SO}_2)_2$, and mixtures thereof.

15. An electrochemical cell according to Claim 14, wherein the lithium salt is selected from the group consisting of
25 LiPF_6 and LiClO_4 .

16. An electrochemical cell according to Claim 15, wherein the solvent is a 50:50 mixture of propylene carbonate and dimethoxy ethane.

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17. An electrochemical cell according to Claim 15, wherein the carbonaceous material is isotropic graphite with a degree of graphitization greater than or equal to 0.4.

18. An electrochemical cell according to Claim 17, wherein the organic solvent is selected from the group consisting of a mixture of ethylene carbonate and diethyl carbonate, and a mixture of ethylene carbonate and dimethyl carbonate.

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19. An electrochemical cell according to Claim 14, wherein the organic solvent is selected from the group consisting of propylene carbonate, ethylene carbonate, 2-methyl tetrahydrofuran, tetrahydrofuran, dimethoxyethane, diethoxyethane, dimethyl carbonate, diethyl carbonate, methyl acetate, methylformate, γ -butyrolactone, 1,3-dioxolane, sulfolane, acetonitrile, butyronitrile, trimethylphosphate, dimethylformamide and mixtures thereof.

20. An electrochemical cell according to Claim 19, wherein the anode comprises a carbonaceous material.

21. An electrochemical cell according to Claim 20, wherein the anode comprises petroleum coke.

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22. An electrochemical cell according to Claim 21, wherein the electrolyte comprises 1 M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in a 50/50 mixture by volume of propylene carbonate and dimethoxyethane.

23. A secondary lithium ion electrochemical cell, comprising a lithium intercalation anode comprising petroleum coke, a non-aqueous electrolyte comprising 1M $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ in a 50/50 mixture by volume of propylene carbonate and dimethoxyethane, a cathode and a separator between the anode and cathode, wherein the initial cathode material comprises a dried slurry of orthorhombic LiMnO_2 characterized by the specific orthorhombic crystal structure described by the space group Pmmn and the unit cell dimensions $a=4.572 \text{ \AA}$, $b=5.757 \text{ \AA}$ and $c=2.805 \text{ \AA}$, and by the x-ray diffraction

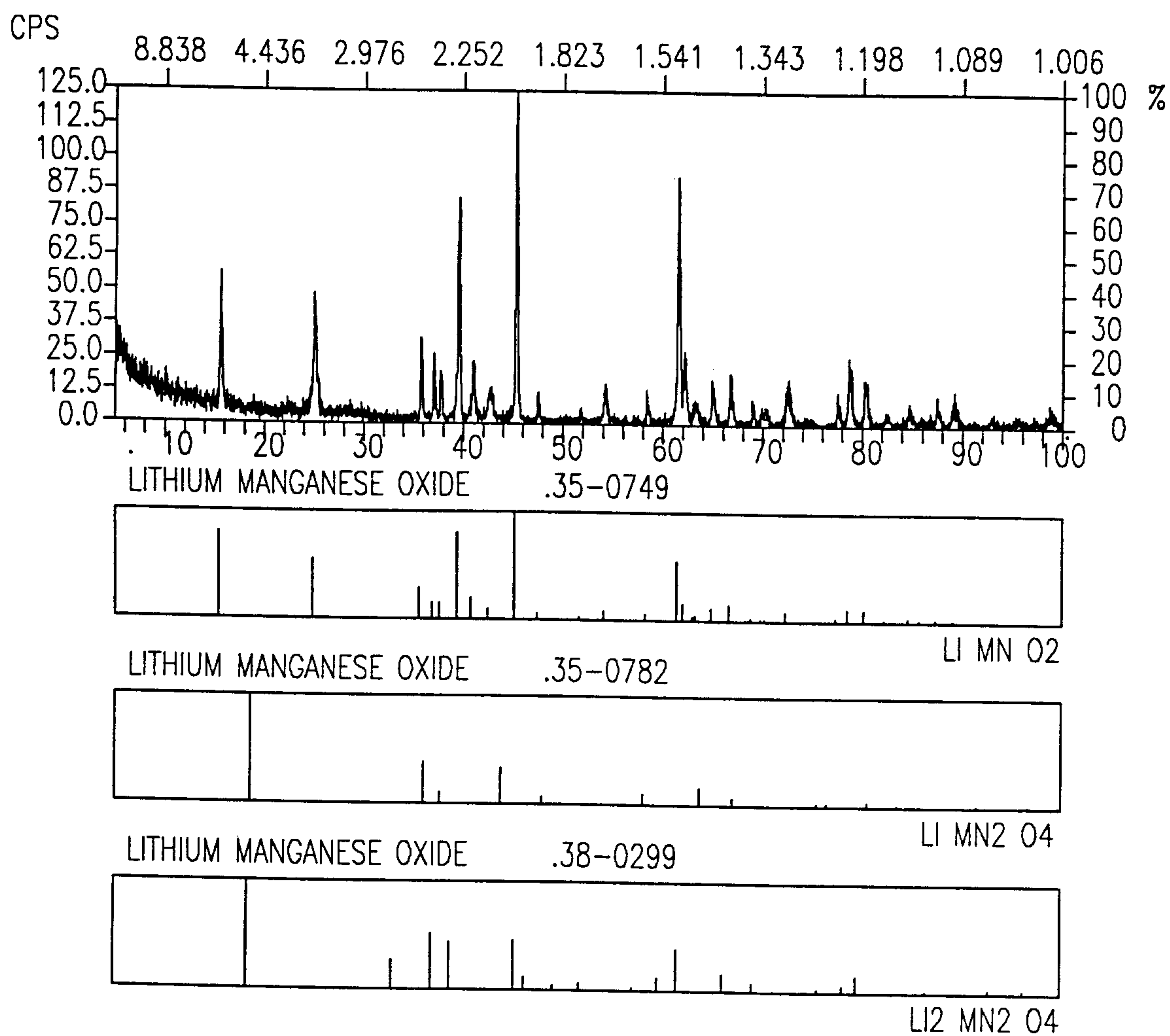
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pattern shown in figures 1 and 2 as active material, two weight percent of ethylenepropylenediene monomer and ten weight percent of carbon black, in cyclohexane.

