



(86) Date de dépôt PCT/PCT Filing Date: 2002/06/26

(87) Date publication PCT/PCT Publication Date: 2003/01/30

(85) Entrée phase nationale/National Entry: 2003/12/30

(86) N° demande PCT/PCT Application No.: GB 2002/002905

(87) N° publication PCT/PCT Publication No.: 2003/009407

(30) Priorité/Priority: 2001/07/14 (0117235.2) GB

(51) Cl.Int.⁷/Int.Cl.⁷ H01M 4/50

(71) Demandeur/Applicant:

THE UNIVERSITY COURT OF THE UNIVERSITY OF
ST ANDREWS, GB

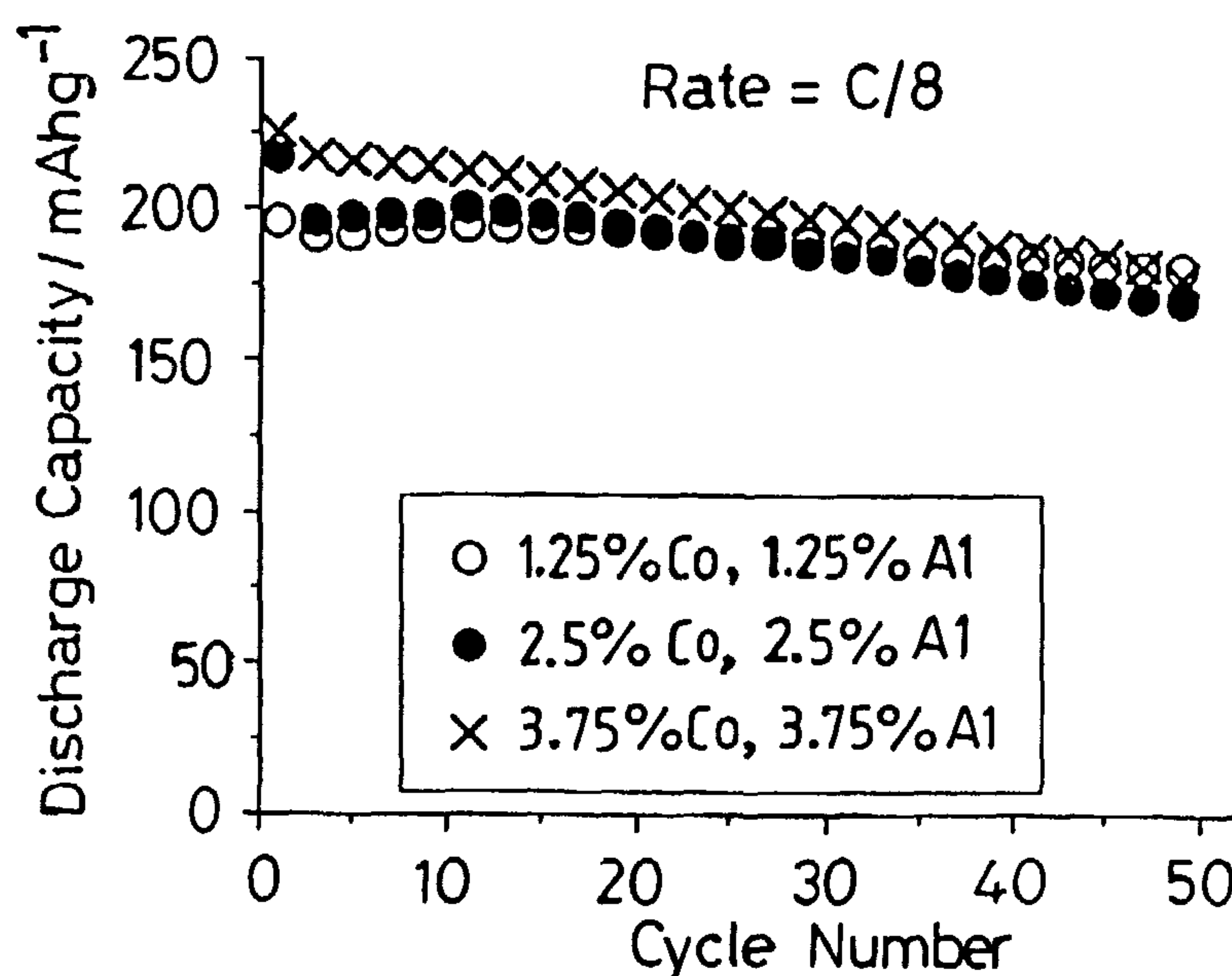
(72) Inventeurs/Inventors:

BRUCE, PETER GEORGE, GB;
ROBERTSON, ALASTAIR DOUGLAS, GB

(74) Agent: KIRBY EADES GALE BAKER

(54) Titre : AMELIORATIONS CONCERNANT DES CELLULES ELECTROCHIMIQUES

(54) Title: IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL CELLS



(57) Abrégé/Abstract:

There is provided a manganese oxide material, wherein the material comprises a host material $Q_qM_nM_zO_x$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In a particularly preferred material Q is Li and M is either Co, Ni, Al, or Li. Particularly preferred combinations of M and a dopant are Ni,Co; Al,Co; Li,Cu; Li,Al; and Li,Zn. A method of preparing the material is also disclosed.

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
30 January 2003 (30.01.2003)

PCT

(10) International Publication Number
WO 03/009407 A2

(51) International Patent Classification⁷: **H01M 4/50**

Fife DD6 8DU (GB). **ROBERTSON, Alastair, Douglas**
[GB/GB]; 71 Hogarth Drive, Cupar, Fife KY15 5YU (GB).

(21) International Application Number: PCT/GB02/02905

(74) Agent: **KEITH W NASH & CO**; 90-92 Regent Street,
Cambridge CB2 1DP (GB).

(22) International Filing Date: 26 June 2002 (26.06.2002)

(25) Filing Language: English

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(26) Publication Language: English

(30) Priority Data:
0117235.2 14 July 2001 (14.07.2001) GB

(71) Applicant (*for all designated States except US*): **THE UNIVERSITY COURT OF THE UNIVERSITY OF ST ANDREWS** [GB/GB]; College Gate, North Street, St Andrews, Fife KY16 9AJ (GB).

