Office de la Propriété
Intellectuelle
du Canada

Un organisme
d'Industrie Canada

Canadian
Intellectual Property
Office

An agency of
Industry Canada

CA 2568211 C 2009/11/17

(11)(21) **2 568 211**

(12) **BREVET CANADIEN**
CANADIAN PATENT

(13) **C**

---

(22) **Date de dépôt/Filing Date**: 2000/12/22

(41) **Mise à la disp. pub./Open to Public Insp.**: 2001/07/26

(45) **Date de délivrance/Issue Date**: 2009/11/17

(62) **Demande originale/Original Application**: 2 466 366

(30) **Priorité/Priority**: 2000/01/18 (US09/484,919)

(51) Cl.Int./Int.Cl. *C01B 25/37* (2006.01),
C01B 25/45 (2006.01), *C01D 15/00* (2006.01),
H01M 4/58 (2006.01)

(72) **Inventeurs/Inventors**:
BARKER, JEREMY, GB;
SAIDI, M. YAZID, US;
SWOYER, JEFFREY L., US

(73) **Propriétaire/Owner**:
VALENCE TECHNOLOGY, INC., US

(74) **Agent**: MCFADDEN, FINCHAM

---

(54) Titre : PRODUCTION DE MATERIAUX CONTENANT DU LITHIUM
(54) Title: PREPARATION OF LITHIUM-CONTAINING MATERIALS

(57) Abrégé/Abstract:

The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions and a method of making such materials. The disclosed method comprises a method of making a lithium mixed metal compound by reaction of starting material which comprises mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture. The starting materials comprise at least one metal containing compound, a lithium compound having a melting point greater than 450°C, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state. The method comprises heating said wet mixture in a non-oxidizing atmosphere at a temperature sufficient to form a reaction product which comprises lithium and said reduced metal ion.

ABSTRACT

The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions and a method of making such materials. The disclosed method comprises a method of making a lithium mixed metal compound by reaction of starting material which comprises mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture. The starting materials comprise at least one metal containing compound, a lithium compound having a melting point greater than 450°C, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state. The method comprises heating said wet mixture in a non-oxidizing atmosphere at a temperature sufficient to form a reaction product which comprises lithium and said reduced metal ion.

PREPARATION OF LITHIUM-CONTAINING MATERIALS

This application is a divisional of Canadian Application Serial No.: 2,395,115, filed December 22, 2000 (division of Canadian Application Serial No. 2,394,318, filed December 22, 2000).

Field of the Invention

This invention relates to improved materials usable as electrode active materials and to their preparation.

Background of the Invention

Lithium batteries are prepared from one or more lithium electrochemical cells containing electrochemically active (electroactive) materials. Such cells typically include an anode (negative electrode), a cathode (positive electrode), and an electrolyte interposed between spaced apart positive and negative electrodes. Batteries with anodes of metallic lithium and containing metal chalcogenide cathode active material are known. The electrolyte typically comprises a salt of lithium dissolved in one or more solvents, typically nonaqueous (aprotic) organic solvents. Other electrolytes are solid electrolytes typically called polymeric matrixes that contain an ionic conductive medium, typically a metallic powder or salt, in combination with a polymer that itself may be ionically conductive which is electrically insulating. By convention, during discharge of the cell, the negative electrode of the cell is defined as the anode. Cells having a metallic lithium anode and metal chalcogenide cathode are charged in an initial condition. During discharge, lithium ions from the metallic anode pass through the liquid electrolyte to the electrochemical active (electroactive) material of the cathode whereupon they release electrical energy to an external circuit.

It has recently been suggested to replace the lithium metal anode with an insertion anode, such as a lithium metal chalcogenide or lithium metal oxide. Carbon anodes, such as coke and graphite, are also insertion materials. Such negative electrodes are used with lithium- containing insertion cathodes, in order to form an electroactive couple in a cell. Such cells, in an initial condition, are not charged. In order to be used to deliver electrochemical energy, such cells must be charged in order to transfer lithium to the anode from the lithium- containing cathode. During discharge the lithium is transferred from the anode back to the cathode. During a subsequent recharge, the lithium is transferred back to the anode where it re-inserts. Upon subsequent charge and discharge, the lithium ions (Li^+) are transported between the electrodes. Such rechargeable batteries, having no free metallic species are called rechargeable ion batteries or rocking chair batteries. See U.S. Patent Nos. 5,418,090; 4,464,447; 4,194,062; and 5,130,211.

Preferred positive electrode active materials include $LiCoO_2$, $LiMn_2O_4$, and $LiNiO_2$. The cobalt compounds are relatively expensive and the nickel compounds are difficult to synthesize. A relatively economical positive electrode is $LiMn_2O_4$, for which methods of synthesis are known. The lithium cobalt oxide ($LiCoO_2$), the lithium manganese oxide ($LiMn_2O_4$), and the lithium nickel oxide ($LiNiO_2$) all have a common disadvantage in that the charge capacity of a cell comprising such cathodes suffers a significant loss in capacity. That is, the initial capacity available (amp hours/gram) from $LiMn_2O_4$, $LiNiO_2$, and $LiCoO_2$ is less than the theoretical capacity because significantly less than 1 atomic unit of lithium engages in the electrochemical reaction. Such an initial capacity value is significantly diminished during the first cycle operation and such capacity further diminishes on every successive cycle of operation. For $LiNiO_2$ and $LiCoO_2$ only about 0.5 atomic units of lithium is reversibly cycled during cell operation. Many attempts have been made to reduce capacity fading, for example, as described in U.S. Patent No. 4,828,834 by Nagaura et al. However, the presently known and commonly used, alkali transition metal oxide compounds suffer from relatively low capacity. Therefore, there remains the difficulty of obtaining a lithium-containing electrode material having acceptable capacity without disadvantage of significant capacity loss when used in a cell.

Summary of the Invention

The invention provides novel lithium-mixed metal materials which, upon electrochemical interaction, release lithium ions, and are capable of reversibly cycling lithium ions. The invention provides methods for the preparation of materials useful in manufacturing a rechargeable lithium battery which comprises an electrode formed from the novel lithium-mixed metal materials. Methods for making the novel lithium-mixed metal materials and methods for using such lithium-mixed metal materials in electrochemical cells are also provided. The lithium-mixed metal materials comprise lithium and at least one other metal besides lithium. Preferred materials are lithium-mixed metal phosphates which contain lithium and two other metals besides lithium. Accordingly, the invention provides a rechargeable lithium battery which comprises an electrolyte; a first electrode having a compatible active material; and a second electrode comprising the novel materials. In one aspect, the novel materials are lithium-mixed metal phosphates which preferably used as a positive electrode active material, reversibly cycle lithium ions with the compatible negative electrode active material. Desirably, the lithium-mixed metal phosphate is represented by the nominal general formula $Li_aMI_bMII_c(PO_4)_d$. Such compounds include $Li_1MI_aMII_bPO_4$ and $Li_3MI_aMII_b(PO_4)_3$; therefore, in an initial condition $0 \le a \le 1$ or $0 \le a \le 3$, respectively. During cycling, x quantity of lithium is released where $0 \le x \le a$. In the general formula, the sum of b plus c is up to about 2. Specific examples are $Li_1MI_{1-y}MII_yPO_4$ and $Li_3MI_{2-y}MII_y(PO_4)_3$, where "y" is defined hereinafter.

