US006677082B2

(12) **United States Patent**
Thackeray et al.

(10) **Patent No.: US 6,677,082 B2**
(45) **Date of Patent: Jan. 13, 2004**

(54) **LITHIUM METAL OXIDE ELECTRODES FOR LITHIUM CELLS AND BATTERIES**

(75) Inventors: **Michael M. Thackeray**, Naperville, IL (US); **Christopher S. Johnson**, Naperville, IL (US); **Khalil Amine**, Downers Grove, IL (US); **Jaekook Kim**, Naperville, IL (US)

(73) Assignee: **The University of Chicago**, Chicago, IL (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 120 days.

(21) Appl. No.: **09/887,842**

(22) Filed: **Jun. 21, 2001**

(65) **Prior Publication Data**

US 2002/0136954 A1 Sep. 26, 2002

Related U.S. Application Data

(60) Provisional application No. 60/213,618, filed on Jun. 22, 2000.

(51) **Int. Cl.**[7] **H01M 4/50**

(52) **U.S. Cl.** **429/224**; 429/223; 429/231.1; 429/231.6; 429/231.3; 423/599

(58) **Field of Search** 429/231.1, 223, 429/224, 218.1, 231.6, 231.3; 423/599

(56) **References Cited**

U.S. PATENT DOCUMENTS

5,153,081	A	10/1992	Thackeray et al.	
5,393,622	A	2/1995	Nitta et al.	
6,017,654	A *	1/2000	Kumta et al.	429/231.95
6,221,531	B1	4/2001	Vaughey et al.	
6,551,743	B1 *	4/2003	Nakanishi et al.	429/223
2002/0136954	A1	9/2002	Thackeray et al.	
2003/0022063	A1	1/2003	Paulsen et al.	
2003/0027048	A1	2/2003	Lu et al.	

FOREIGN PATENT DOCUMENTS

WO WO 00/23380 * 4/2000

OTHER PUBLICATIONS

Material Res. Bulletin vol. 15, pp. 783–789, 1980, "A New Cathode Material for Batteries of High Energy Density", K. Mizushima et al.

Electrochemical Society vol. 144, No. 8, Aug. 1997, Morphology Effects on The Electrochemical Performance of . . . , W. Li et al., pp. 2773–2779.

Electrochemical and Solid State . . . 117–119 (1998) Novel . . . Compounds as Cathode Material for Safer Lithium–Ion Batteries, Yuan Gao et al.

Journal of Power Sources 90 (2000) 76–81, "Lithium Nickelate Electrodes With Enhanced . . . Thermal Stability," Hajime Arai et al.

Electrochemical Society vol. 144, Sep., 9, 1997, Electrochemical and Thermal Behavior of . . . , Hajime Arai et al., pp. 3117–3125.

Nature, vol. 381, Jun. 6, 1996, Synthesis of Layered . . . Lithium Batteries, A. Robert Armstrong et al. pp. 499–500.

Mat. Res. Bull. vol. 26, pp. 463–473, 1991, Lithium Manganese Oxides From . . . Battery Applications, M.H. Rossouw et al.

Journal of Solid State Chemistry, 104, 464–466 (1993), Synthesis and Structural Characterization . . . Lithiated Derivative . . . , M.H. Rossouw et al.

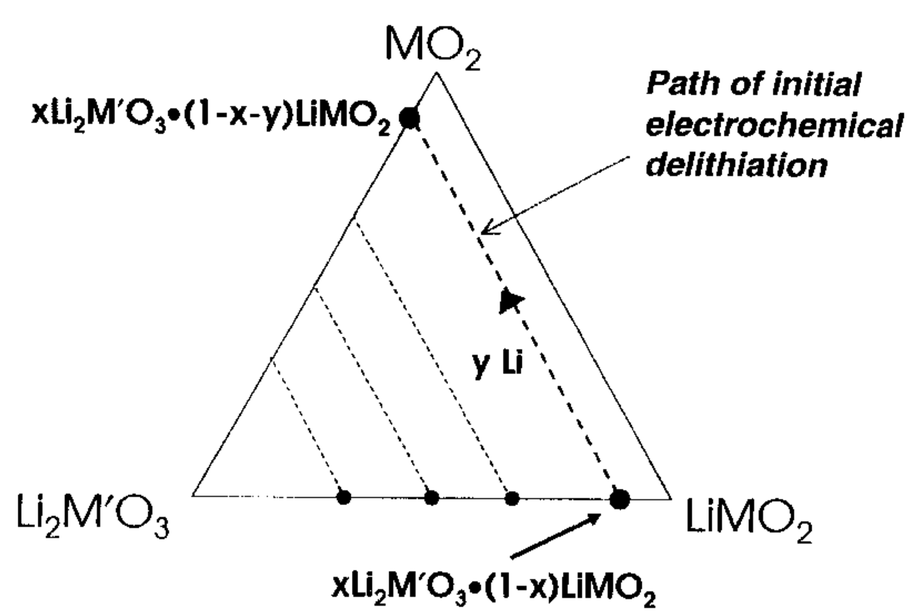
(List continued on next page.)

Primary Examiner—Laura Weiner
(74) *Attorney, Agent, or Firm*—Emrich and Dithmar

(57) **ABSTRACT**

A lithium metal oxide positive electrode for a non-aqueous lithium cell is disclosed. The cell is prepared in its initial discharged state and has a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more trivalent ion with at least one ion being Mn or Ni, and where M' is one or more tetravalent ion. Complete cells or batteries are disclosed with anode, cathode and electrolyte as are batteries of several cells connected in parallel or series or both.

16 Claims, 8 Drawing Sheets



(M′= e.g., Mn, Ti, Zr) (M= e.g., Mn, Ni)

OTHER PUBLICATIONS

The Electrochemical Society, Inc. Meeting Abstract No. 16, Boston, Nov. 1–6, 1998, Layered Lithium–Manganese Oxide . . . Precursors, Christopher S. Johnson et al.
Journal of Power Sources 81–82 (1999) 491–495, "Structural and Electrochemical Analysis . . . ", C. S. Johnson et al.
10th International Meeting on Lithium Batteries, "Lithium 2000", Como, Italy, May 28–Jun. 2, 2000, Abstract No. 17, B. Amundsen et al.
Solid State Ionics 118 (1999) 117–120, Preparation and Electrochemical Properties . . . , K. Numata et al.
Solid State Ionics, vol. 57m, p. 311 (1992), R. Rossen et al.
Power Sources, vol. 74, p. 46 (1998), M. Yoshio et al.
J. Electrochem. Soc., vol. 145, p. 1113 (1998) Yuoshio M. et al.
Chem. Commun. vol. 17, p. 1833 (1998); Armstrong A. R. et al.
J. Mat. Chem., vol. 9, p. 193 1999); P. G. Bruce et al.
J. Solid State Chem., vol. 145, p. 549 (1999). Armstrong, A. R.
J. Power Source, vol. 54, p. 205 (1995); Davidson, I. J. et al.
K. Mizushima, P.J. Wiseman and J.B. Goodenough, Mat. Res. Bull, 15 783–789 (1980).
W. Li and J.C. Currie, J. Electrochem. Soc., 144, 2773–2779 (1997.
Y. Gao, M.V. Yakovleva and W.B. Ebner, Electrochem. and Solid–State Lett., 1, 117–119 (1998).
H. Arai, M. Tsuda and Y. Sakurai, J. Power Sources, 90, 76–81 (2000).
H. Arai, S. Okada, Y. Sakurai and J. Yamaki, . Electrochem. soc., 144, 3117–3125 (1997).
Armstrong and P.G. Bruce, Nature, 381, 499–500 (1996).
M.H. Rossouw and M. M. Thackeray, J.Solid State Chem. 104, 464–473 1993).
M.H. Rossouw, D.C. Liles and M.M. Thakeray, J. Solid State Chem. 104, 464–466 (1993).
C.S. Johnson, J.T. Vaughey, M.M. Thackeray, T.E. Bofinger and S.A. Hackney, Ext. Abstract No. 136, 194th Meeting of the Electrochemical Society Boston, USA, Nov. 1–6, 1998.
S. Johnson, S.D. Korte, J.T. Vaughey, M.M.Thackeray, T.E. Bofinger, Y. Shao–Horn and S.A. Hackney, J. PowerSources 81–82, 491–495 (1999).
B. Amundsen, 10th International Meeting on Lithium Batteries, Como, Italy, May 28–Jun. 2, 2000.
K. Numata and S. Yamanaka, Solid State ionics, 118, 117 (1999).