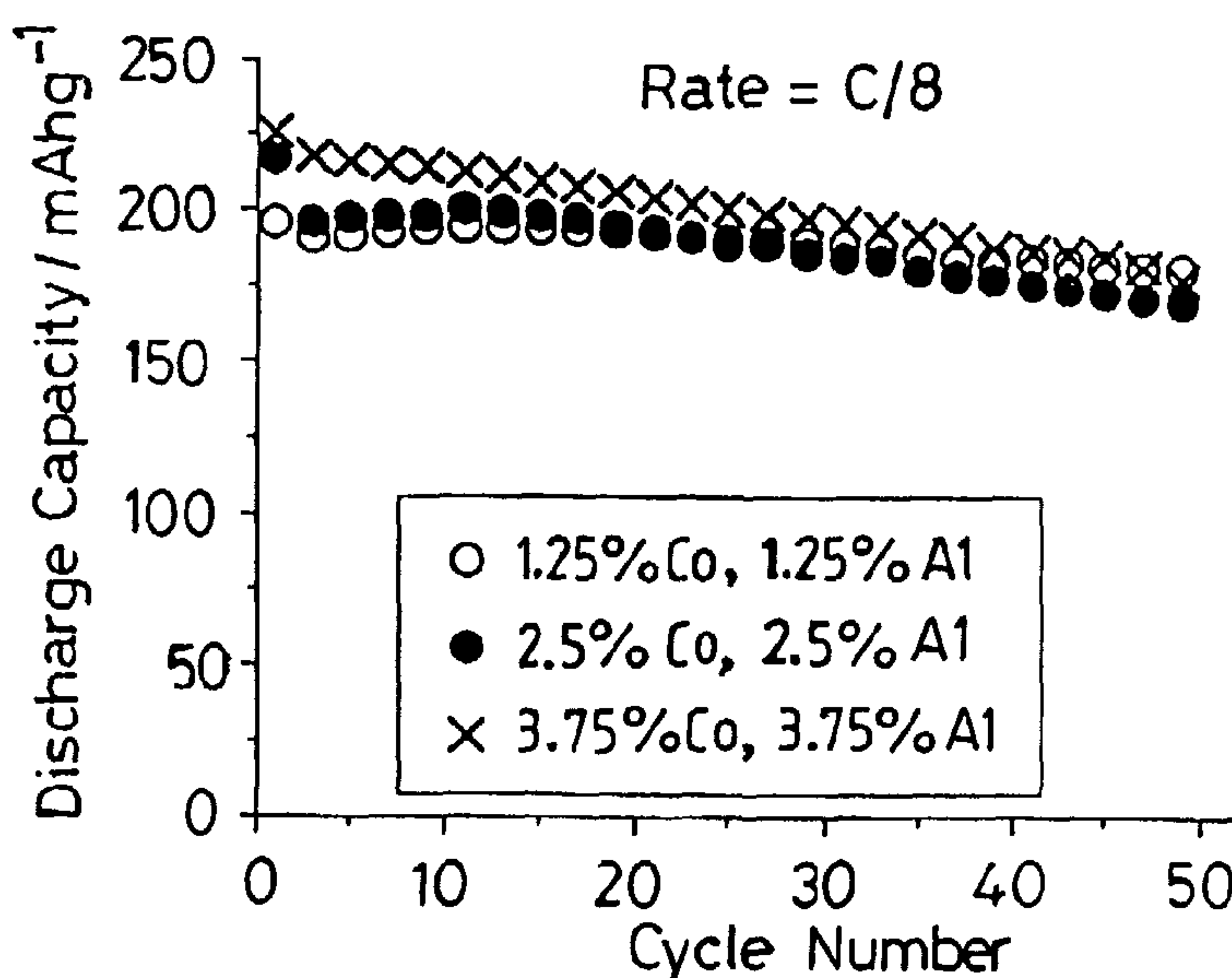
(84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(72) Inventors; and

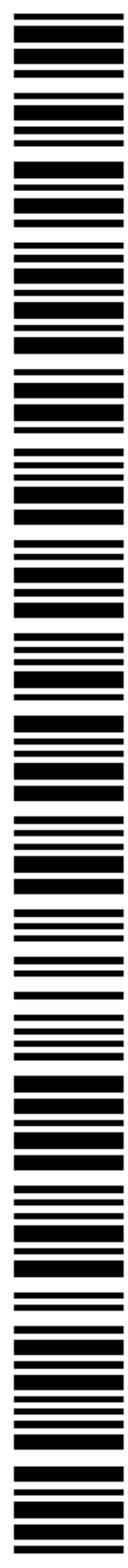
(75) Inventors/Applicants (*for US only*): **BRUCE, Peter, George** [GB/GB]; 14 Linden Avenue, Newport-on-Tay,

[Continued on next page]

(54) Title: IMPROVEMENTS IN OR RELATING TO ELECTROCHEMICAL CELLS



(57) Abstract: There is provided a manganese oxide material, wherein the material comprises a host material $Q_qMn_yM_zO_x$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In a particularly preferred material Q is Li and M is either Co, Ni, Al, or Li. Particularly preferred combinations of M and a dopant are Ni,Co; Al,Co; Li,Cu; Li,Al; and Li,Zn. A method of preparing the material is also disclosed.



WO 03/009407 A2

WO 03/009407 A2



Published:

— *without international search report and to be republished
upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Title: Improvements in or Relating to Electrochemical Cells**Field of Invention**

This invention concerns electrochemical cells and relates to material with a layered structure for use in such cells, a method for producing the layered materials, and a cell having the layered materials as the positive electrode.

Background to the Invention

Electrochemical cells generally have a negative electrode, a positive electrode, and an electrolyte placed between the electrodes. The electrolyte is chosen so that transfer of ions between the two electrodes occurs, thus producing an electrical current. One example of an electrochemical cell is a rechargeable battery. The use of layered materials such as lithium cobalt oxide, LiCoO_2 , as the positive electrode in such a rechargeable battery is well established. The layered material consists of sheets of oxygen ions stacked one on top of the other. Between the first and second layers of oxygen are located the cobalt ions, with the lithium ions being located between the second and third oxygen layers. Use of LiCoO_2 in rechargeable batteries allows greater energy storage per unit weight and volume than is possible in conventional rechargeable batteries such as nickel-cadmium. However LiCoO_2 has disadvantages in that it is somewhat toxic, is less safe than is desirable, has limited energy storage capacity, and the cobalt containing materials from which it is produced are expensive and scarce.