In one aspect, MI and MII are the same. In a preferred aspect, MI and MII are different from one another. At least one of MI and MII is an element capable of an oxidation state higher than that initially present in the lithium-mixed metal phosphate compound. Correspondingly, at least one of MI and MII has more than one oxidation state in the phosphate compound, and more than one oxidation state above the ground state M^0. The term oxidation state and valence state are used in the art interchangeably.

In another aspect, both MI and MII may have more than one oxidation state and both may be oxidizable from the state initially present in the phosphate compound. Desirably, MII is a metal or semi-metal having a +2 oxidation state, and is selected from Groups 2, 12 and 14 of the Periodic Table. Desirably, MII is selected from non-transition metals and semi-metals. In one embodiment, MII has only one oxidation state and is nonoxidizable from its oxidation state in the lithium-mixed metal compound. In another embodiment, MII has more than one oxidation state. Examples of semi-metals having more than one oxidation state are selenium and tellurium; other non-transition metals with more than one oxidation state are tin and lead. Preferably, MII is selected from Mg (magnesium), Ca (calcium), Zn (zinc), Sr (strontium), Pb (lead), Cd (cadmium), Sn (tin), Ba (barium), and Be (beryllium), and mixtures thereof. In another preferred aspect, MII is a metal having a +2 oxidation state and having more than one oxidation state, and is oxidizable from its oxidation state in lithium-mixed metal compound.

Desirably, MI is selected from Fe (iron), Co (cobalt), Ni (nickel), Mn (manganese), Cu (copper), V (vanadium), Sn (tin), Ti (titanium), Cr (chromium), and mixtures thereof. As can be seen, MI is preferably selected from the first row of transition metals and further includes tin, and MI preferably initially has a +2 oxidation state.

In one aspect, the product $LiMI_{1-y}MII_yPO_4$ may have an olivine structure and the product $Li_3MI_{1-y}(PO_4)_3$ is a rhombohedral or monoclinic Nasicon structure. In another aspect, the term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent. In still another aspect, any portion of P (phosphorous) may be substituted by Si (silicon), S (sulfur), and/or As (arsenic); and any portion of O (oxygen) may be substituted by halogen, preferably F (fluorine). These aspects are also disclosed in U.S. Patent Application Serial Numbers 09/105,748 issued as U.S. 6,136,472 on October 24, 2000, 09/274,371 issued as U.S. 6,153,333 on November 28, 2000 and in U.S. Patent No. 5,871,866 issued February 16, 1999; each of the listed applications and patents are co-owned by the assignee of the present invention.

The metal phosphates are alternatively represented by the nominal general formulas such as $Li_{1-x}MI_{1-y}MII_yPO_4$ $(0 \leq x \leq 1)$, and $Li_{3-x}MI_{2-y}MII_y(PO_4)_3$ signifying capability to release and reinsert lithium. The term "general" refers to a family of compounds, with M, x and y representing variations therein. The expressions 2-y and 1-y each signify that the relative amount of MI and MII may vary. In addition, as stated above, MI may be a mixture of metals meeting the earlier stated criteria for MI. In addition, MII may be a mixture of metallic elements meeting the stated criteria for MII. Preferably, where MII is a mixture, it is a mixture of 2 metallic elements; and where MI is a mixture, it is a mixture of 2 metals. Preferably, each such metal and metallic element has a +2 oxidation state in the initial phosphate compound.

The active material of the counter electrode is any material compatible with the lithium-mixed metal phosphate of the invention. Where the lithium-mixed metal phosphate is used as a positive electrode active material, metallic lithium, lithium-containing material, or non-lithium-containing material may be used as the negative electrode active material. The negative electrode is desirably a nonmetallic insertion material. Desirably, the negative electrode comprises an active material from the group consisting of metal oxide, particularly transition metal oxide, metal chalcogenide, carbon, graphite, and mixtures thereof. It is preferred that the anode active material comprises a carbonaceous material such as graphite. The lithium-mixed metal phosphate of the invention may also be used as a negative electrode material.

In another embodiment, the present invention provides a method of preparing a compound of the nominal general formula $Li_aMI_bMII_c(PO_4)_d$ where $0 < a \leq 3$; the sum of b plus c is greater than zero and up to about 2; and $0 < d \leq 3$. Preferred compounds include $Li_3MI_bMII_c(PO_4)_3$ where b plus c is about 2; and $LiMI_bMII_cPO_4$ where b plus c is about 1. The method comprises providing starting materials in particle form. The starting (precursor) materials include a lithium-containing compound, one or more metal containing compounds, a compound capable of providing the phosphate $(PO_4)^{-3}$ anion, and carbon. Preferably, the lithium-containing compound is in particle form, and an example is lithium salt. Preferably, the phosphate-containing anion compound is in particle form, and examples include metal phosphate salt and diammonium hydrogen phosphate (DAHP) and ammonium dihydrogen phosphate (ADHP). The lithium compound, one or more metal compounds, and phosphate compound are included in a proportion which provides the stated nominal general formula. The starting materials are mixed together with carbon, which is included in an amount sufficient to reduce the metal ion of one or more of the metal-containing starting materials without full reduction to an elemental metal state. Excess quantities of carbon and one or more other starting materials (i.e., 5 to 10% excess) may be used to enhance product quality. A small amount of carbon, remaining after the reaction, functions as a conductive constituent in the ultimate electrode formulation. This is an advantage since such remaining carbon is very intimately mixed with the product active material. Accordingly, large quantities of excess carbon, on the order of 100% excess carbon are useable in the process. The carbon present during compound formation is thought to be intimately dispersed throughout the precursor and product. This provides many advantages, including the enhanced conductivity of the product. The presence of carbon particles in the starting materials is also thought to provide nucleation sites for the production of the product crystals.

According to a preferred embodiment, the invention provides a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound having a melting point greater than 450°C, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and heating said starting materials in a non-oxidizing atmosphere at a temperature sufficient to form a reaction product comprising lithium and said reduced metal ion.

Another preferred embodiment of the invention provides a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and

heating said starting materials at a temperature sufficient to form a reaction product comprising lithium and said reduced metal ion; wherein said lithium compound is selected from the group consisting of lithium carbonate, lithium phosphate, lithium oxide, lithium vanadate, and mixtures thereof.

Still another preferred embodiment of the invention is a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising a metal compound; a lithium compound; carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and a compound containing a polyanion capable of forming a crystal lattice; and

heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said polyanion.

In another aspect of the present invention, there is provided, in a preferred embodiment, a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising a metal oxide; lithium carbonate; carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and a compound containing a phosphate group; and

heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said phosphate group.

In another aspect of this invention there is provided a method of making a compound which comprises:

mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound selected from the group consisting of lithium acetate ($LiOOCCH_3$), lithium nitrate ($LiNO_3$), lithium oxalate ($Li_2C_2O_4$), lithium oxide (Li_2O), lithium phosphate (Li_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), lithium vanadate ($LiVO_3$), and lithium carbonate (Li_2CO_3), and carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and

heating said starting materials at a temperature sufficient to form a single phase reaction product.