* cited by examiner

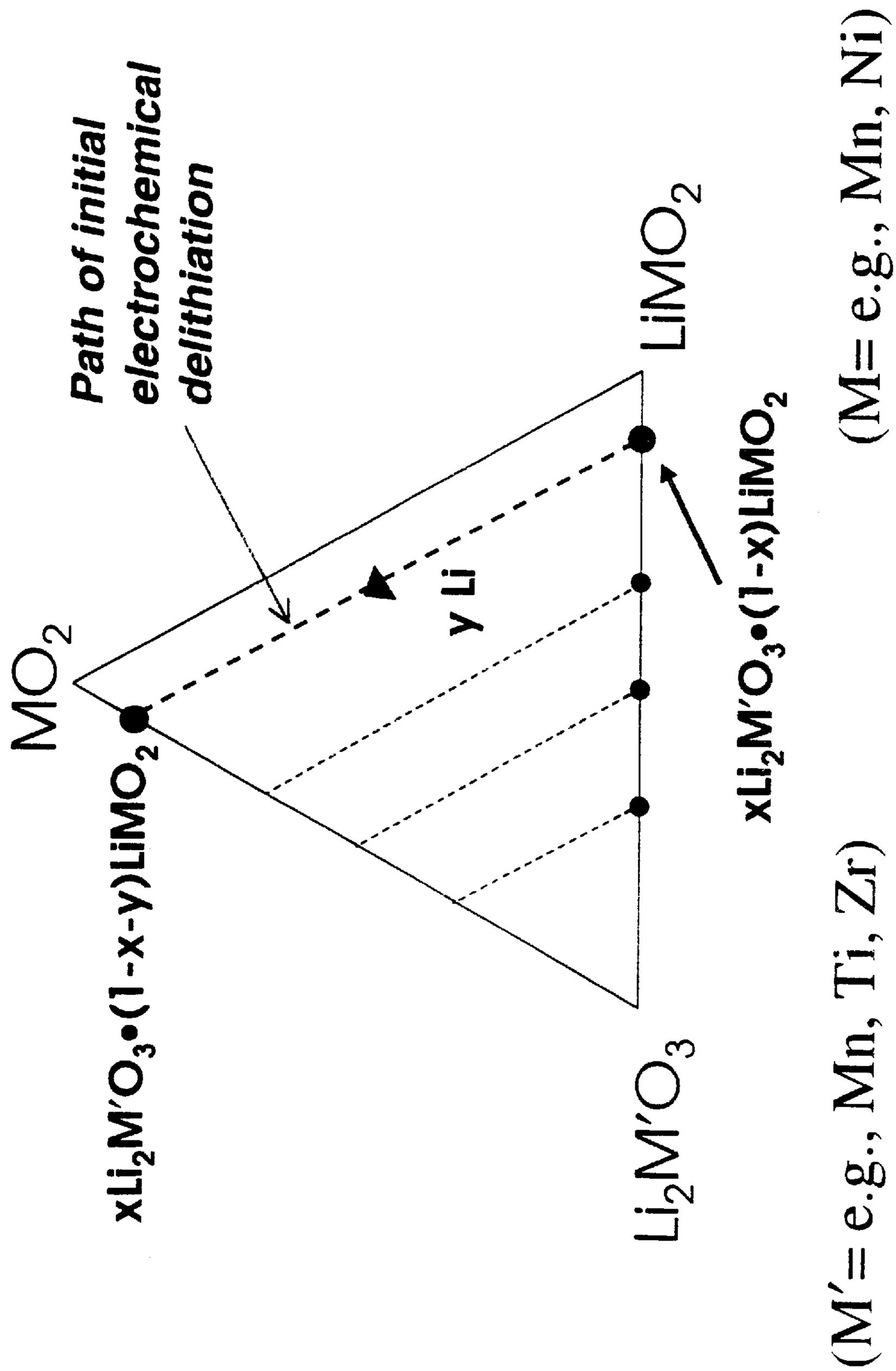

Path of initial electrochemical delithiation
MO_2
$xLi_2M'O_3 \bullet (1-x-y)LiMO_2$
y Li
$LiMO_2$
$xLi_2M'O_3 \bullet (1-x)LiMO_2$
$Li_2M'O_3$
(M= e.g., Mn, Ni)
(M'= e.g., Mn, Ti, Zr)