Attempts have been made to use other compounds with a similar layered structure to that of, LiCoO_2 , such as LiNiO_2 , and LiFeO_2 . EP 0 017 400 discloses a range of compounds having layers of the $\alpha\text{-NaCrO}_2$ structure. In an International Patent Application, Publication No. WO97/26683, we disclosed the synthesis and viability of materials of the form $\text{Q}_q\text{M}_y\text{M}_z\text{O}_2$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and the material is a layered structure.

It is one aim of the present invention to provide a further layered manganese oxide material which can be used in electrochemical cells.

Summary of the Invention

According to one aspect of the present invention, there is provided a manganese oxide material, wherein the material comprises a host material $Q_qMn_yM_zO_x$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure. Any number of dopants may be substituted into the host material, with the number of simultaneously occurring dopants possible only being restricted by the requirement to retain a layered structure. Such a material may be written as $Q_qMn_yM_zA_aB_bC_c\dots\gamma_nO_x$, where A, B, C.... γ_n are dopants. Typically for such a material the values of z, a, b, c,...,n will be chosen to sum equal to one.

A layered structure is one in which the ions are arranged in a series of generally planar layers, or sheets, stacked one on top of another. In general, each layer contains ions of one particular element. Thus, when z is equal to zero and q is greater than zero, the layering will consist of sheets of oxide ions which are separated by alternating layers of Q ions and Mn ions, i.e. the layers order as a layer of oxide ions, a layer of Mn ions, a layer of oxide ions, a layer of Q ions and a layer of oxide ions; this is repeated throughout the structure.

Q is preferably chosen from Group I elements, i.e. K, Li, Rb, and in a particularly preferred material is Li so that the host material is of the form $Li_wMn_yM_zO_x$, where w is any number greater than zero.

Where z is not equal to zero, the M ions will occupy sites in the Mn layers, and if desired M within the host material can be viewed as a first dopant with at least one further dopant being substituted within the material.

Where z is not equal to zero, the element M is typically chosen from Group II elements, the transition elements or from Group III elements. Suitable elements include Be, Mg, Ca, Sc,

Ti, V, Cr, Fe, Co, Ni, Cu, Zn, Al, Ga, P. However Group I elements such as Li may also be used as a dopant.

In a particularly preferred material according to the invention, Q is Li and M is either Co, Ni, Al, or Li.

Preferably at least one dopant is chosen from Group II elements, the transition elements or from Group III elements. Suitable elements include Ni, Al, Co, Mg, Zn and Cu.

Particularly preferred combinations of M and a dopant are Ni, Co; Al, Co; Li, Co; Li, Ni; Li, Mg; Li, Cu; Li, Al; and Li, Zn.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing an intermediate material $X_xMn_yM_zA_aB_bO_x$ (or any number of elements n additional to M, A and B), where X is a Group I element not being lithium, M, A and B are any element, a, x and y are each any number greater than zero, and z, and b are any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form $Li_wMn_yM_zA_aB_bO_x$, where w is any number greater than zero, and the material has a layered structure. If M is to be incorporated, then z is chosen to be greater than zero.

Preferably X is chosen to be Na, so that the intermediate material is of the form $Na_xMn_yM_zA_aB_bO_x$.

The reactant may be any suitable lithium salt, such as LiBr or LiCl. Preferably the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux. Typically n-pentanol, n-hexanol, ethanol or n-octanol are used as the reflux agent, with the reflux period being 96 hours.

In a particularly preferred exchange reaction, the ion exchange occurs at room temperature and in water.

According to a further aspect of the invention, there is provided a method of preparing a manganese oxide material of the invention, comprising processing a precursor material $Q_qMn_yM_zA_aB_bO_x$, where Q and M are each any element, q and y are each any number greater than zero, z and b are any number greater than or equal to zero, and a is greater than zero by carrying out an ion removal reaction, so as to remove Q and produce a material of the form $Mn_yM_zA_aB_bO$, with a layered structure.

Ion removal is conveniently achieved by electrochemical extraction, using the precursor material as the working electrode in an electrochemical cell. This is of particular advantage in preparation of materials of the form $Mn_yM_zA_aB_bO_x$. For preparation of these materials, Q is preferably chosen from the Group I or Group II elements, such as Na, K, Rb, Mg or Ca. The $Mn_yM_zA_aB_bO_x$ may be subsequently processed to insert lithium so as to produce $Li_wMn_yM_zA_aB_bO_x$.

According to another aspect of the invention, there is provided an electrochemical cell, wherein the positive electrode is of the form $Li_qMn_yM_zA_aB_bO_x$ where M, A and B are any elements, x, y, z and a are any number greater than zero, and q and b are each any number greater than or equal to zero. The use of the manganese in the electrode avoids the need for use of cobalt or nickel which is of advantage as manganese is less toxic, safer, more abundant and cheaper than cobalt and nickel.

A rechargeable battery is an example of an electrochemical cell with which the invention may be used.

The invention will now be described by way of example, and with reference to the accompanying Figures in which:

Figures 1(a) and 1(b) show the observed diffraction data of a material according to the invention, where M is Li and the dopant is Co, Figure 1(a) being an X-ray diffraction trace and Figure 1(b) a neutron diffraction trace;

Figure 2 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Ni and the dopant Co;

Figure 3 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Co and the dopant Al; and Figure 4 shows the discharge capacity of a cell incorporating a further material according to the invention on successive discharge cycles, where M is Li and the dopant is either Cu or Al or Zn.

Description

The preparation of materials of the form $Q_qMn_yM_zO_2$ incorporating one or more dopants, and the experimental verification of the structure of such materials and their properties as an electrode for an electrochemical cell will be described. If desired, one can view $Q_qMn_yO_2$ as the base or host material into which M and or at least one other dopant are substituted, producing a double dopant system. However substitution is only limited by the requirement to have a layered structure, and multiple dopants can be substituted into the original structure.