Still another preferred embodiment of the invention, there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form, said starting materials comprising a first metal compound, a lithium compound, a second metal compound, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and heating said starting materials at a temperature sufficient to form a reaction product comprising lithium and said reduced metal ion, wherein the second metal compound has a second metal ion which is not reduced and which forms a part of said reaction product.

In still another aspect of the present invention, there is provided in a preferred embodiment, a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form, said starting materials comprising a metal compound, a lithium compound, a phosphate compound, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and heating said starting materials at a temperature sufficient to form a reaction product comprising lithium and said reduced metal ion, wherein said reaction product is a lithium metal phosphate.

In another aspect of this invention there is provided a two-stage method for making a lithium iron phosphate, wherein the first stage comprises mixing starting materials comprising iron oxide, diammonium hydrogen phosphate and carbon, and heating said first stage mixed starting materials at a temperature sufficient to produce iron phosphate; and the second stage comprises mixing starting materials comprising said iron phosphate and lithium phosphate, and heating said second stage mixed starting materials at a temperature sufficient to form the lithium iron phosphate represented by the nominal formula $LiFePO_4$.

According to another preferred embodiment, the invention provides a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials consisting of lithium carbonate, iron phosphate, diammonium hydrogen phosphate, a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide, and carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and

heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said phosphate group.

Still another preferred embodiment of the invention there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises:

mixing starting materials in particle form, said starting materials comprising an oxide of a transition metal selected from Groups 4 to 11 inclusive of the Periodic Table having a +2 valence state, a compound of a metal selected from Groups 2, 12, and 14 of the Periodic Table having a +2 valence state; a lithium compound selected from the group consisting of lithium carbonate and lithium dihydrogen phosphate, a phosphate group containing compound selected from the group diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof; and carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state; and

heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said phosphate group.

The starting materials are intimately mixed and then reacted together where the reaction is initiated by heat and is preferably conducted in a nonoxidizing, inert atmosphere, whereby the lithium, metal from the metal compound(s), and phosphate combine to form the $Li_aMI_bMII_c(PO_4)_d$ product. Before reacting the compounds, the particles are intermingled to form an essentially homogeneous powder mixture of the precursors. In one aspect, the precursor powders are dry-mixed using a ball mill, such as zirconia media. Then the mixed powders are pressed into pellets. In another aspect, the precursor powders are mixed with a binder. The binder is selected so as to not inhibit reaction between particles of the powders. Therefore, preferred binders decompose or evaporate at a temperature less than the reaction temperature. Examples include mineral oils (i.e., glycerol, or C-18 hydrocarbon mineral oil) and polymers which decompose (carbonize) to form a carbon residue before the reaction starts, or which evaporate before the reaction starts. In still another aspect, intermingling is conducted by forming a wet mixture using a volatile solvent and then the intermingled particles are pressed together in pellet form to provide good grain-to-grain contact.

Although it is desired that the precursor compounds be present in a proportion which provides the stated general formula of the product, the lithium compound may be present in an excess amount on the order of 5 percent excess lithium compared to a stoichiometric mixture of the precursors. And the carbon may be present at up to 100% excess compared to the stoichiometric amount. The method of the invention may also be used to prepare other novel products, and to prepare known products. A number of lithium compounds are available as precursors, such as lithium acetate ($LiOOCCH_3$), lithium hydroxide, lithium nitrate ($LiNO_3$), lithium oxalate ($Li_2C_2O_4$), lithium oxide (Li_2O), lithium phosphate (Li_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), lithium vanadate ($LiVO_3$), and lithium carbonate (Li_2CO_3). The lithium carbonate is preferred for the solid state reaction since it has a very high melting point and commonly reacts with the other precursors before melting. Lithium carbonate has a melting point over 600°C and it decomposes in the presence of the other precursors and/or effectively reacts with the other precursors before melting. In contrast, lithium hydroxide melts at about 400°C. At some reaction temperatures preferred herein of over 450°C the lithium hydroxide will melt before any significant reaction with the other precursors occurs to an effective extent. This melting renders the reaction very difficult to control. In addition, anhydrous LiOH is highly hygroscopic and a significant quantity of water is released during the reaction. Such water needs to be removed from the oven and the resultant product may need to be dried. In one preferred aspect, the solid state reaction made possible by the present invention is much preferred since it is conducted at temperatures at which the lithium-containing compound reacts with the other reactants before melting. Therefore, lithium hydroxide is useable as a precursor in the method of the invention in combination with some precursors, particularly the phosphates. The method of the invention is able to be conducted as an economical carbothermal-based process with a wide variety of precursors and over a relatively broad temperature range.

The aforesaid precursor compounds (starting materials) are generally crystals, granules, and powders and are generally referred to as being in particle form. Although many types of phosphate salts are known, it is preferred to use diammonium hydrogen phosphate $(NH_4)_2HPO_4$ (DAHP) or ammonium dihydrogen phosphate $(NH_4)H_2PO_4$ (ADHP). Both ADHP and DAHP meet the preferred criteria that the precursors decompose in the presence of one another or react with one another before melting of such precursor. Exemplary metal compounds are Fe_2O_3, Fe_3O_4, V_2O_5, VO_2, $LiVO_3$, NH_4VO_3, $Mg(OH)_2$, Cao, MgO, $Ca(OH)_2$, MnO_2, Mn_2O_3, $Mn_3(PO_4)_2$, CuO, SnO, SnO_2, TiO_2, Ti_2O_3, Cr_2O_3, PbO_2, PbO, $Ba(OH)_2$, BaO, $Cd(OH)_2$. In addition, some starting materials serve as both the source of metal ion and phosphate, such as $FePO_1$, $Fe_3(PO_4)_2$, $Zn_3(PO_4)_2$, and $Mg_3(PO_4)_2$. Still others contain both lithium ion and phosphate such as Li_3PO_4 and LiH_2PO_4. Other exemplary precursors are H_3PO_4 (phosphoric acid); and P_2O_5 (P_4O_{10}) phosphoric oxide; and HPO_3 meta phosphoric acid, which is a decomposition product of P_2O_5. If it is desired to replace any of the oxygen with a halogen, such as fluorine, the starting materials further include a fluorine compound such as LiF. If it is desired to replace any of the phosphorous with silicon, then the starting materials further include silicon oxide (SiO_2). Similarly, ammonium sulfate in the starting materials is useable to replace phosphorus with sulfur.

The starting materials are available from a number of sources. The following are typical. Vanadium pentoxide of the formula V_2O_5 is obtainable from any number of suppliers including Kerr McGee, Johnson Matthey, or Alpha Products of Davers, Massachusetts. Vanadium pentoxide has a CAS number of 1314-62-1. Iron oxide Fe_3O_3 is a common and very inexpensive material available in powder form from the same suppliers. The other precursor materials mentioned above are also available from well known suppliers, such as those listed above.

The method of the invention may also be used to react starting materials in the presence of carbon to form a variety of other novel products, such as gamma-LiV_2O_5 and also to produce known products. Here, the carbon functions to reduce metal ion of a starting metal compound to provide a product containing such reduced metal ion. The method is particularly useful to also add lithium to the resultant product, which thus contains the metallic element ions, namely, the lithium ion and the other metal ion, thereby forming a mixed metal product. An example is the reaction of vanadium pentoxide (V_2O_5) with lithium carbonate in the presence of carbon to form gamma-LiV_2O_5. Here the starting metal ion $V^{+5}V^{+5}$ is reduced to $V^{+4}V^{+5}$ in the final product. A single phase gamma-LiV_2O_5 product is not known to have been directly and independently formed before.