FIG. 1

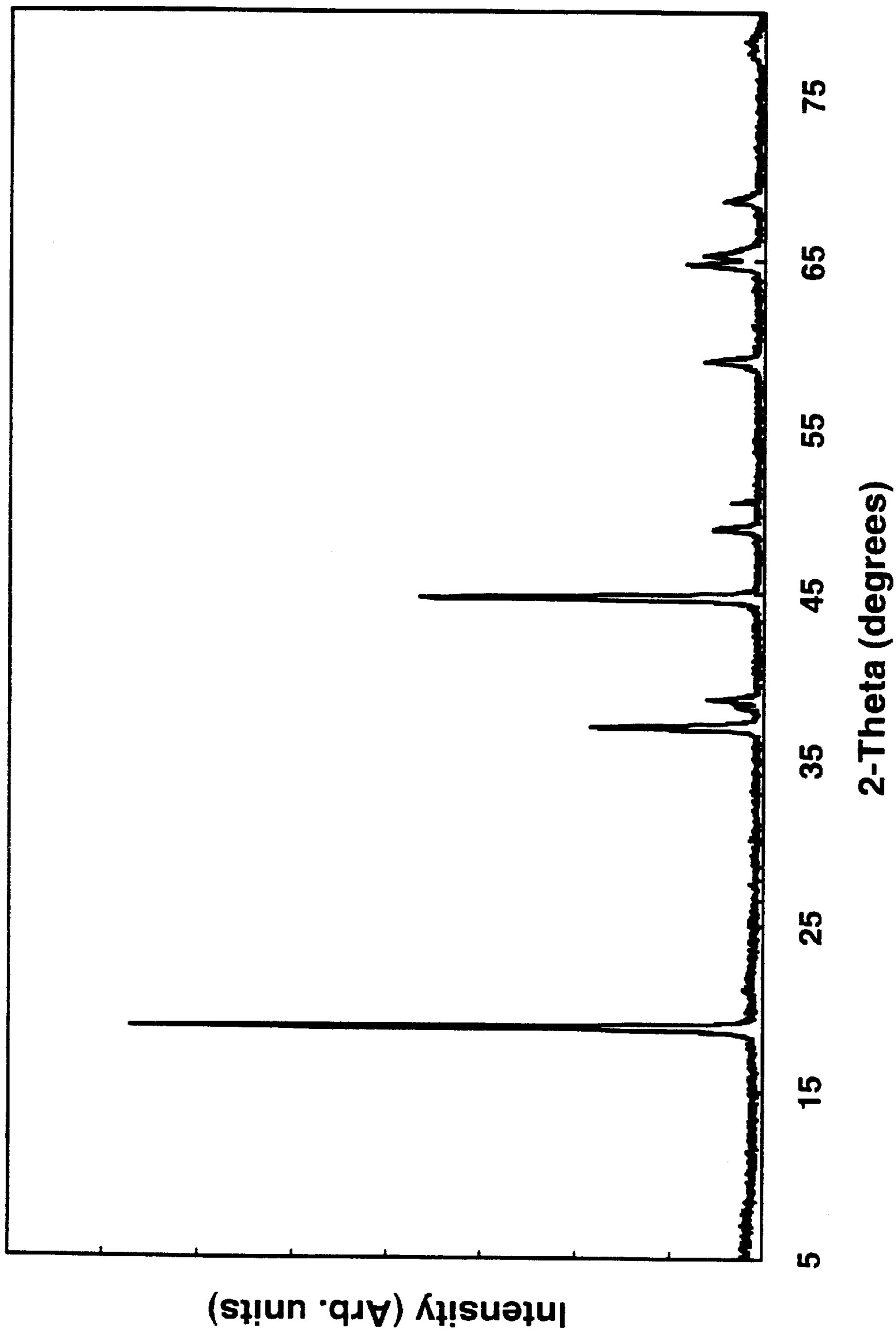


FIG. 2

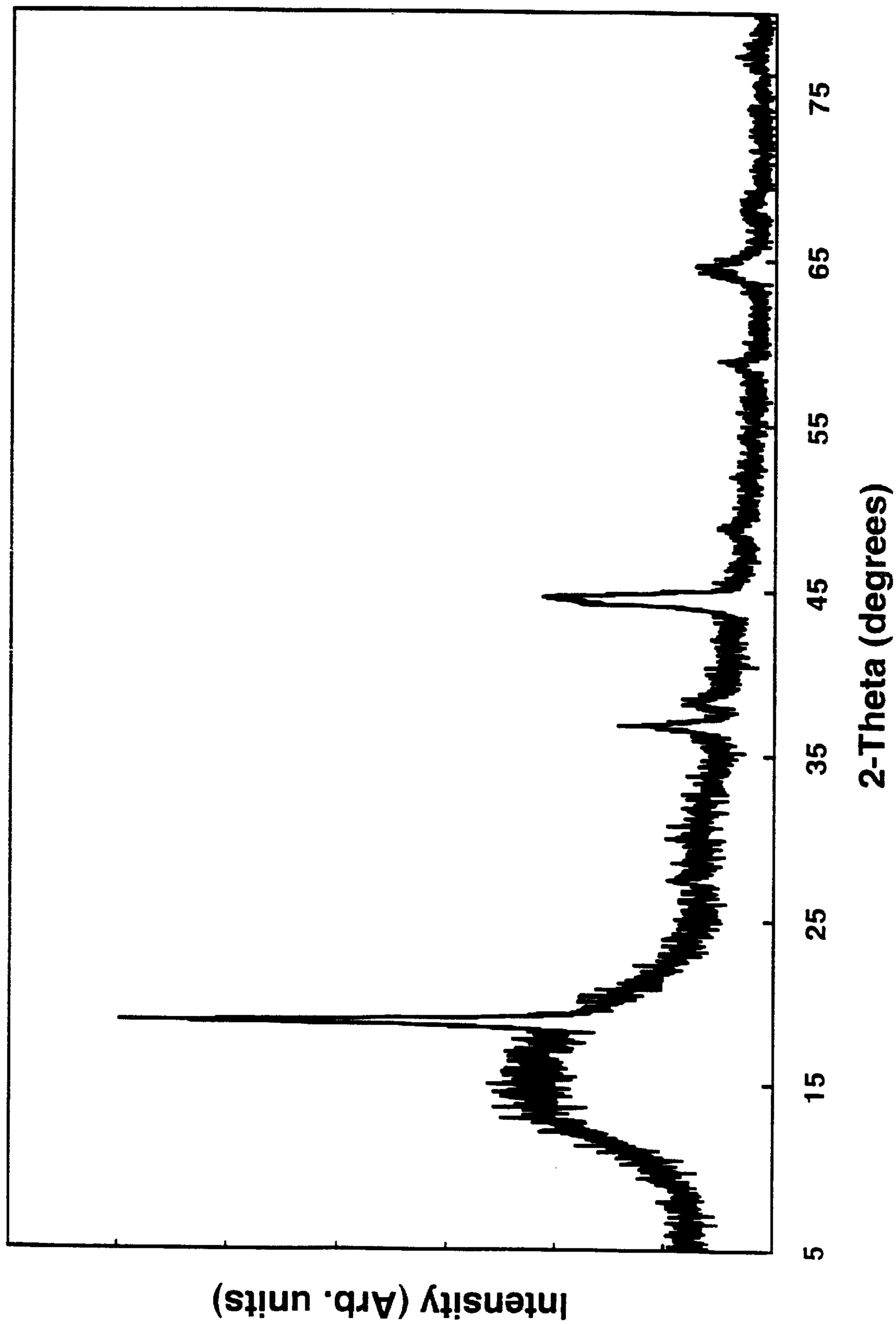


FIG. 3

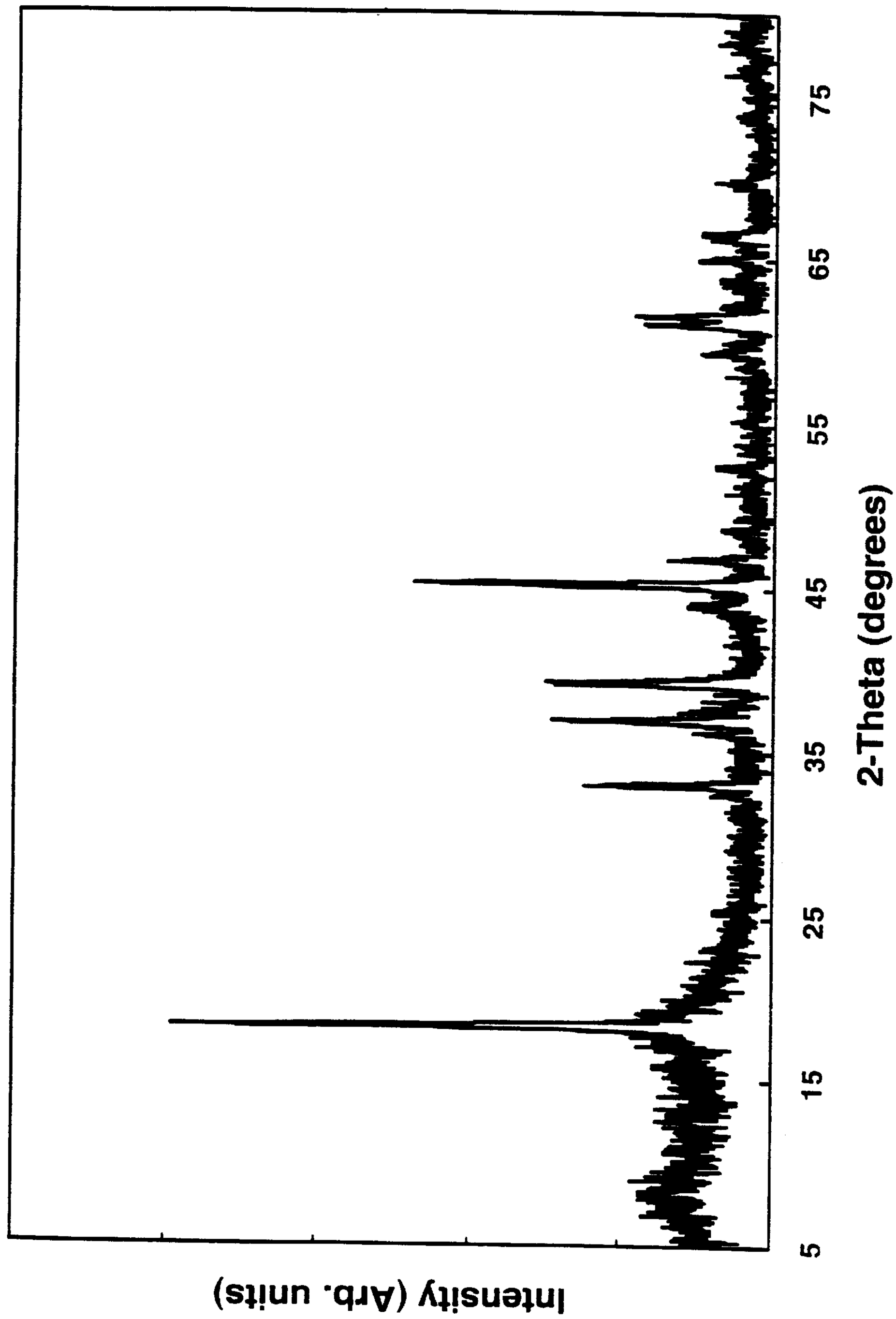


FIG. 4

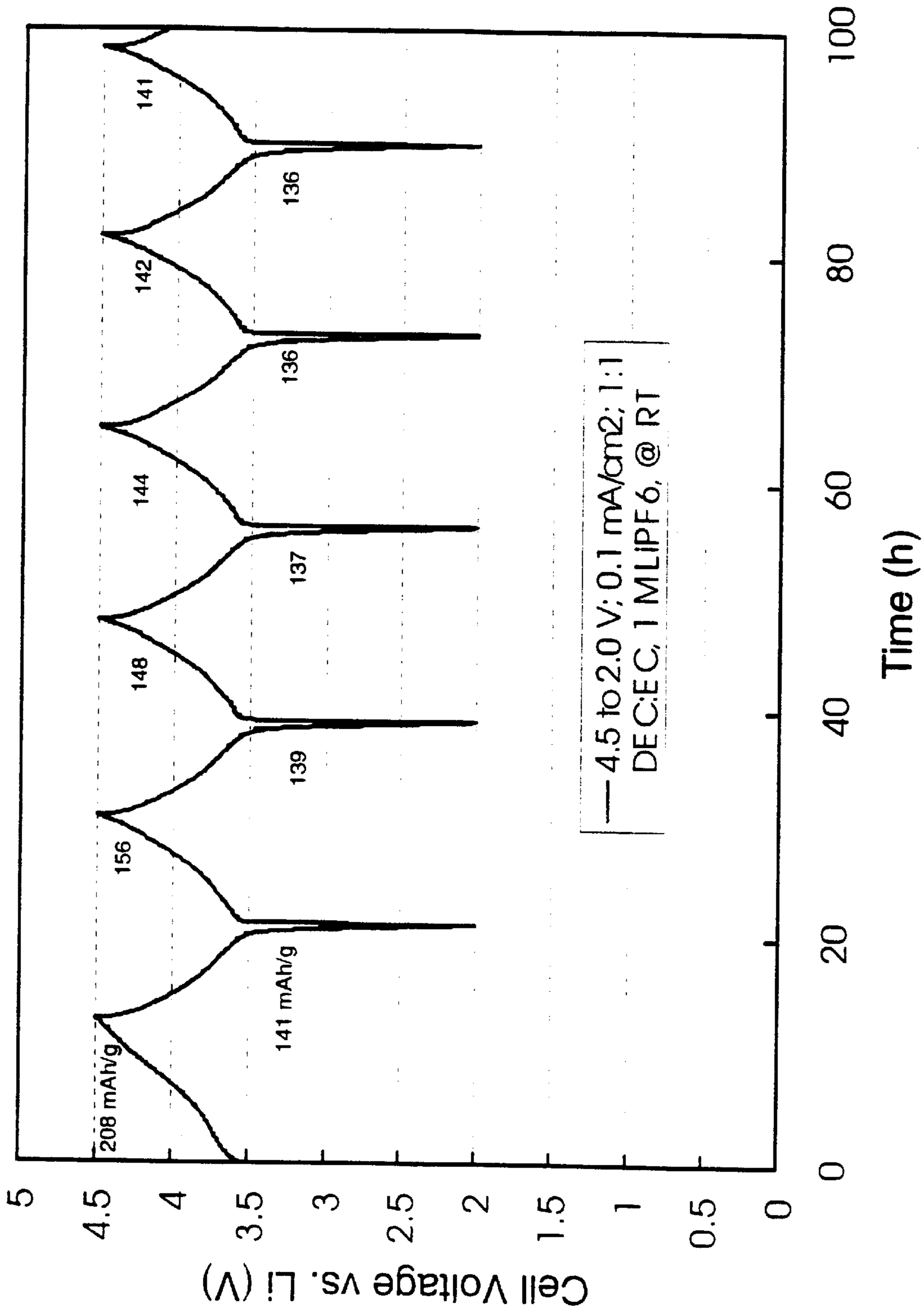

Cell Voltage vs. Li (V)
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
Time (h)
0
20
40
60
80
100
208 mAh/g