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Figure 1

DATE:02/17/92 TIME:15:00 PT:1.80000 STEP:0.03000 WL:1.54060



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Figure 2

DATE:01/12/93 TIME:10:30 PT:0.90000 STEP:0.03000 WL:1.54060

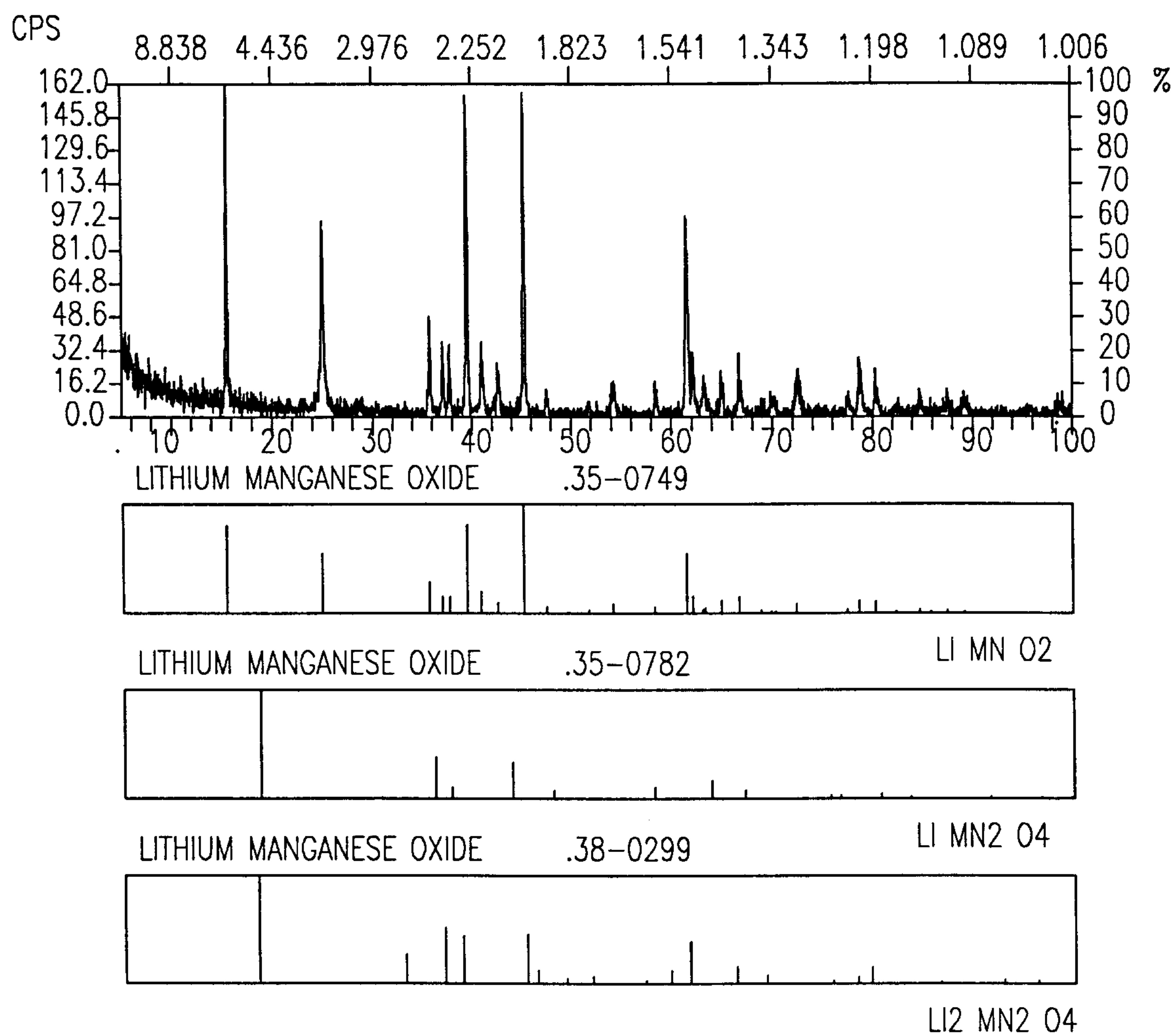


Figure 3

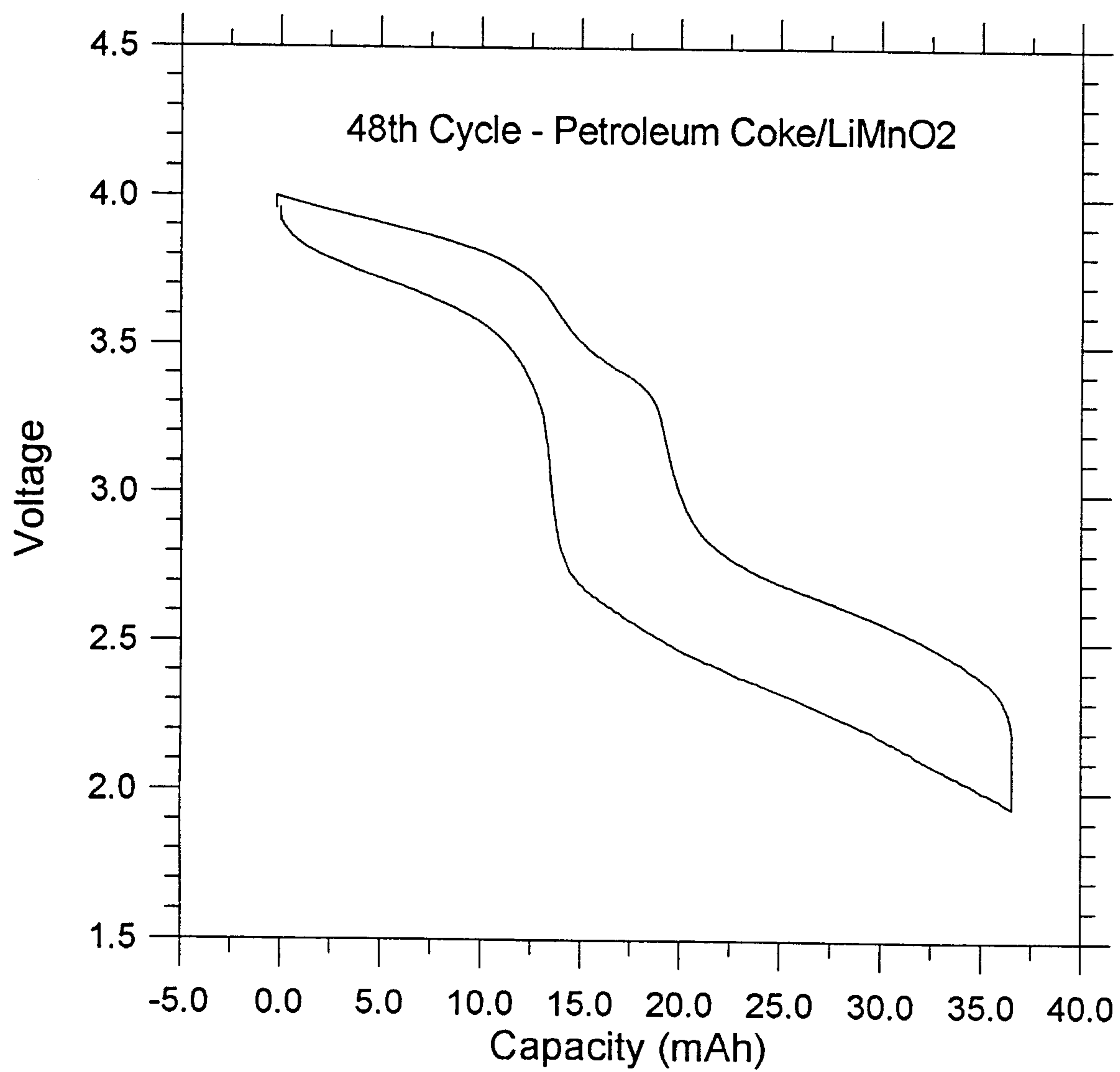
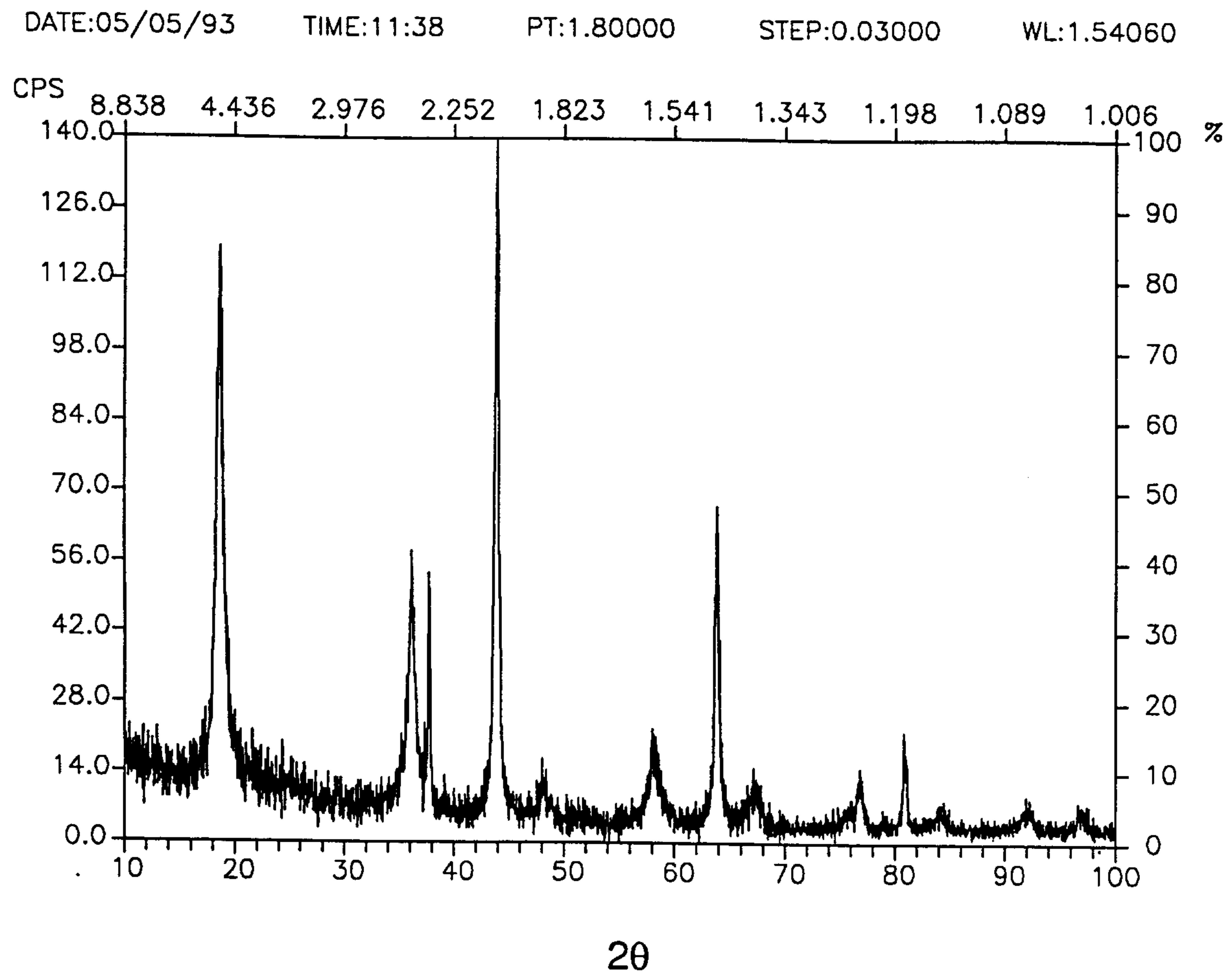