As described earlier, it is desirable to conduct the reaction at a temperature where the lithium compound reacts before melting. The temperature should be about 400°C or greater, and desirably 450°C or greater, and preferably 500°C or greater, and generally will proceed at a faster rate at higher temperatures. The various reactions involve production of CO or CO_2 as an effluent gas. The equilibrium at higher temperature favors CO formation. Some of the reactions are more desirably conducted at temperatures greater than 600°C; most desirably greater than 650°C; preferably 700°C or greater; more preferably 750°C or greater. Suitable ranges for many reactions are about 700 to 950°C, or about 700 to 800°C.

Generally, the higher temperature reactions produce CO effluent and the stoichiometry requires more carbon be used than the case where CO_2 effluent is produced at lower temperature. This is because the reducing effect of the C to CO_2 reaction is greater than the C to CO reaction. The C to CO_2 reaction involves an increase in carbon oxidation state of +4 (from 0 to 4) and the C to CO reaction involves an increase in carbon oxidation state of +2 (from ground state zero to 2). Here, higher temperature generally refers to a range of about 650°C to about 1000°C and lower temperature refers to up to about 650°C. Temperatures higher than 1200°C are not thought to be needed.

In one aspect, the method of the invention utilizes the reducing capabilities of carbon in a unique and controlled manner to produce desired products having structure and lithium content suitable for electrode active materials. The method of the invention makes it possible to produce products containing lithium, metal and oxygen in an economical and convenient process. The ability to lithiate precursors, and change the oxidation state of a metal without causing abstraction of oxygen from a precursor is heretofore unexpected. These advantages are at least in part achieved by the reductant, carbon, having an oxide whose free energy of formation becomes more negative as temperature increases. Such oxide of carbon is more stable at high temperature than at low temperature. This feature is used to produce products having one or more metal ions in a reduced oxidation state relative to the precursor metal ion oxidation state. The method utilizes an effective combination of quantity of carbon, time and temperature to produce new products and to produce known products in a new way.

Referring back to the discussion of temperature, at about 700°C both the carbon to carbon monoxide and the carbon to carbon dioxide reactions are occurring. At closer to 600°C the C to CO_2 reaction is the dominant reaction. At closer to 800°C the C to CO reaction is dominant. Since the reducing effect of the C to CO_2 reaction is greater, the result is that less carbon is needed per atomic unit of metal to be reduced. In the case of carbon to carbon monoxide, each atomic unit of carbon is oxidized from ground state zero to plus 2. Thus, for each atomic unit of metal ion (M) which is being reduced by one oxidation state, one half atomic unit of carbon is required. In the case of the carbon to carbon dioxide reaction, one quarter atomic unit of carbon is stoichiometrically required for each atomic unit of metal ion (M) which is reduced by one oxidation state, because carbon goes from ground state zero to a plus 4 oxidation state. These same relationships apply for each such metal ion being reduced and for each unit reduction in oxidation state desired.

It is preferred to heat the starting materials at a ramp rate of a fraction of a degree to 10°C per minute and preferably about 2°C per minute. Once the desired reaction temperature is attained, the reactants (starting materials) are held at the reaction temperature for several hours. The heating is preferably conducted under non-oxidizing or inert gas such as argon or vacuum.

Advantageously, a reducing atmosphere is not required, although it may be used if desired. After reaction, the products are preferably cooled from the elevated temperature to ambient (room) temperature (i.e., 10°C to 40°C). Desirably, the cooling occurs at a rate similar to the earlier ramp rate, and preferably 2°C/minute cooling. Such cooling rate has been found to be adequate to achieve the desired structure of the final product. It is also possible to quench the products at a cooling rate on the order of about 100°C/minute. In some instances, such rapid cooling (quench) may be preferred.

The present invention resolves the capacity problem posed by widely used cathode active material. It has been found that the capacity and capacity retention of cells having the preferred active material of the invention are improved over conventional materials. Optimized cells containing lithium-mixed metal phosphates of the invention potentially have performance improved over commonly used lithium metal oxide compounds. Advantageously, the new method of making the novel lithium-mixed metal phosphate compounds of the invention is relatively economical and readily adaptable to commercial production.

Another feature of one embodiment of the invention includes an electrochemical cell or battery based on lithium-mixed metal phosphates. Still another feature is to provide an electrode active material which combines the advantages of good discharge capacity and capacity retention. It is also a desirable feature of the present invention to provide electrodes which can be manufactured economically. Yet another feature of one embodiment is to provide a method for forming electrode active material which lends itself to commercial scale production for preparation of large quantities.

Another embodiment of the method of the present invention comprises of a method of making a lithium mixed metal polyanion compound by reacting a mixture of a lithium compound and at least one metal containing compound, said compounds in particle form, the improvement comprising of an incorporating carbon into said mixture in an amount sufficient to reduce the oxidation state of at least one metal ion of the metal containing compound without full reduction to an elemental state and carrying out the reaction in the presence of said carbon.

Another embodiment of the method of the present invention consists of a method of making a lithium mixed metal compound by reaction of starting materials which comprises: (a) in a first stage, mixing starting materials in particle form, the starting materials consisting of iron oxide, diammonium hydrogen phosphate and carbon, said carbon being present in an amount sufficient to reduce the oxidation state of the iron oxide without full reduction to an elemental state, and heating said starting materials in a non-oxidizing atmosphere at a temperature sufficient to produce iron phosphate; and(b) in a second stage, mixing starting materials consisting of said iron phosphate and lithium phosphate and heating said second stage mixed starting materials at a temperature sufficient to form lithium iron phosphate represented by the nominal formula $LiFePO_4$.

A further aspect of the method of the present invention relates to an improvement in a method of making a lithium mixed metal compound by reaction of starting materials in which the reaction, in a first stage comprises heating in a non-oxidizing atmosphere and at a temperature sufficient to form iron phosphate, a mixture of starting materials in particle form, said starting materials being iron oxide and diammonium hydrogen phosphate, and in a second stage, mixing starting materials consisting of said iron phosphate and lithium phosphate and heating said second stage mixed starting materials at a temperature sufficient to form lithium iron phosphate represented by the nominal formula $LiFePO_4$, the improvement which comprises incorporating, in the starting materials of the first stage, and prior to said heating of said starting materials of said first stage, carbon in an amount sufficient to reduce the oxidation state of the iron ion of said iron oxide without full reduction to an elemental state.

Yet another aspect of the method of the present invention relates to a method of making a lithium mixed metal compound by reaction of starting materials comprising mixing starting materials in particle form, said starting materials comprising a metal oxide; a lithium compound selected from lithium carbonate and lithium dihydrogen phosphate; and a compound containing a phosphate group; and in which the reaction involves heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, said reduced metal ion, and said phosphate group, the improvement comprising incorporating into said starting materials carbon in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state.