141 mAh/g
156
148
144
142
141
139
137
136
136
4.5 to 2.0 V; 0.1 mA/cm2; 1:1
DEC:EC, 1 MLiPF6, @ RT

FIG. 5

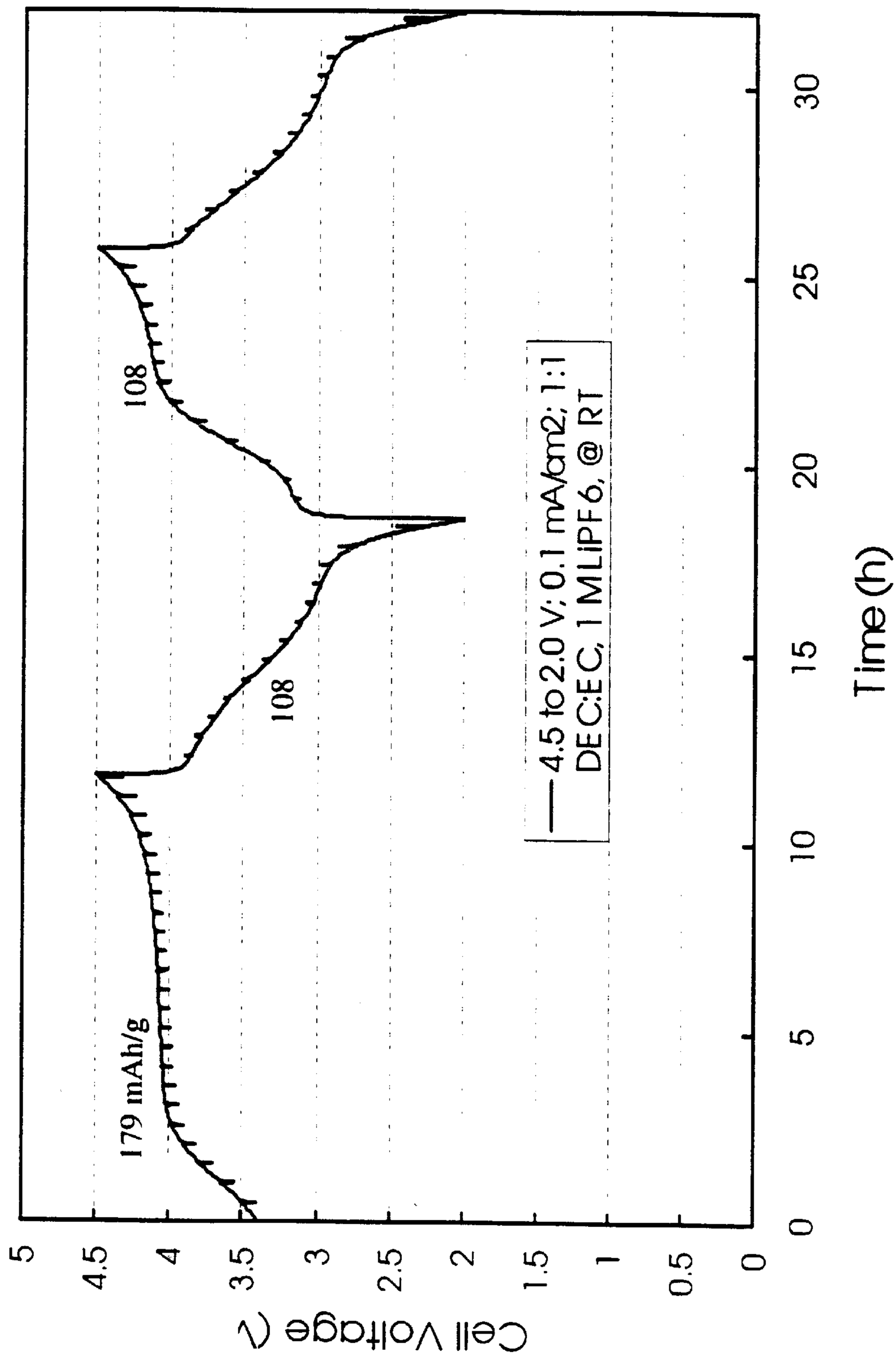

179 mAh/g
108
108
4.5 to 2.0 V; 0.1 mA/cm2; 1:1
DEC:EC, 1 MLiPF6, @ RT
Cell Voltage (V
5
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0
5
10
15
20
25
30
Time (h)