Preparation

Preparation of the materials requires two stages:

- 1) The preparation of the intermediate material, sodium manganese oxide, $NaMnO_2$ combined with the dopants, i.e. of the form $Na_qMn_yM_zA_aB_bO_x$, where A is one additional dopant, and B is another additional dopant; and
- 2) Ion exchange reaction.

Stage 1

(a) Solid State Preparation

Appropriate quantities of the Na source such as Na_2CO_3 , a Manganese oxide such as Mn_2O_3 , MnO or MnO_2 and oxides of the dopant elements are weighed out and intimately ground together with or without a dispersant such as acetone. As will be apparent to a person skilled in the art, $NaOH$, $Na(CH_3CO_2)$ or any other solid Na compound which decomposes on heating to yield the oxide can be used instead of Na_2CO_3 , and any solid Mn source which decomposes on heating to yield the oxide can be used to provide a source of Mn. Any

source of the elements M, A, B etc. which decomposes on heating to yield the oxide can be used to supply the dopants.

The resulting homogenous mixture of Na source, Mn source and dopant sources is heated in a furnace until a material of the form $\text{Na}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$ is produced. Whether an air, reducing or oxidising atmosphere is required within the furnace depends on the elements M, A, B and the furnace heating and cooling characteristics chosen will depend on M, A and B. Typically temperatures of between 250°C and 1500°C are chosen for anything between 1-96 hours and the samples may be furnace cooled or cooled more quickly.

The intermediate material can also be prepared from solution, and where required solution preparation is as follows.

(b) Solution Preparation

Suitable salts of Na, Mn, M, A, B etc. which are soluble in H_2O , ethanol, n-hexanol or similar solvents, for example Na_2CO_3 , NaCH_3CO_2 , $\text{Mn}(\text{CH}_3\text{CO}_2)_2$ and $\text{A}(\text{CH}_3\text{CO}_2)_n$, $\text{B}(\text{CH}_3\text{CO}_2)_s$ are weighed out and added to the solvent. After mixing, the solvent is removed by heating and if required using reduced pressure. The resulting homogenous mixture is then heated at a low temperature between 80-150°C for between 1-5 hours, and then at temperatures between 250-1500°C for 1-96 hours in air, or if appropriate depending on the combination of elements M, A, B in a more reducing or more oxidising atmosphere. As before the samples may be furnace cooled or cooled more quickly, such as by air cooling.

Stage 2

An excess, typically 8-15 fold of a Lithium salt such LiBr , LiCl or LiNO_3 , is added to a solvent such as ethanol, butanol, n-hexanol, n-octanol, acetonitrile, water or a combination of some of these. To this mixture is added the intermediate material prepared either by solid state reaction or from solution as above, and the various constituents allowed to react for between 6 and 96 hours at a suitable temperature. Where the reaction is carried out at elevated temperatures, then a condenser is fitted permitting reflux. For example ion exchange in ethanol may be carried out by refluxing at 80°C or in the case of n-hexanol 160°C. Particularly of interest is that the ion exchange reaction is possible at room

temperature and in water. After reaction the mixture is subjected to filtration under suction and then washed with a solvent used for exchange, typically alcohol or alcohol and water, before being dried.

Alternatively ion exchange is carried out in a molten salt containing a Lithium source. For this, the sample is mixed with the ion exchange medium and heated until the medium is molten. The temperature is maintained for 1-96 hours until exchange is complete. After cooling the ion exchange medium is removed by washing in H₂O, alcohol or other solvent. The resulting material is dried by heating under vacuum.

The structure of the resultant product was then examined by X-ray diffraction or by neutron diffraction. Determination of the structure by neutron diffraction requires the observed diffraction data from a representative sample of the product to be compared to theoretical diffraction data for a variety of structural models. The correct structural model produces the best fit between theoretical and observed data. Typically trial models are selected by looking at the structures of similar families of compounds, or from the structures of the compounds that formed the product.

Time-of-flight powder neutron diffraction data were collected on the POLARIS high intensity, medium resolution diffractometer at the ISIS pulsed source at the Rutherford Appleton Laboratory. Data from the highest resolution backscattering bank of detectors were used for structural analysis.

Figure 1(a) shows the X-ray diffraction pattern of $\text{Li}_x\text{Mn}_{0.95}\text{Li}_{0.025}\text{Co}_{0.025}\text{O}_2$, with thus M being Li and the additional dopant being Co and Figure 1(b) shows the neutron diffraction pattern of the same compound. Various other combinations of dopants have been investigated including the following (where the first element is equivalent to M in the general formula given above and the second element the additional dopant): Co, Ni; Co, Al; Li, Co; Li, Ni; Li, Al; Li, Mg; Li, Zn; Li, Cu.

The materials produced in accordance with the present invention have a layered structure in which the Mn, Li and O ions are arranged separately in a series of generally planar layers, or

sheets, stacked one on top of another, with the dopants substituting into these layers. Generally the dopants substitute randomly into the Mn layers, although some of the dopant ions may be present in the Li layers. The layering will thus consist of sheets of oxide ions which are separated by alternating layers of Li ions and Mn ions, i.e. the layers order as a layer of oxide ions, a layer of Mn ions, a layer of oxide ions, a layer of Q ions and a layer of oxide ions; this is repeated throughout the structure.

The layered structure possesses a crystal symmetry lower than rhombohedral and is generally monoclinic. The monoclinic structure possesses one 2-fold axis and/or one plane of symmetry, its unit cell possessing three unequal axes, one axis being perpendicular to the other two axes which are inclined at an oblique angle. In such a structure the Mn ions are not equally spaced from all nearest neighbour oxide ions, i.e. the three oxide ions in the adjacent upper layer and the three oxide ions in the adjacent lower layer, but rather are distorted from equal spacing so that the Mn-O bond distance varies. An equivalent view of this is that the layered structure comprises layers of MnO₆ polyhedra separated by layers of other ions, for example lithium ions.