The present invention also includes a method of making a lithium mixed metal compound by reaction of starting materials which comprises mixing starting materials in particle form, said starting materials consisting of iron oxide, a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; lithium carbonate; a phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and carbon, said carbon being present in an amount sufficient to reduce the oxidation state of the iron ion of said iron oxide without full reduction to an elemental state; and heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, reduced iron ion, and said phosphate group.

An additional embodiment of the invention includes a method of making a lithium mixed metal compound by reaction of starting materials which comprises mixing starting materials in particle form, said starting materials being lithium carbonate; iron phosphate; diammonium hydrogen phosphate; a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; and heating said starting materials at a temperature sufficient to form a single phase reaction product comprising lithium, the reduced iron ion, and said phosphate group, the improvement which comprises incorporating carbon into said starting materials in an amount sufficient to reduce the oxidation state of the iron ion of said iron phosphate without full reduction to an elemental state.

Further aspects of the present invention include a method of making a compound which comprises mixing starting materials in particle form, said starting materials comprising at least one metal containing compound and a lithium compound selected from the group consisting of lithium acetate ($LiOOCCH_3$), lithium nitrate ($LiNO_3$), lithium oxalate ($Li_2C_2O_4$), lithium oxide (Li_2O), lithium phosphate (Li_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), lithium vanadate ($LiVO_3$), and lithium carbonate (Li_2CO_3); and heating said starting materials at a temperature sufficient to form a single phase reaction product, the improvement which comprises incorporating carbon into said starting materials in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state.

According to a further aspect of the present invention, there is provided a reactive composition comprising a mixture of starting materials in particle form, said starting materials comprising at least one metal containing compound, a lithium compound and carbon, said carbon being present in at least an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state upon heating of the mixture.

In the above composition the lithium compound preferably has a melting point greater than 450°C. Still further, most desirably the lithium compound is selected from the group consisting of lithium carbonate, lithium phosphate, lithium oxide, lithium vanadate, and mixtures thereof. In a preferred composition, the metal of said metal containing compound is selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and mixtures thereof. More desirably, the metal containing compound is selected from the group consisting of Fe_2O_3, V_2O_5, $FePO_4$, VO_2, Fe_3O_4, $LiVO_3$, NH_4VO_3, and mixtures thereof.

In other preferred embodiments of the invention, the above composition starting materials which include a second metal containing compound having a second metal ion which is not reduced and which is adapted to form a part of a reaction product of said composition. Desirably, such starting materials include a second metal containing compound which is a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

In another embodiment of the above composition of the present invention, the said second metal containing compound is selected from the group consisting of magnesium hydroxide and calcium hydroxide. In addition, desirably the starting materials include a phosphate compound and said composition when reacted forms a reaction product which is a lithium metal phosphate. In other embodiments, the phosphate compound may be selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof.

In another embodiment of this invention the above composition, said metal compound is a metal oxide or a metal phosphate. Desirably, the metal compound is V_2O_5, and said lithium compound is lithium carbonate.

According to another aspect of the present invention, there is provided a reactive composition in particle form for forming a lithium iron phosphate represented by the nominal formula $LiFePO_4$, wherein said reactive mixture consists of an iron phosphate and lithium phosphate, in which the iron phosphate is the reaction product of iron oxide, diammonium hydrogen phosphate and carbon, the carbon being present in said reactive composition in at least an amount sufficient to reduce the oxidation state of the iron ion of said iron oxide without full reduction to an elemental state.

In a still further aspect of the present invention, there is provided a reactive composition for forming a single phase reaction product comprising lithium, reduced iron ion, and a phosphate group, said composition comprising a mixture of starting materials in particle form, said starting materials consisting of iron oxide, a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; lithium carbonate; a phosphate selected from the group consisting of diammonium hydrogen phosphate and ammonium dihydrogen phosphate; and carbon, said carbon being present in at least an amount sufficient to reduce the oxidation state of the iron ion of said iron oxide without full reduction to an elemental state.

In yet a further embodiment of the present invention there is also provided a reactive composition for making a single phase reaction product comprising lithium, reduced iron ion, and a phosphate group, said composition comprising a mixture of starting materials in particle form, said starting materials consisting of: lithium carbonate; iron phosphate; diammonium hydrogen phosphate; a hydroxide selected from the group consisting of magnesium hydroxide and calcium hydroxide; and carbon, said carbon being present in at least an amount sufficient to reduce the oxidation state of the iron ion of said iron phosphate without full reduction to an elemental state.

Another embodiment of the present invention involves a reactive composition comprising a mixture of starting materials in particle form, wherein said starting materials comprise carbon, at least one metal oxide and one further metal compound, the metal of said metal oxide being selected from (a) Ca; (b) Sn; and (c) a transition metal selected from Groups 4 to 11 inclusive of the Periodic Table having a +2 valence state, and the further metal compound being a compound of a metal selected from Groups 2, 12, and 14 of the Periodic Table having a +2 valence state; a lithium compound selected from the group consisting of lithium carbonate and lithium dihydrogen phosphate; and a phosphate compound selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof, said carbon being present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state.

In a preferred composition of the present invention, desirably the starting materials consist of carbon, lithium carbonate, iron oxide and a phosphate of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof.

A still further embodiment of the present invention involves a reactive composition suitable for making a single phase compound which comprises mixed starting materials in particle form, said starting materials comprising at least one metal containing compound, a lithium compound selected from the group consisting of lithium acetate ($LiOOCCH_3$), lithium nitrate ($LiNO_3$), lithium oxalate ($Li_2C_2O_4$), lithium oxide (Li_2O), lithium phosphate (Li_3PO_4), lithium dihydrogen phosphate (LiH_2PO_4), lithium vanadate ($LiVO_3$), and lithium carbonate (Li_2CO_3), and carbon present in an amount at least sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state.

In the preceding composition, desirably the metal of said metal containing compound is a metal selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr, and mixtures thereof. A further preferred feature of such a composition is where the metal containing compound is selected from the group consisting of Fe_2O_3, V_2O_5, $FePO_4$, VO_2, Fe_3O_4, $LiVO_3$, NH_4VO_3, and mixtures thereof.

Other preferred forms of the above composition include embodiments where the starting materials include a second metal compound having a second metal ion not capable of being reduced and which will form a part of a reaction product. Desirably, the second metal compound is a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Most preferably, the second metal compound is selected from the group consisting of magnesium hydroxide and calcium hydroxide.

In the preceding compositions, preferably the starting materials include a phosphate compound which is selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, and mixtures thereof. Another preferred embodiment of the above compositions is where the metal containing compound is a metal oxide or a metal phosphate. Preferably, the metal containing compound is V_2O_5, and said lithium compound is lithium carbonate.

In yet another embodiment of the present invention, there is provided a reactive composition for making a lithium mixed metal compound comprising a mixture of starting materials in particle form, said starting materials comprising a first metal compound, a lithium compound, a second metal compound, and carbon, where said carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state, said second metal compound having a second metal ion which is nonreducable and which is adapted to form a part of a reaction product.

The present invention also provides another embodiment of a reactive composition suitable for making a lithium mixed metal reaction product comprising lithium and a reduced metal ion, said composition comprising a mixture of starting materials in particle form, said starting materials comprising one or more metal containing compounds, a lithium compound, a phosphate compound, and carbon, where said carbon is present in an amount at least sufficient to reduce the oxidation state of at least one metal ion of said starting materials without full reduction to an elemental state.