FIG. 6

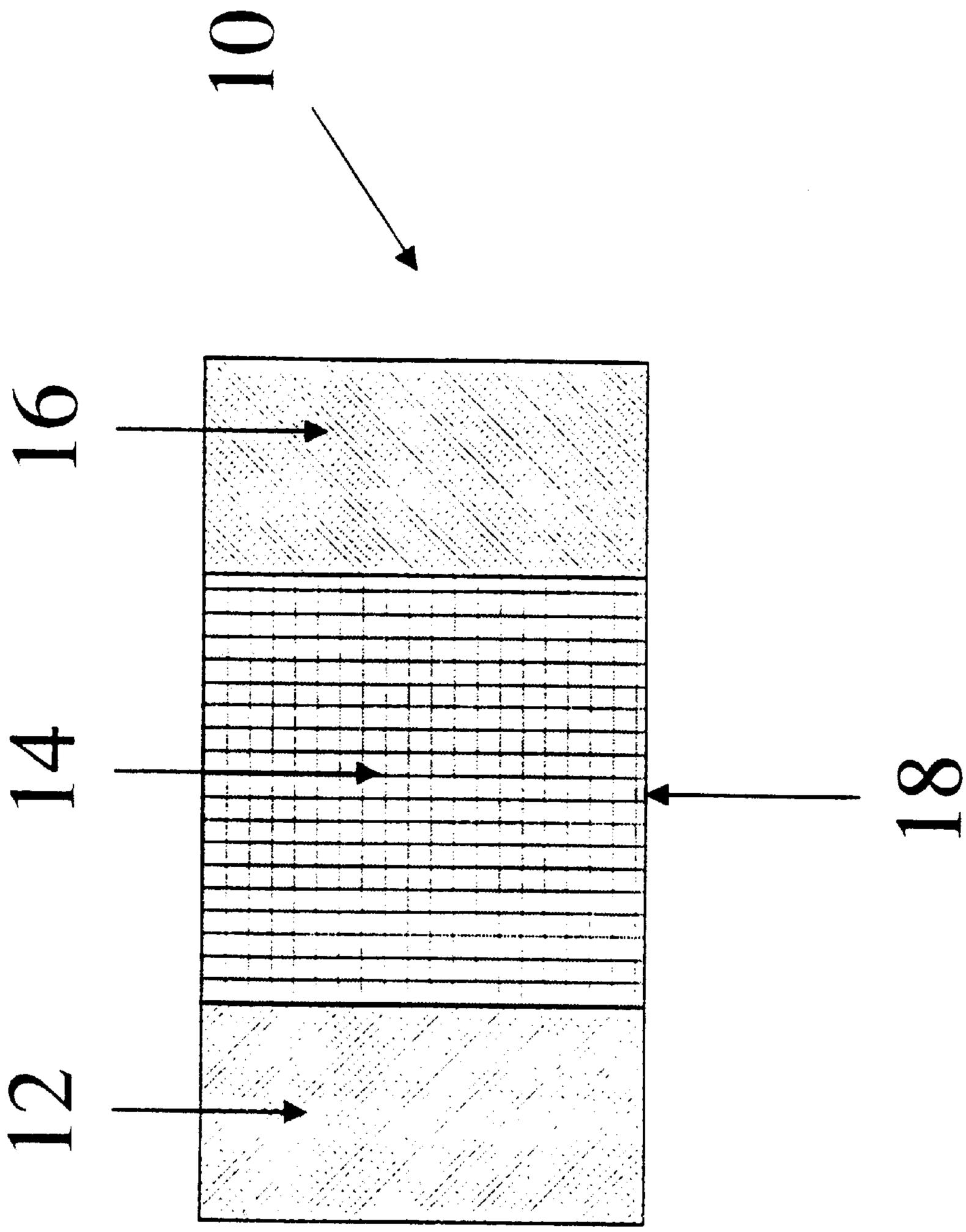


FIG. 7

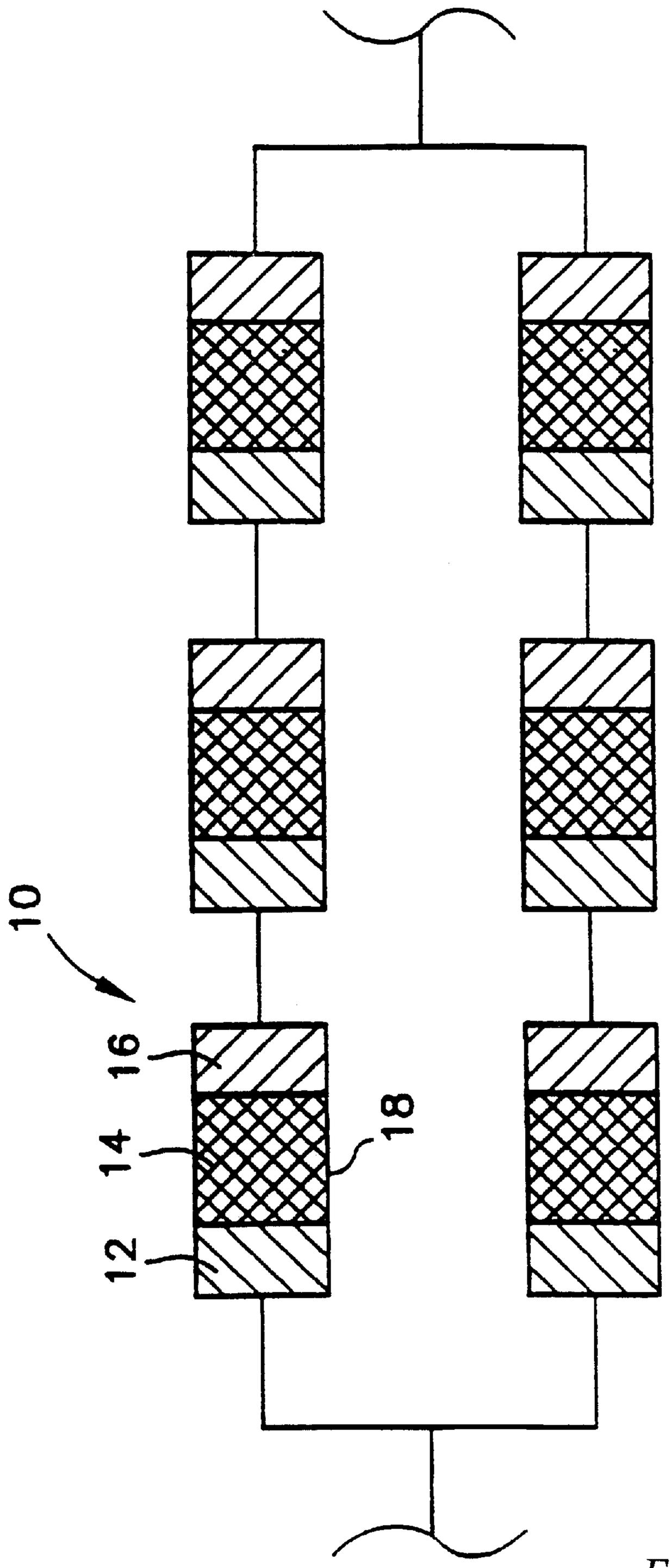


FIG. 8

LITHIUM METAL OXIDE ELECTRODES FOR LITHIUM CELLS AND BATTERIES

RELATED APPLICATIONS

This application claims priority under 35 U.S.C. §1.78(a)(3) provisional application Serial No. 60/213,618 filed Jun. 22, 2000, the entire contents of which are incorporated herein by reference.

CONTRACTUAL ORIGIN OF THE INVENTION

The United States Government has rights in this invention pursuant to Contract No. W-31-109-ENG-38 between the U.S. Department of Energy (DOE) and The University of Chicago representing Argonne National Laboratory.

BACKGROUND OF THE INVENTION

This invention relates to lithium metal oxide positive electrodes for non-aqueous lithium cells and batteries. More specifically, it relates to lithium-metal-oxide electrode compositions and structures, having in their initial state in an electrochemical cell, a general formula $xLiMO_2.(1-x)Li_2M'O_3$ alternatively $Li_{2-x}M_xM'_{1-x}O_{3-x}$ in which $0<x<1$ and where M is one or more trivalent ion with at least one ion being Mn, and where M is one or more tetravalent ions selected preferably from Mn, Ti and Zr; or, where M is one or more trivalent ion with at least one ion being Ni, and where M' is one or more tetravalent ion with at least one ion being Mn. In one embodiment of the invention, the Mn content should be as high as possible, such that the $LiMO_2$ component is essentially $LiMnO_2$ modified in accordance with this invention. In a further embodiment of the invention, the transition metal ions and lithium ions may be partially replaced by minor concentrations of one or more mono- or multivalent cations such as H^+ derived from the electrolyte by ion-exchange with Li^+ ions, and/or Mg^{2+} and Al^{3+} to impart improved structural stability or electronic conductivity to the electrode during electrochemical cycling.