Lattice parameter data for selected materials are given below:

Nominal y	a/ Angstrom	c/Angstrom	c/a
0.025	2.8652 (4)	14.674 (2)	5.121
0.05	2.8731 (3)	14.638 (1)	5.095
0.10	2.8667 (3)	14.612 (2)	5.097
0.20	2.8699 (3)	14.620 (1)	5.094

Table 1: Lattice parameter data for Li_xMn_{1-y}Ni_{y/2}Co_{y/2}O₂ system

Nominal y	a/ Angstrom	c/Angstrom	c/a
0.05	2.8672 (3)	14.618 (1)	5.098

Table 2: Lattice parameter data for Li_xMn_{1-y}Li_{y/2}Ni_{y/2}O₂ system

Nominal y	a/ Angstrom	C/Angstrom	c/a
0.05	2.8614 (3)	14.614 (1)	5.107

Table 3: Lattice parameter data for $\text{Li}_x\text{Mn}_{1-y}\text{Li}_{y/2}\text{Co}_{y/2}\text{O}_2$ system

Nominal y	a/ Angstrom	C/Angstrom	c/a
0.05	2.8690 (4)	14.641 (2)	5.103

Table 4: Lattice parameter data for $\text{Li}_x\text{Mn}_{1-y}\text{Li}_{y/2}\text{Mg}_{y/2}\text{O}_2$ system

The performance of various materials in accordance with the present invention in an electrochemical cell is shown in Figures 2 to 4. These Figures show the discharge capacity of the material used in an electrolytic cell during successive discharge cycles. The cell was cycled at 30° C at a constant current C of 0.5mAcm^{-2} between the potential limit 2.4 and 4.6 V to simulate the behaviour of a rechargeable battery. These Figures demonstrate that lithium can be chemically or electrochemically extracted from and reinserted into these materials, i.e. it is an intercalation/insertion electrode.

Figure 2 shows the discharge capacity in mAhg^{-1} over 150 cycles at C/8 and 1C for $\text{Li}_x\text{Mn}_{0.95}\text{Ni}_{0.025}\text{Co}_{0.025}\text{O}_2$, i.e. where M is Ni and the additional dopant is Co.

Figure 3 shows the discharge capacity in mAhg^{-1} over 50 cycles at C/8 for $\text{Li}_x\text{Mn}_{1-y}\text{Co}_{y/2}\text{Al}_{y/2}\text{O}_2$, i.e. where M is Co and the additional dopant is Al, for varying percentages of Co and Al. The discharge capacity is similar for all three compositions shown and is similar to the discharge at C/8 for $\text{Li}_x\text{Mn}_{0.95}\text{Ni}_{0.025}\text{Co}_{0.025}\text{O}_2$.

Figure 4 shows the discharge capacity in mAhg^{-1} over 150 cycles at a rate of C/4/ 50mA g^{-1} between voltage limits of 2.4-4.6V for $\text{Li}_x\text{Mn}_{0.95}\text{M}_{0.025}\text{A}_{0.025}\text{O}_2$, i.e. where M is Li and the additional dopant A is Cu, or Al or Zn. Better discharge properties are seen for the materials having the dopant pairs Li, Cu and Li Al.

Claims

1. A manganese oxide material, wherein the material comprises a host material $Q_qMn_yM_zO_x$, where Q and M are each any element, y is any number greater than zero, and q and z are each any number greater than or equal to zero, and at least one dopant substituted into the host material, the manganese oxide material having a layered structure.
2. A manganese oxide material according to claim 1, wherein Q is chosen from Group I elements.
3. A manganese oxide material according to claim 2, wherein Q is Li and the host material is of the form $Li_wMn_yM_zO_x$, where w is any number greater than zero.
4. A manganese oxide material according to any of the preceding claims, wherein the element M is chosen from Group I, Group II elements, the transition elements or from Group III elements.
5. A manganese oxide material according to any of the preceding claims, wherein Q is Li and M is either Co, Ni, Al, or Li.
6. A manganese oxide material according to any of the preceding claims, wherein at least one dopant is chosen from Group II elements, the transition elements or from Group III elements.
7. A method of preparing a manganese oxide material comprising processing an intermediate material $X_xMn_yM_zA_aB_bO_x$ (or any number of elements n additional to M, A and B), where X is a Group I element not being lithium, M, A and B are any element, a, x and y are each any number greater than zero, and z and b are any number greater than or equal to zero, by an ion exchange reaction with a reactant containing lithium ions, so as to replace X with lithium and produce a material of the form $Li_wMn_yM_zA_aB_bO_x$, where w is any number greater than zero, and the material has a layered structure.

8. A method according to claim 7, wherein X is Na, so that the intermediate material is of the form $\text{Na}_x\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$.
9. A method according to claim 7 or claim 8, wherein the ion exchange reaction is achieved by heating the reactant and intermediate material under reflux.
10. A method according to claim 9, wherein the ion exchange reaction occurs at room temperature and in water.
11. A method of preparing a manganese oxide material comprising processing a precursor material $\text{Q}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$, where Q and M are each any element, q and y are each any number greater than zero, z and b are any number greater than or equal to zero, and a is greater than zero by carrying out an ion removal reaction, so as to remove Q and produce a material of the form $\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}$, with a layered structure.
12. A method according to claim 11, wherein ion removal is conveniently achieved by electrochemical extraction, using the precursor material as the working electrode in an electrochemical cell.
13. An electrochemical cell, wherein the positive electrode is of the form $\text{Li}_q\text{Mn}_y\text{M}_z\text{A}_a\text{B}_b\text{O}_x$ where M, A and B are any elements, x, y, z and a are any number greater than zero, and q and b are each any number greater than or equal to zero.
14. A rechargeable battery comprising an electrochemical cell according to claim 13.