Another form of the present invention involves a reactive composition for forming a lithium iron phosphate represented by the nominal formula $LiFePO_4$, said composition being a mixture of starting materials in particle form comprising iron oxide, diammonium hydrogen phosphate and carbon.

In the preceding embodiments, desirably the second metal compound comprises a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Preferably the above compositions are compositions which have the second metal compound chosen from the group consisting of magnesium hydroxide and calcium hydroxide.

In a further desirable embodiment of the above compositions, the phosphate compound is selected from the group consisting of diammonium hydrogen phosphate, ammonium dihydrogen phosphate, lithium dihydrogen phosphate, and mixtures thereof. Also, desirably, the first metal compound is selected from the group consisting of Fe_2O_3, V_2O_5, $FePO_4$, VO_2, Fe_3O_4, $LiVO_3$, NH_4VO_3, and mixtures thereof. Preferably, the composition is one where the metal of said first metal compound is a compound of a metal selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Ti and Cr. The above compositions may be compositions where the second metal compound is a compound of a metal selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba and Be.

A particularly preferred embodiment according to one aspect of the present invention is where any of the above compositions have carbon present in a stoichiometric excess, which is desirably up to 100% stoichiometric excess.

In another embodiment of the present invention, there is provided as a novel product, a reaction product produced by any one of the previously described methods. In such a reaction product obtained by the previously described methods, the product can contain residual carbon from the reaction, and in which the residual carbon is in intimate admixture with the components of the reaction product. The reaction product obtained by the previously described methods can be a product which comprises crystals of lithium material, wherein the crystals are nucleated onto the carbon particles.

In another embodiment of the present invention, there is also provided a composition comprising a lithium mixed metal polyanion compound; and a carbon dispersed throughout the lithium mixed metal polyanion compound, wherein the composition is prepared by a process comprising the step of reacting, in particle form, a lithium compound and at least one metal compound in the presence of carbon wherein the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the metal compound without full reduction to an elemental state.

Desirably, the preceding composition is obtained by a reaction step which comprises providing as starting materials a lithium compound, a metal compound, and carbon, in powder form, mixing the powders, and heating the mixture for a time and at a temperature sufficient to produce the reaction product. Desirably, carbon is present in stoichiometric excess during the reaction step. Preferably, the reaction step comprises reacting a finely divided mixture of a lithium compound, a metal compound and carbon.

In the preceding compositions, desirably the lithium mixed metal polyanion compound comprises a mixed metal phosphate of general formula

$$Li_aMI_bMII_c(PO_4)_d$$

wherein $0 < a \leq 3$, $0< b+c \leq 2$, $0 < d \leq 3$, and wherein MI and 8. MII are the same or different, and at least one of MI and MII has more than one oxidation state above the ground state. Preferably, MI and MII are the same. In other cases, MI and MII have more than one oxidation state above the ground state. A preferred embodiment is where MII has a +2 oxidation state. In such an embodiment desirably MII comprises an element from groups 2, 12,or 14 of the periodic table. A particularly preferred embodiment is where MII is selected from the group consisting of magnesium, calcium, zinc, strontium, lead, cadmium, tin, barium, beryllium, and mixtures thereof.

In the preceding compositions preferably MI is selected from the group consisting of iron, cobalt, nickel, manganese, copper, vanadium, tin, titanium, chromium, and mixtures thereof. In another embodiment, MI comprises one or more metals selected from the group consisting of first row transition metals and tin, and wherein MII is selected from the group consisting of magnesium, calcium, zinc, strontium, lead, cadmium, tin, barium, beryllium, and mixtures thereof.

A still further aspect of the present invention relates to a composition comprising a lithium mixed metal material represented by general formula

$$LiMI_{1-y}MII_yPO_4$$

and carbon particles dispersed throughout the lithium mixed metal material in particle form, wherein the composition is prepared by a process comprising the step of reacting a lithium compound and at least one metal compound in the presence of carbon wherein the carbon is present in an amount sufficient to reduce at least one metal ion of the metal compound without full reduction to elemental state, wherein $0 \leq y \leq 1$, MI and MII are the same or different and each comprise a metal or mixture of metals, and at least one of MI and MII has more than one oxidation state above the ground state.

In the preceding composition, the lithium mixed metal material may have an olivine structure. As preferred embodiments, MI is selected from the group consisting of iron, cobalt, manganese, copper, vanadium, tin, titanium, chromium, and mixture thereof, and MII is selected from the group consisting of magnesium, calcium, zinc, strontium, lead, cadmium, tin barium, beryllium, and mixtures thereof. Another embodiment is where MI has more than one oxidation state above the ground state, and MII has an oxidation state of +2. Desirably, MI comprises iron or cobalt. Another embodiment is where MI comprises iron, cobalt or mixtures thereof and where MII comprises magnesium, calcium, zinc or mixtures thereof.

In the above formula, preferably the composition is one in which $0 < y \le 0.5$, desirably $0 < y \le 0.2$.

The present invention also provides an embodiment of a composition in which the composition comprises a lithium mixed metal material represented by formula

$$LiFe_{1-y}Mg_yPO_4$$

wherein $0 < y \le 0.2$; and carbon particles dispersed throughout the lithium mixed metal material, the material being in particle form, wherein the composition is prepared by a process comprising the step of reacting a lithium compound and at least one metal compound in the presence of carbon wherein the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the metal compound without full reduction to an elemental state. In this composition, desirably the lithium mixed metal material is a compound of the general formula

$$LiFe_{1-y}Ca_yPO_4$$

wherein $0 < y \le 0.2$. Another embodiment of the invention is a composition wherein the lithium mixed metal material is a compound of the general formula

$$LiFe_{1-y}Zn_yPO_4$$

wherein $0 < y \le 0.2$.

Yet a further aspect of the present invention provides a composition of the type outlined above, wherein the lithium mixed metal material is a compound of the general formula

$$LiCo_{1-y}Mg_yPO_4$$

wherein $0 < y \leq 0.2$.

Another embodiment of the invention wherein the lithium mixed metal material is a compound of the general formula

$$LiCo_{1-y}Ca_yPO_4$$

wherein $0 < y \leq 0.2$.

A further embodiment of the invention is where the lithium mixed metal material is a compound of the general formula

$$LiCo_{1-y}Zn_yPO_4$$

wherein $0 < y \leq 0.2$.

Yet another aspect of the invention is a composition comprising carbon particles and crystals of a lithium mixed metal material in particle form, wherein the crystals are nucleated onto the particles, wherein the composition is made by a process comprising the step of reacting a lithium compound and a metal compound in the presence of carbon.

In a further embodiment the invention provides a composition comprising carbon particles and crystals of a lithium mixed metal material in particle form, wherein the crystals are nucleated onto the particles, wherein the composition is made by a process comprising the step of reacting a lithium compound and a metal compound in the presence of a stoichiometric excess of carbon.

In yet another embodiment the invention includes a composition comprising a lithium mixed metal material in particle form represented by general formula

$$Li_3MI_yMII_{2-y}(PO_4)_3, \text{ and}$$

carbon particles dispersed throughout the lithium mixed metal material, wherein the composition is prepared by a process comprising the step of reacting a lithium compound and a metal compound in the presence of carbon, wherein $0 \leq y \leq 2$, MI and MII are the same or different and each comprise a metal or mixture of metals and at least one of MI and MII has more than one oxidation state above the ground state.