SUMMARY OF THE INVENTION

Lithium-metal oxide compounds of general formula $LiMO_2$, where M is a trivalent transition metal cation Co, Ni, Mn, Ti, V, Fe, and with electrochemically inactive substituents such as Al are very well known and are of interest as positive electrodes for rechargeable lithium batteries. The best-known electrode material is $LiCoO_2$, which has a layered-type structure and is relatively expensive compared to the isostructural nickel and manganese-based compounds. Efforts are therefore being made to develop less costly electrodes, for example, by partially substituting the cobalt ions within $LiCoO_2$ by nickel, such as in $LiNi_{0.8}Co_{0.2}O_2$ or by exploiting the manganese-based system $LiMnO_2$. Such layered compounds are sometimes stabilized by partially replacing the transition metal cations within the layers by other metal cations, either alone or in combination. For example, Mg^{2+} ions may be introduced into the structure to improve the electronic conductivity of the electrode, or Al^{3+} or Ti^{4+} ions to improve the structural stability of the electrode at high levels of delithiation. Examples of such compounds are $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$ and $LiNi_{0.75}Co_{0.15}Ti_{0.05}Mg_{0.05}O_2$.

A major problem of layered $LiMO_2$ compounds containing either Co or Ni (or both) is that the trivalent transition metal cations, M, are oxidized during charge of the cells to a metastable tetravalent oxidation state. Such compounds are highly oxidizing materials and can react with the electrolyte or release oxygen. These electrode materials can, therefore, suffer from structural instability in charged cells when, for example, more than 50% of the lithium is extracted from their structures; they require stabilization to combat such chemical degradation.

Although the layered manganese compound $LiMnO_2$ has been successfully synthesized in the laboratory, it has been found that delithiation of the structure and subsequent cycling of the Li_xMnO_2 electrode in electrochemical cells causes a transition from the layered MnO_2 configuration to the configuration of a spinel-type $[Mn_2]O_4$ structure. This transformation changes the voltage profile of the Li/Li_xMnO_2 cell such that it delivers capacity over both a 4V and a 3V plateau; cycling over the 3V plateau is not fully reversible which leads to capacity fade of the cell over long-term cycling. Other types of $LiMnO_2$ structures exist, such as the orthorhombic-form, designated O-$LiMnO_2$ in which sheets of MnO_6 octahedra are staggered in zig—zig fashion unlike their arrangement in layered $LiMnO_2$. However, O-$LiMnO_2$ behaves in a similar way to layered $LiMnO_2$ in lithium cells; it also converts to a spinel-like structure on electrochemical cycling.

Therefore, further improvements must be made to $LiMO_2$ electrodes, particularly $LiMnO_2$, to impart greater structural stability to these electrode materials during electrochemical cycling in lithium cells and batteries. This invention addresses the stability of $LiMO_2$ electrode structures, particularly $LiMnO_2$, and makes use of a $Li_2M'O_3$ component to improve their stability.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention consists of certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in the appended claims, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the present invention.

FIG. **1** depicts a schematic representation of a $Li_2M'O_3$-MO_2-$LiMO_2$ phase diagram, in which M is a trivalent ion (or ions) and M is a tetravalent ion (or ions);

FIG. **2** depicts the X-ray diffraction pattern of a $xLi_2MnO_3.(1-x)LiNi_{0.8}Co_{0.2}O_2$ electrode composition;

FIG. **3** depicts the X-ray diffraction pattern of a $xLi_2Mn_{1-x}Ti_xO_3.(1-x)LiNi_{0.8}Co_{0.2}O_2$ electrode composition;

FIG. **4** depicts the X-ray diffraction pattern of a $xLi_2TiO_3.(1-x)LiMnO_2$ electrode composition;

FIG. **5** depicts the electrochemical profile of a $Li/xLi_2MnO_3.(1-x)LiNi_{0.8}Co_{0.2}O_2$ electrochemical cell;

FIG. **6** depicts the electrochemical profile of a $Li/xLi_2TiO_3.(1-x)LiMnO_2$ electrochemical cell;

FIG. **7** depicts a schematic representation of an electrochemical cell; and

FIG. **8** depicts a schematic representation of a battery consisting of a plurality of cells connected electrically in series and in parallel.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

This invention relates to stabilized $LiMO_2$ electrodes whereby an electrochemically inert rocksalt phase Li_2MO_3 is introduced as a component to the overall electrode structure as defined, in its initial state, by the general formula $xLiMO_2.(1-x)Li_2M'O_3$ alternatively $Li_{2-x}M_xM'_{1-x}O_{3-x}$ in

which $0<x<1$, preferably $0.8 \leqq x<1$, and more preferably $0.9 \leqq x<1$, and where M is one or more trivalent ions having at least one ion selected from Mn and where M' is one or more tetravalent ion selected preferably from Mn, Ti and Zr, or alternatively, where M is one or more trivalent ions having at least one ion selected from Ni and where M' one or more tetravalent ions having at least one ion selected from Mn. These compounds can be visualized as lying on the $LiMO_2$-$Li_2M'O_3$ tie-line of the $Li_2M'O_3$-MO_2-$LiMO_2$ phase diagram shown schematically in FIG. **1**.

The rocksalt phase Li_2MnO_3 has a layered-type structure in which discrete layers of lithium ions alternate with layers containing Mn and Li ions (in a 2:1 ratio) between the close-packed oxygen sheets. Note that, in this respect, the formula Li_2MnO_3 can be written in layered notation as $Li(Mn_{2/3}Li_{1/3})O_2$, in which the Li and Mn within round brackets represent the ions in one layer. A difference between Li_2MnO_3 and the layered $LiMO_2$ compounds is that the Mn ions in Li_2MnO_3 are tetravalent and cannot be easily electrochemically oxidized by lithium extraction, whereas in the $LiMO_2$ compounds the transition metal cations M are trivalent and can be electrochemically oxidized. Because Li_2MnO_3 has a rocksalt phase, there is no energetically favorable interstitial space for additional lithium; therefore, Li_2MnO_3 cannot operate as an insertion electrode and cannot be electrochemically reduced. The $xLiMO_2.(1-x)Li_2M'O_3$ structure can be regarded essentially as a compound with a common oxygen array for both the $LiMO_2$ and Li_2MnO_3 components, but in which the cation distribution can vary such that domains of the two components exist side by side. Such a domain structure does not rule out the possibility of cation mixing and structural disorder, particularly at domain or grain boundaries. In a generalized $xLiMO_2.(1-x)Li_2M'O_3$ layered structure, one layer contains M, M' and Li ions between sheets of close-packed oxygen ions, whereas the alternate layers are occupied essentially by lithium ions alone. By analogy, in a $xLiMO_2.(1-x)Li_2M'O_3$ structure that contains monoclinic $LiMnO_2$ as the $LiMO_2$ component, it is believed that the tetravalent M' ions can partially occupy the M positions in the monoclinic layered $LiMnO_2$ structure, thereby providing increased stability to the overall structure.

Thus in the electrodes of the present invention, the M and M' ions can be disordered in the electrode structure. It is preferable that the Mn content should be as high as possible, such that the $LiMO_2$ component is essentially $LiMnO_2$. In a further embodiment of the invention, the transition metal ions and lithium ions may be partially replaced by minor concentrations (typically less than 10 atom percent) of other mono- or multivalent cations such as Al^{3+} or Mg^{2+} to impart improved structural stability or electronic conductivity to the electrode during electrochemical cycling. In addition, the $xLiMO_2.(1-x)Li_2M'O_3$ structures of the invention may include H^+ ions, for example, resulting from the removal acidic H^+ species from the electrolyte by ion-exchange with Li^+ ions. It stands to reason, therefore, that the present invention includes the introduction of mono- or divalent cations into the structure, and that the electrodes of the invention may depart slightly from the ideal stoichiometry as defined by the formula $xLiMO_2.(1-x)Li_2M'O_3$.