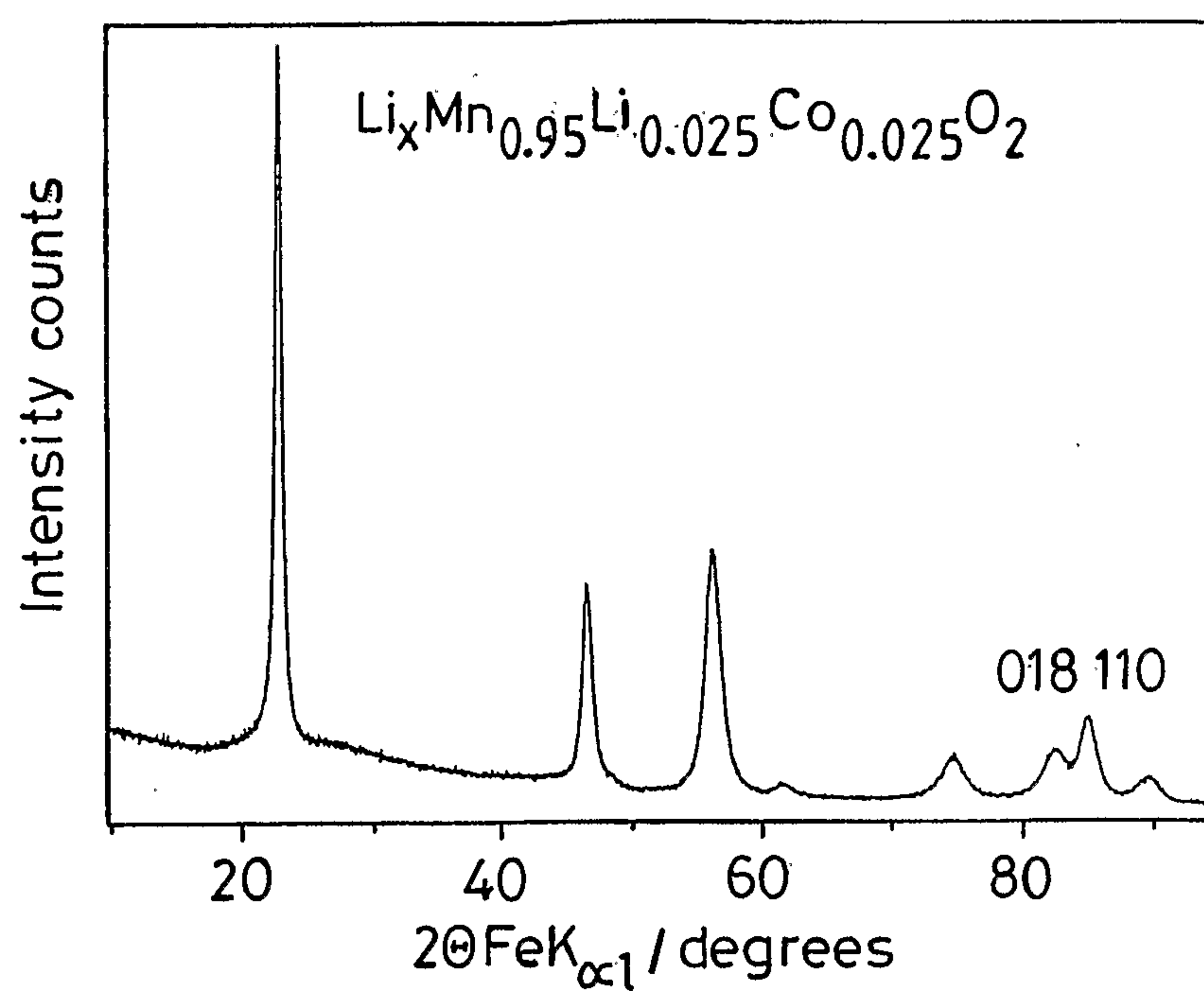


Fig. 1(a)

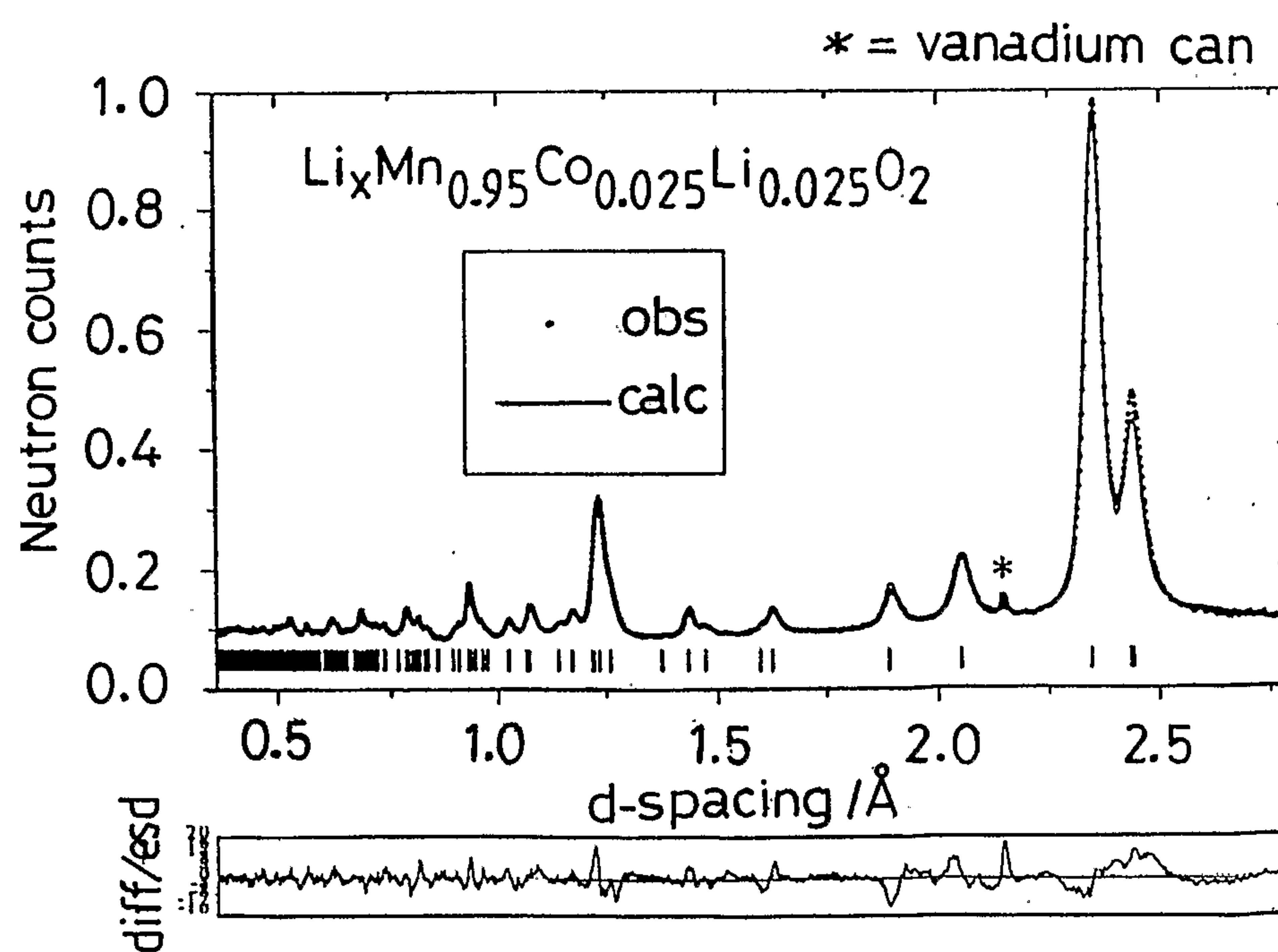


Fig. 1(b)