In the preceding embodiment, the lithium mixed metal material may have a nasicon structure; preferably MI and MII are different. Further, in preceding embodiments, MI is desirably selected from the group consisting of iron, cobalt, nickel, manganese, copper, vanadium, tin, titanium, chromium and mixtures thereof, and wherein MII is selected from the group consisting of magnesium, calcium, zinc, strontium, lead, cadmium, tin, barium, beryllium, and mixtures thereof.

These and other aspects, features, and advantages will become apparent from the following description of the preferred embodiments, claims, and accompanying drawings.

According to one aspect of the present invention there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture, the starting

compound, a lithium compound having a melting point greater than 450°C, and carbon, where the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state; and heating the wet mixture in a non-oxidizing atmosphere at a temperature sufficient to form a reaction product comprising lithium and the reduced metal ion.

According to another aspect of the present invention there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture, the starting materials comprising at least one or more metal containing compound, a lithium compound, and carbon, where the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state; and heating the wet mixture at a temperature sufficient to form a reaction product comprising lithium and the reduced metal ion; wherein the lithium compound is selected from the group consisting of lithium carbonate, lithium phosphate, lithium oxide, lithium vanadate, and mixtures thereof.

According to yet another aspect of the present invention there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture, the starting materials comprising at least one metal containing compound; a lithium compound; carbon present in an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state; and a compound containing a polyanion capable of forming a crystal lattice; and heating the wet mixture at a temperature sufficient to form a single phase reaction product comprising lithium, the reduced metal ion, and the polyanion.

According to still yet another aspect of the present invention there is provided a method of making a lithium mixed metal compound by reaction of starting materials which comprises: mixing starting materials in particle form with a volatile solvent or binder to form a wet mixture, the starting materials comprising a first metal compound, a lithium compound, a second metal compound, and carbon, where the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state; and heating the wet mixture at a temperature sufficient to form a reaction product comprising lithium and the reduced metal ion, wherein the second metal compound has a second metal ion which is not reduced and which forms a part of the reaction product.

According to still yet another aspect of the present invention there is provided a reactive composition comprising: a wet mixture of starting materials in particle form and a volatile solvent or binder, the starting materials comprising at least one metal containing compound, a lithium compound and carbon, the carbon being present in at least an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state upon heating of the wet mixture.

According to still yet another aspect of the present invention there is provided a reactive composition for making a lithium mixed metal compound comprising a wet mixture of starting materials in particle form and a volatile solvent or binder, the starting materials comprising a first metal compound, a lithium compound, a second metal compound, and carbon, where the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the starting materials without full reduction to an elemental state, the second metal compound having a second metal ion which is nonreducable and which is adapted to form a part of a reaction product.

According to still yet another aspect of the present invention there is provided a composition comprising: a lithium mixed metal polyanion compound; and carbon dispersed throughout the lithium mixed metal material, wherein the composition is prepared by a process comprising mixing a lithium compound, a volatile solvent or binder and at least one metal compound in the presence of carbon, wherein the carbon is present in an amount sufficient to reduce the oxidation state of at least one metal ion of the metal compound without full reduction to an elemental state, to form a wet mixture; and heating the wet mixture at a temperature and for a time sufficient to produce the lithium mixed metal polyanion.

According to still yet another aspect of the present invention there is provided a composition comprising a lithium mixed metal material represented by general formula

$$LiMI_{1-y}MII_{y}PO_{4}$$

and carbon dispersed throughout the lithium mixed metal material, wherein the composition is prepared by a process comprising the step of mixing a lithium compound, a volatile, and at least one metal compound in the presence of carbon wherein the carbon is present in an amount sufficient to reduce at least one metal ion of the metal compound without full reduction to elemental state, wherein $0 \leq y \leq 1$, MI and MII are the same or different and each comprise a metal or mixture of metals, and at least one of MI and MII has more than one oxidation state above the ground state.

Brief Description of the Drawings

Figure 1 shows the results of an x-ray diffraction analysis, of the $LiFePO_4$ prepared according to the invention using CuKα radiation, λ = 1.5405A. Bars refer to simulated pattern from refined cell parameters, Space Group, SG = Pnma (62). The values are a = 10.2883A (0.0020), b = 5.9759A (0.0037), c = 4.6717A (0.0012) 0.0072, cell volume = $287.2264A^3$ (0.0685). Density, p = 3.605 g/cc, zero = 0.452 (0.003). Peak at full width half maximum, PFWHM = 0.21. Crystallite size from XRD data = 704A.

Figure 2 is a voltage/capacity plot of $LiFePO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts at a temperature of about 23°C. The cathode contained 19.0mg of the $LiFePO_4$ active material, prepared by the method of the invention. The electrolyte comprised ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and included a 1 molar concentration of $LiPF_6$ salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a glass fiber separator which is interpenetrated by the solvent and the salt.

Figure 3 shows multiple constant current cycling of $LiFePO_4$ active material cycled with a lithium metal anode using the electrolyte as described in connection with Figure 2 and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions, 23°C and 60°C. Figure 3 shows the excellent rechargeability of the lithium iron phosphate/lithium metal cell, and also shows the excellent cycling and specific capacity (mAh/g) of the active material.

Figure 4 shows the results of an x-ray diffraction analysis, of the $LiFe_{0.9}Mg_{0.1}PO_4$ prepared according to the invention, using CuKα radiation, λ = 1.5405A. Bars refer to simulated pattern from refined cell parameters SG = Pnma (62). The values are a = 10.2688A (0.0069), b = 5.9709A (0.0072), c = 4.6762A (0.0054), cell volume = 286.7208A (0.04294), p = 3.617 g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite = 950A.

Figure 5 is a voltage/capacity plot of $LiFe_{0.9}Mg_{0.1}PO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.9mg of the $LiFe_{0.9}Mg_{0.1}PO_4$ active material prepared by the method of the invention.

Figure 6 shows multiple constant current cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions, 23°C and 60°C. **Figure 6** shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

Figure 7 is a voltage/capacity plot of $LiFe_{0.8}Mg_{0.2}PO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°C. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 16mg of the $LiFe_{0.8}Mg_{0.2}PO_4$ active material prepared by the method of the invention.

Figure 8 shows the results of an x-ray diffraction analysis, of the $LiFe_{0.9}Ca_{0.1}PO_4$ prepared according to the invention, using CuKα radiation, λ = 1.5405A. Bars refer to simulated pattern from refined cell parameters SG = Pnma (62). The values are a = 10.3240A (0.0045), b = 6.0042A (0.0031), c = 4.6887A (0.0020), cell volume = 290.6370A (0.1807), zero = 0.702 (0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite = 680A.

Figure 9 is a voltage/capacity plot of $LiFe_{0.8}Ca_{0.2}PO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.5mg of the $LiFe_{0.8}Ca_{0.2}PO_4$ active material prepared by the method of the invention.

Figure 10 is a voltage/capacity plot of $LiFe_{0.8}Zn_{0.2}PO_4$-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 4.0 volts at 23°C. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 18.9mg of the $LiFe_{0.8}Zn_{0.2}PO_4$ active material prepared by the method of the invention.