It has been shown in the past that Li_2MnO_3 (and isostructural $Li_2Mn_{1-x}Zr_xO_3$) which is electrochemically inactive, can be used as a precursor material to form an electrochemically active charged $xMnO_2.(1-x)Li_2MnO_3$ electrode structure in which x is approximately equal to 0.91; this value of x translates to a composition of the layered structure $Li_{1.1}Mn_{0.9}O_2$. These charged $xMnO_2.(1-x)Li_2MnO_3$ compounds have been prepared by leaching Li_2O from the Li_2MnO_3 ($Li_2O.MnO_2$) structure with acid such as sulphuric acid (U.S. Pat. No. 5,153,081). However, the acid treatment causes a shear of the oxygen array, such that the resulting $xMnO_2.(1-x)Li_2MnO_3$ structures are no longer close-packed but have an oxygen arrangement that provides octahedral and trigonal prismatic sites in alternate layers. During relithiation, for example with LiI in acetonitrile, it has been demonstrated that the oxygen sheets shear back to close-packing and that the phase transformation yields a $xLiMnO_2.(1-x)Li_2MnO_3$-type structure. However, such phase transformations are undesirable in rechargeable battery systems, because they can adversely affect the efficiency and rechargeability of the electrode. Thus, a major advantage of this invention is that this phase transformation can be avoided by starting directly with a discharged $xLiMnO_2.(1-x)Li_2MnO_3$ electrode in the cell because the non-aqueous removal of lithium does not appear to cause the phase transition to yield the structure (non-close-packed) generated by acid leaching of Li_2MnO_3 .

Furthermore, it is important to note that even though the relithiation of a $xMnO_2.(1-x)Li_2MnO_3$ electrode of the prior art in an electrochemical cell yields the same formulation as the electrodes of the present invention, i.e., $xLiMnO_2.(1-x)Li_2MnO_3$, the applicants believe that the structures of the electrode materials of the present invention are significantly different from those of the prior art and will be unequivocally distinguished from one another by high-resolution transmission electron microscopy, i.e., differences will be evident in the microstructural features of the $xLiMnO_2$-$(1-x)Li_2MnO_3$ electrodes of the present invention and those of the prior art. For example, because the lithiated **20** $xLiMnO_2$-$(1-x)Li_2MnO_3$ electrode structures of the prior art are derived from a non-close-packed $xMnO_2$-$(1-x)Li_2MnO_3$ structure, which is obtained by the acid leaching of, and Li_2**0** removal from, a Li_2MnO_3 precursor as described above, the microstructures of the prior art electrode materials will be characterized by high concentrations of defects and stacking faults, as is evident by the broad peaks in their X-ray diffraction patterns, in contrast to the electrode materials of the present invention that are more crystalline and ordered as reflected by the relatively sharp and well-resolved peaks in their X-ray diffraction patterns (FIGS. **2**, **3** and **4**).

Another disadvantage of the acid-treated compounds of the prior art ('081 patent) $xMnO_2.(1-x)Li_2MnO_3$, is that they represent charged positive electrodes, whereas lithium-ion batteries require positive electrodes in the discharged state, for example, $LiMO_2$ electrodes (M=Co, Ni, Mn). Moreover, the charged $xMnO_{2.1}$-$x)Li_2MnO_3$ electrodes of the prior art require dehydration before use so that they can be used effectively in lithium cells. By contrast, the $xLiMnO_2.(1-x)Li_2MnO_3$ electrodes of this invention are prepared in the discharged state and are essentially anhydrous materials and are more stable to heat-treatment and long-term storage in air compared to the $xMnO_2.(1-x)Li_2MnO_3$ materials of the prior art, which are known to transform on storage to a gamma-MnO_2-type structure as reported by Johnson et al in J. Power Sources 81–82, 491 (1999).

In one embodiment, this invention extends to include $xLiMO_2.(1-x)Li_2M'O_3$ electrodes stabilized by isostructural rocksalt $Li_2M'O_3$ compounds other than M'=Mn, Ti, Zr as described in the preceding sections. Examples of such compounds are Li_2RuO_3, Li_2ReO_3, Li_2IrO_3, and Li_2PtO_3 which may contribute a portion of the electrochemical capacity of the electrode.

One of the difficulties that has been encountered in synthesizing $xLiMO_2.(1-x)Li_2M'O_3$ electrodes, in which M

is Mn, has been to keep the valency of the manganese ions equal, or close to its trivalent state. This has been successfully accomplished by the inventors with a hydrothermal method or process under basic conditions using LiOH and/or KOH. This invention, therefore, extends to include a hydrothermal process or method for synthesizing $xLiMO_2.(1-x)Li_2M'O_3$ compounds in which M is one or more trivalent ion with at least one ion being Mn, and in which M' is a tetravalent ion. Such methods of synthesis are undertaken in a pressurized autoclave, preferably between 5 and 35 atmospheres and at temperatures ranging between 100 and 250° C. and most preferably at 10–20 atm and temperatures between 180 and 230° C. for about 6 to 12 hours or more if necessary. For example, $0.15LiMnO_2.85Li_2TiO_3$ electrodes have been successfully prepared by this process from precursor materials consisting of manganese oxide (Mn_2O_3), lithium hydroxide ($LiOH.H_2O$) and titanium isopropoxide ($Ti[OCH(CH_3)_2]_4$) in a potassium hydroxide (KOH) solution at 220° C. and at 15 atmospheres pressure.

It has been recently demonstrated that layered lithium-chromium-manganese-oxide and lithium-cobalt-manganese-oxide electrodes of general formula $xLiCrO_2.(1-x)Li_2MnO_3$ and $xLiCoO_2.(1-x)Li_2MnO_3$ provide electrochemical stability when cycled between 4.5 and 2.0 V in electrochemical lithium cells. In particular, a $Li(Cr_{0.4}Mn_{0.4}Li_{0.2})O_2$ electrode (alternatively, $0.4LiCrO_2.0.4Li_2MnO_3$) delivers approximately 150 mAh/g at 25° C. and 200 mAh/g at 55° C. at an average cell voltage of 3.5 V vs. Li. However, because the Li_2MnO_3 component is electrochemically inactive, the electrochemical capacity derived from the cell is due to the oxidation of Cr^{3+} to Cr^{6+} during the electrochemical charging of the cells. This system has an immediate disadvantage because it is known that the high oxidation states of chromium such as those found in Cr_3O_8 are dangerous and are a major health hazard whereas the electrodes of the present invention operate predominantly off a M^{3+}/M^{4+} couple, notably a $Mn^{3+/4+}$ couple. For the cobalt compound, $xLiCoO_2.(1-x)Li_2MnO_3$, no significant advantage is gained in overcoming the cost limitations of the electrode because the cobalt ions, not the manganese ions, provide all the electrochemical capacity of the electrode.

The following examples of stabilized $xLiMnO_2.(1-x)Li_2MnO_3$ electrodes containing either manganese and/or nickel describe the principles of the invention as contemplated by the inventors, but they are not to be construed as limiting examples.

EXAMPLE 1

The material $0.2Li_2MnO_3.0.8LiNi_{0.8}Co_{0.2}O_2$ that can be written, alternatively, as $Li(Ni_{0.58}Mn_{0.18}Co_{0.15}Li_{0.09})O_2$ was prepared by the reaction of $Ni(NO_3)_2$, $Co(NO_3)_2$, MnO_2, and LiOH in the required stoichiometric amounts at 800° C. in air or oxygen for about 16 hours. The powder X-ray diffraction pattern of this compound indicates an essentially single-phase product with a layered-type structure (FIG. **2**).

EXAMPLE 2

The material $0.2Li_2Mn_{1-x}Ti_xO_3.0.8LiNi_{0.8}Co_{0.2}O_2$, where x=0.5, which can be written, alternatively, as $Li(Ni_{0.58}Mn_{0.09}Ti_{0.09}Co_{0.15}Li_{0.09})O_2$ was prepared by the reaction of $Ni(NO_3)_2$, $Co(NO_3)_2$, MnO_2, TiO_2 (anatase) and LiOH in the required stoichiometric amounts at 800° C. in air or oxygen for about 16 hours. The powder X-ray diffraction pattern of this compound indicates an essentially single-phase product with a layered-type structure (FIG. **3**).

EXAMPLE 3

The material $0.15Li_2TiO_3.0.85LiMnO_2$ that can be written, alternatively, as $Li(Ti_{0.14}Mn_{0.79}Li_{0.07})O_2$ was prepared by the hydrothermal reaction of Mn_2O_3, TiO_2 (anatase) and LiOH in the required stoichiometric amounts at 220° C. and 15 atmospheres pressure for about 10 hours. The powder X-ray diffraction pattern of this compound indicates an essentially single-phase product with a layered-type structure (FIG. **4**).