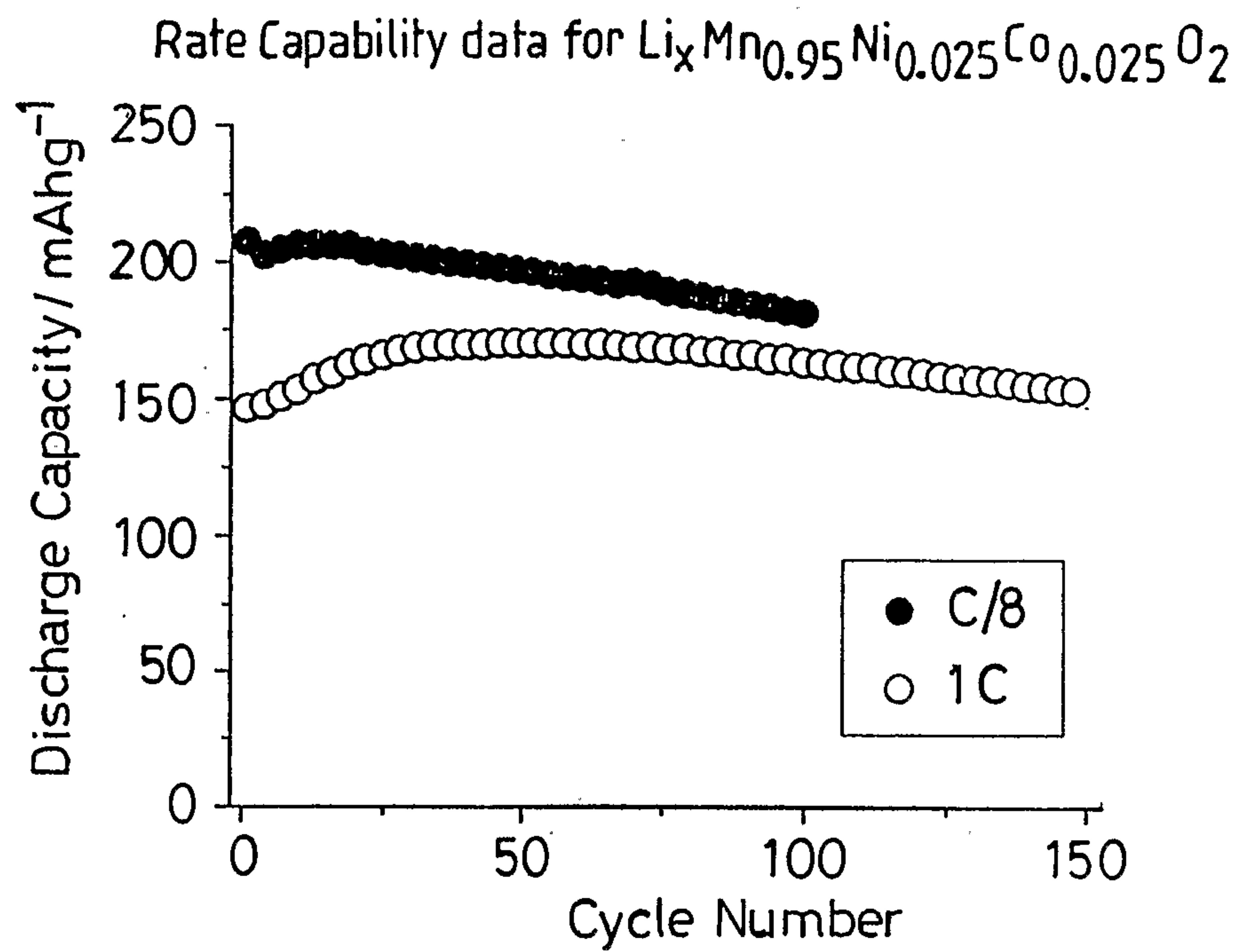


Fig. 2

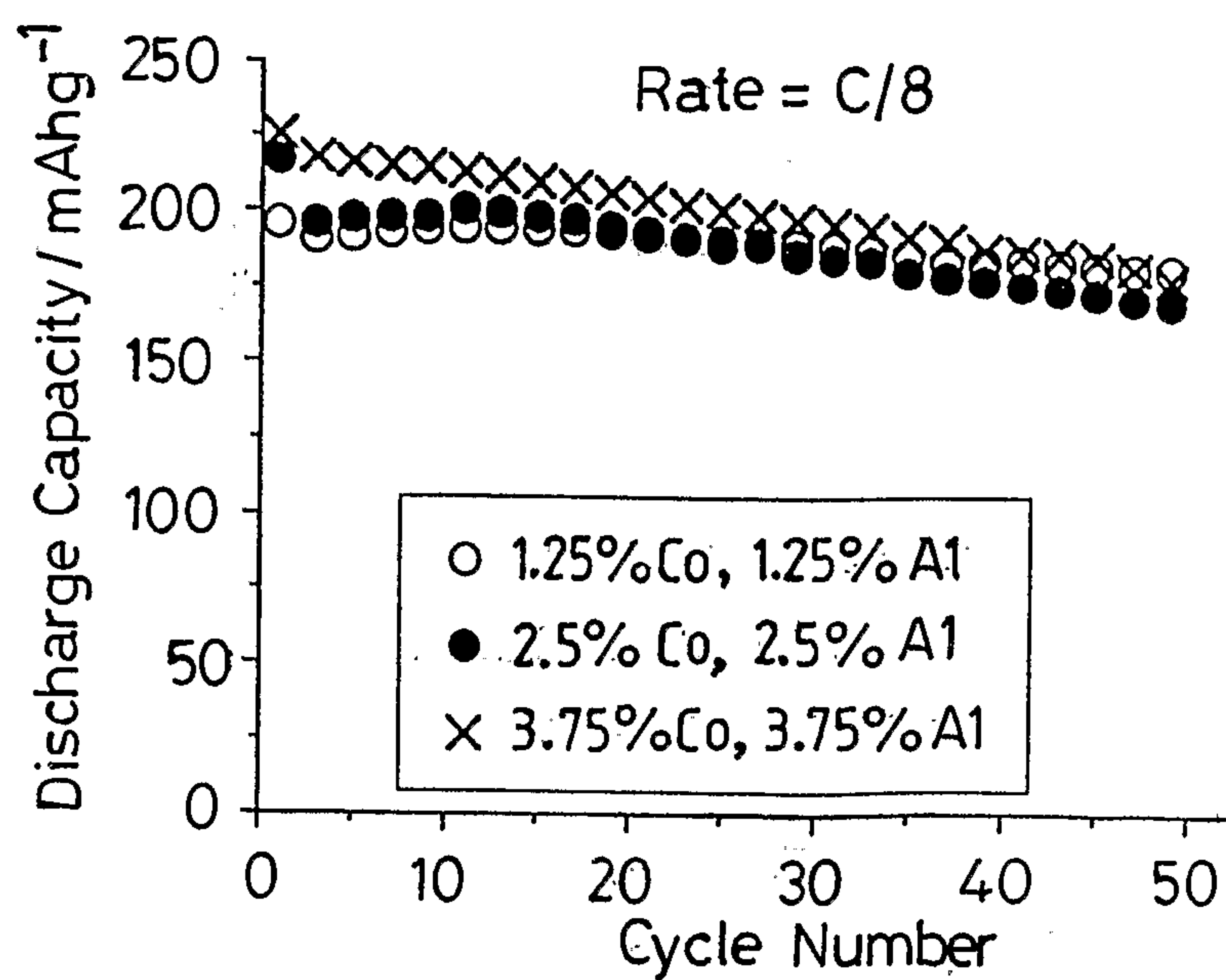