Figure 4



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Figure 5

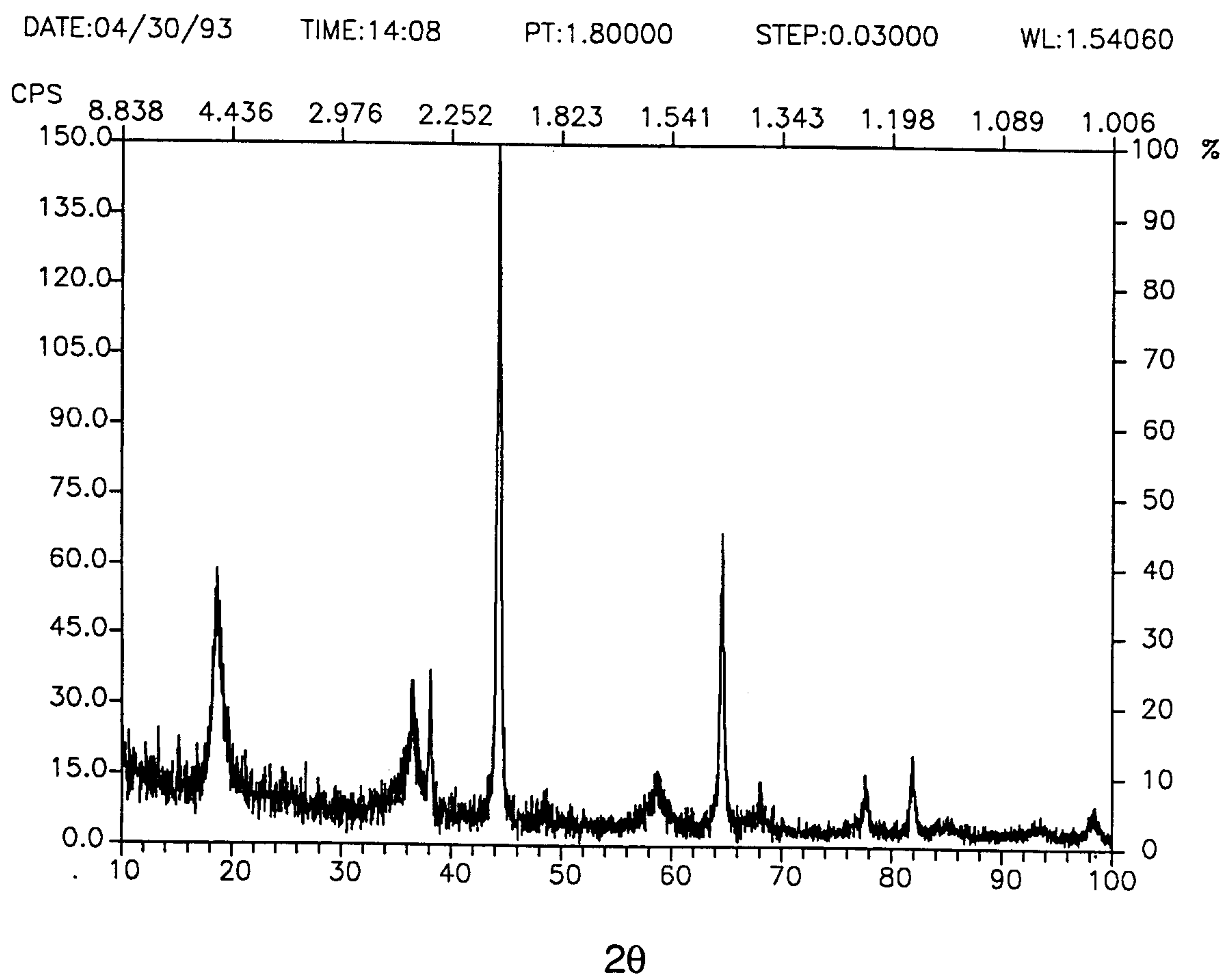


Figure 6