EXAMPLE 4

The $xLiMO_2.(1-x)Li_2M'O_3$ electrode materials were evaluated in coin cells (size 2032) 20 mm diameter and 3.2 mm high against a counter lithium electrode. The cells had the configuration: Li/1M $LiPF_6$ in ethylene carbonate (EC), diethyl carbonate (DEC) (1:1)electrolyte/$xLiMO_2.(1-x)Li_2M'O_3$, in which the $xLiMO_2.(1-x)Li_2M'O_3$ electrode consisted of $0.2Li_2MnO_3.0.8LiNi_{0.8}Co_{0.20}O_2$ or $0.15Li_2TiO_3.0.85LiMnO_2$. Other electrolytes well known in the art may be used. Laminated electrodes were made containing approximately 7 to 10 mg of the $xLiMO_2.(1-x)Li_2M'O_3$ powder, i.e., approximately 82% by weight of the laminate electrode, intimately mixed with approximately 10% by weight of a polyvinylidene difluoride (Kynar PVDF polymer binder) and approximately 8% by weight of a suitable carbon (i.e. graphite, such as Timcal SFG-6, or acetylene black, such as Chevron XC-72) in 1-methyl-2-pyrrolidinone (NMP). Other binders are well known in the art and may be substituted here. The slurries were coated with a doctor blade onto an aluminum foil substrate current collector. The coatings were dried in vacuum at temperatures from 70° C. for about 12 hours, and punched out as electrode laminates. Metallic lithium foil was used as the counter electrode. $Li/xLiMO_2.(1-x)Li_2M'O_3$ cells were discharged and charged at constant current (typically 0.1 mA/cm^2) within the voltage range 4.5 to 2.0 V.

Typical electrochemical data for $Li/xLiMO_2.(1-x)Li_2M'O_3$ cells are provided in various plots, as shown in FIG. **5**, a $Li/0.2Li_2MnO_3.0.8LiNi_{0.8}Co_{0.2}O_2$ cell; and FIG. **6**, a $Li/0.15Li_2TiO_3.0.85LiMnO_2$ cell. For example, the electrode of Example 1, namely $0.2Li_2MnO_3.0.8LiNi_{0.8}Co_{0.2}O_2$ has a theoretical electrochemical capacity of 212 mAh/g. The electrochemical data in FIG. **5** indicate that an initial capacity of approximately 208 mAh/g can be achieved from this electrode during the 'break-in' process on the initial charge of the cell and, thereafter, a steady rechargeable discharge capacity of approximately 136 mAh/g. For the stabilized $0.15Li_2TiO_3.0.85LiMnO_2$ electrode of Example 3, as seen in FIG. **6**, a capacity of 179 mAh/g was achieved during the 'break-in ' process on the initial charge of the cell, and thereafter a rechargeable capacity of 108 mAh/g was achieved.

The data in the examples provided above indicate that the principle of this invention can be used to stabilize $LiMO_2$ compounds with a $Li_2M'O_3$ component, and specifically those containing M=Ni and/or Mn that are of major significance and interest to the lithium battery industry for replacing the lithium-cobalt-oxide, $LiCoO_2$, as the electrode of choice, thereby reducing cost. The performance and effectiveness of the $xLiMO_2.(1-x)Li_2MO_3$ electrodes ($0<x<1$) of this invention depend on the concentration of the trivalent transition metal ions, M, in the structure, that is the value of "x" which preferably is equal to or greater than 0.8 and less than 1. A major advantage of the compounds of this invention is that the concentration of the trivalent M ions,

the concentration of stabilizing tetravalent M' ions and concentration of monovalent lithium ions can be tailored in such a way to extend and optimize both the capacity of the electrode as well as the stabilizing effect of the $Li_2M'O_3$ component in the structure. For example, an electrode with the composition $0.9LiMn_{0.9}Ni0.1O_2.0.1Li_2TiO_3$ (alternatively $Li_{1.2}Mn_{0.72}Ni_{0.08}Ti_{0.2}O_{2.2}$) has a theoretical capacity of 252 mAh/g, which is only 8% less than that of $LiCoO_2$ used in state-of-the-art lithium cells.

This invention, therefore, relates to a lithium-metal-oxide positive electrode for a non-aqueous electrochemical lithium cell as shown schematically in FIG. **7**, the cell represented by the numeral **10** having a negative electrode **12** separated from a positive electrode **16** by an electrolyte **14**, all contained in an insulating housing **18** with suitable terminals (not shown) being provided in electronic contact with the negative electrode **12** and the positive electrode **16**. Binders and other materials normally associated with both the electrolyte and the negative and positive electrodes are well known in the art and are not described herein, but are included as is understood by those of ordinary skill in this art. FIG. **8** shows a schematic illustration of one example of a battery in which two strings of electrochemical lithium cells, described above, are arranged in parallel, each string comprising three cells arranged in series.

While particular embodiments of the present invention have been shown and described, it will be appreciated by those skilled in the art that changes and modifications may be made without departing from the invention in its broader aspects. Therefore, the aim in the appended claims is to cover all such changes and modifications as fall within the true spirit and scope of the invention.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A lithium metal oxide positive electrode for a non-aqueous lithium cell prepared in its initial discharged state having a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more ions having an average oxidation state of three with at least one ion being Ni, and where M' is one or more ions with an average oxidation state of four with at least one ion being Mn, with both the $LiMO_2$ and $Li_2M'O_3$ components being layered and the ratio of Li to M and M' being greater than one and less than two.

2. A lithium metal oxide positive electrode according to claim **1** in which $0.8 \leqq x<1$.

3. A lithium metal oxide positive electrode according to claim **1** in which $0.9 \leqq x<1$.

4. A lithium metal oxide positive electrode according to claim **1** in which M and M' are disordered in the electrode structure.

5. A lithium metal oxide positive electrode according to claim **1** in which M ions are Ni and Co, and M' is Mn.

6. A lithium metal oxide positive electrode according to claim **1** in which M is Ni and M' is Mn.

7. A lithium metal oxide positive electrode according to claim **1** in which M and M' ions are partially replaced by mono- or multivalent cations.

8. A lithium metal oxide positive electrode according to claim **7** in which M and M' ions are partially replaced by Mg^{2+} or Al^{3+} ions.

9. A lithium metal oxide positive electrode according to claim **1** in which the lithium ions are partially replaced by H^+ cations.

10. The lithium metal oxide positive electrode of claim **1**, wherein M is more than one of V, Mn, Fe, Co, and Ni and wherein M' is one or more of Mn, Ti, Zr, Ru, Re, and Pt.

11. The lithium metal oxide positive electrode of claim **10**, wherein M is more than one of Mn, Co and Ni and M' is one or more of Mn, Ti, and Zr.

12. The lithium metal oxide positive electrode of claim **11**, wherein M ions are Ni and Co and M' is Mn.

13. An electrochemical cell having a negative electrode and a non-aqueous electrolyte and a positive electrode, said positive electrode having in its initial discharged state a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more ions with an average oxidation state of three with at least one ion being Ni and where M' is one or more ions with an average oxidation state of four and at least one ion being Mn with both the $LiMO_2$ and $Li_2M'O_3$ components being layered and the ratio of Li to M and M' being greater than one and less than two.

14. A battery consisting at a plurality of cells, at least some cells including a negative electrode and a non-aqueous electrolyte and a positive electrode, said positive electrode having in its initial discharged state a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more ions with an average oxidation state of three and at least one ion being Ni and where M' is one or more ions with an average oxidation state of four and at least one ion being Mn, with both the $LiMO_2$ and $Li_2M'O_3$ components being layered and the ratio of Li to M and M' being greater than one and less than two.

15. A lithium metal positive oxide electrode prepared in its initial discharged state having a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more ions with an average oxidation state of three and at least one ion being Ni, and where M' is one or more ions having an average oxidation state of four with at least one ion being Mn in which the lithium ions are partially replaced by hydrogen cations.

16. A lithium metal oxide positive electrode for a non-aqueous lithium cell prepared in its initial discharged state in an autoclave at a pressure between 5 and 35 atmospheres and at a temperature between 100–250° C. having a general formula $xLiMO_2.(1-x)Li_2M'O_3$ in which $0<x<1$, and where M is one or more ions with an average oxidation state of three with at least one ion being Ni, and where M' is one or more ions with an average oxidation state of four with at least one ion being Mn.

* * * * *