Fig. 3

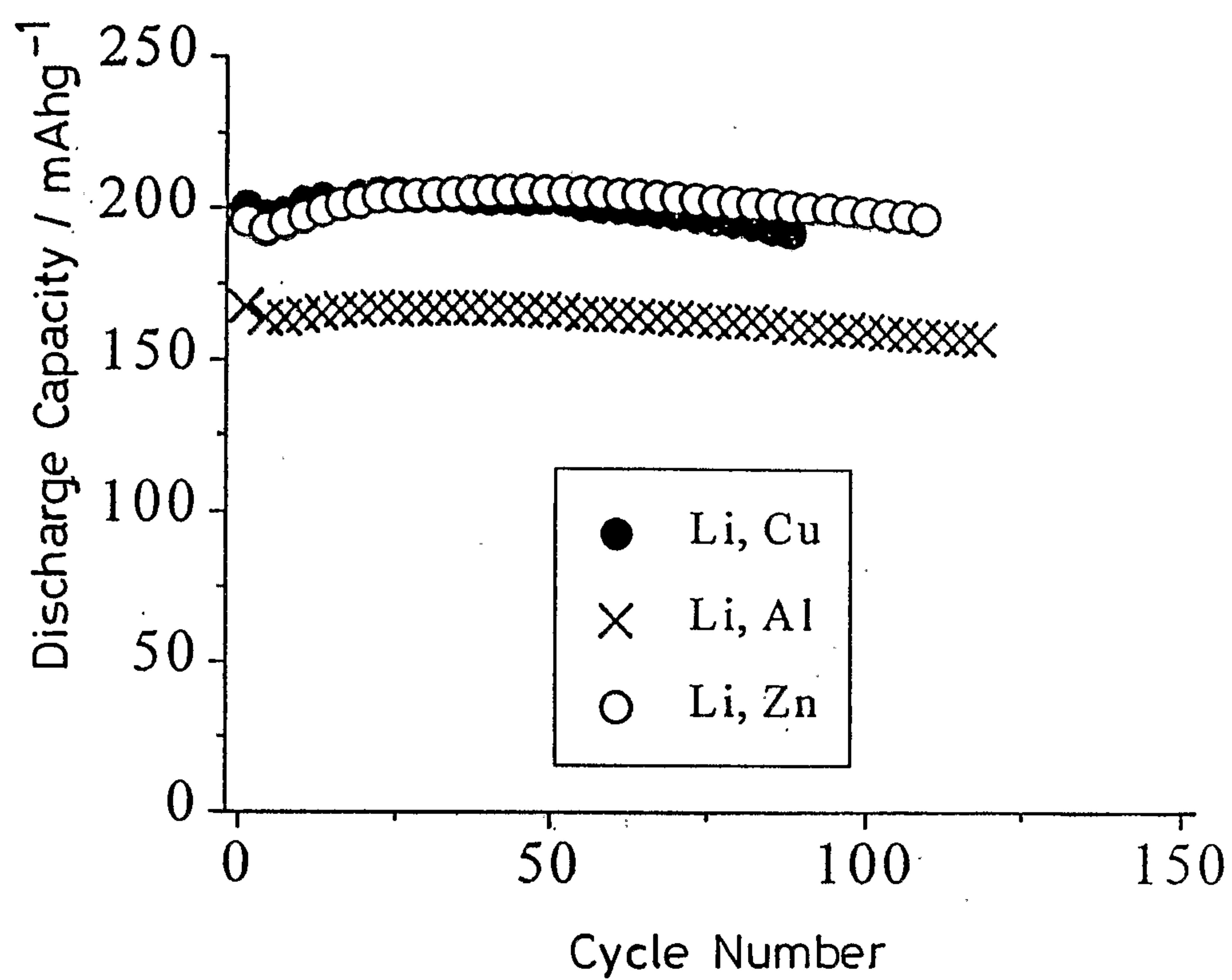


Fig. 4