Figure 11 shows the results of an x-ray diffraction analysis of the gamma-$Li_xV_2O_5$(x = 1, gamma LiV_2O_5) prepared according to the invention using CuKα radiation λ = 1.5405A. The values are a = 9.687A (1), b = 3.603A (2), and c = 10.677A (3); phase type is gamma-$Li_xV_2O_5$ (x = 1); symmetry is orthorhombic; and space group is Pnma.

Figure 12 is a voltage/capacity plot of gamma-

LiV_2O_5-containing cathode cycled with a lithium metal anode using constant current cycling at ± 0.2 milliamps per square centimeter in a range of 2.5 to 3.8 volts at 23°C. Other conditions are as described earlier with respect to **Figure 2**. The cathode contained 21mg of the gamma-LiV_2O_5 active material prepared by the method of the invention.

Figure 13 is a two-part graph based on multiple constant current cycling of gamma-LiV_2O_5 cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 3.8 volts. In the two-part graph, **Figure 13** shows the excellent rechargeability of the lithium-metal-oxide/lithium metal cell. **Figure 13** shows the excellent cycling and capacity of the cell.

Figure 14 shows the results of an x-ray diffraction analysis of the $Li_3V_2(PO_4)_3$ prepared according to the invention. The analysis is based on CuKα radiation, $\lambda = 1.5405A$. The values are a = 12.184A (2), b = 8.679A (2), c = 8.627A (3), and $\beta = 90.457°$ (4).

Figure 15 shows the results of an x-ray diffraction analysis of $Li_3V_2(PO_4)_3$ prepared according to a method described in U.S. Patent No. 5,871,866. The analysis is based on CuKα radiation, $\lambda = 1.5405A$. The values are a = 12.155A (2), b = 8.711A (2), c = 8.645A (3); the angle beta is 90.175 (6); symmetry is Monoclinic; and space group is $P2_1/n$.

Figure 16 is an EVS (Electrochemical Voltage Spectroscopy) voltage/capacity profile for a cell with cathode material formed by the carbothermal reduction method of the invention. The cathode material is 13.8mg of $Li_3V_2(PO_4)_3$. The cell includes a lithium metal counter electrode in an electrolyte comprising ethylene carbonate (EC) and dimethyl carbonate (DMC) in a weight ratio of 2:1 and including a 1 molar concentration of $LiPF_6$ salt. The lithium-metal-phosphate containing electrode and the lithium metal counter electrode are maintained spaced apart by a fiberglass separator which is interpenetrated by the solvent and the salt. The conditions are ± 10 mV steps, between about 3.0 and 4.2 volts, and the critical limiting current density is less than or equal to 0.1 mA/cm^2.

Figure 17 is an EVS differential capacity versus voltage plot for the cell as described in connection with **Figure 16**.

Figure 18 shows multiple constant current cycling of $LiFe_{0.8}Mg_{0.2}PO_4$ cycled with a lithium metal anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 4.0 volts at two different temperature conditions, 23°C and 60°C. **Figure 18** shows the excellent rechargeability of the lithium-metal-phosphate/lithium metal cell, and also shows the excellent cycling and capacity of the cell.

Figure 19 is a graph of potential over time for the first four complete cycles of the $LiMg_{0.1}Fe_{0.9}PO_4$/MCMB graphite cell of the invention.

Figure 20 is a two-part graph based on multiple constant current cycling of $LiFe_{0.9}Mg_{0.1}PO_4$ cycled with an MCMB graphite anode using the electrolyte as described in connection with **Figure 2** and cycled, charge and discharge at ± 0.2 milliamps per square centimeter, 2.5 to 3.6 volts, 23°C and based on a C/10 (10 hour) rate. In the two-part graph, **Figure 20** shows the excellent rechargeability of the lithium-metal-phosphate/graphite cell. **Figure 20** shows the excellent cycling and capacity of the cell.

Figure 21 is a graph of potential over time for the first three complete cycles of the gamma-LiV_2O_5/MCMB graphite cell of the invention.

Figure 22 is a diagrammatic representation of a typical laminated lithium-ion battery cell structure.

Figure 23 is a diagrammatic representation of a typical multi-cell battery cell structure.

Detailed Description of the Preferred Embodiments

The present invention provides lithium-mixed metal-phosphates, which are usable as electrode active materials, for lithium (Li^+) ion removal and insertion. Upon extraction of the lithium ions from the lithium-mixed-metal-phosphates, significant capacity is achieved. In one aspect of the invention, electrochemical energy is provided when combined with a suitable counter electrode by extraction of a quantity x of lithium from lithium-mixed-metal-phosphates $Li_{a-x}MI_bMII_c(PO_4)_d$. When a quantity x of lithium is removed per formula unit of the lithium-mixed-metal phosphate, metal MI is oxidized. In another aspect, metal MII is also oxidized. Therefore, at least one of MI and MII is oxidizable from its initial condition in the phosphate compound as Li is removed. Consider the following which illustrate the mixed metal compounds of the invention: $LiFe_{1-y}Sn_yPO_4$, has two oxidizable elements, Fe and Sn; in contrast, $LiFe_{1-y}Mg_yPO_4$ has one oxidizable metal, the metal Fe.

In another aspect, the invention provides methods for preparation of materials useful in a lithium ion battery; typically such a battery comprises an electrolyte; a negative electrode having an insertion active material; and a positive electrode comprising a lithium-mixed-metal-phosphate active material characterized by an ability to release lithium ions for insertion into the negative electrode active material. The lithium-mixed-metal-phosphate is desirably represented by the nominal general formula $Li_aMI_bMII_c(PO_4)_d$. Although the metals MI and MII may be the same, it is preferred that the metals MI and MII are different. Desirably, in the phosphate compound MI is a metal selected from the group: Fe, Co, Ni, Mn, Cu, V, Sn, Ti, Cr and mixtures thereof, and MI is most desirably a transition metal or mixture thereof selected from said group. Most preferably, MI has a +2 valence or oxidation state.

In another aspect, MII is selected from Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof. Most preferably, MII has a +2 valence or oxidation state. The lithium-mixed-metal-phosphate is preferably a compound represented by the nominal general formula $Li_{a-x}MI_bMII_c(PO_4)_d$, signifying the preferred composition and its capability to release x lithium. Accordingly, during cycling, charge and discharge, the value of x varies as x greater than or equal to 0 and less than or equal to a. The present invention resolves a capacity problem posed by conventional cathode active materials. Such problems with conventional active materials are described by Tarascon in U.S. Patent No. 5,425,932, using $LiMn_2O_4$ as an example. Similar problems are observed with $LiCoO_2$, $LiNiO_2$, and many, if not all, lithium metal chalcogenide materials. The present invention demonstrates that significant capacity of the cathode active material is utilizable and maintained.

A preferred novel procedure for forming the lithium-mixed-metal-phosphate $Li_aMI_bMII_c(PO_4)_d$ compound active material will now be described. In addition, the preferred novel procedure is also applicable to formation of other lithium metal compounds, and will be described as such. The basic procedure will be described with reference to exemplary starting materials but is not limited thereby. The basic process comprises conducting a reaction between a lithium compound, preferably lithium carbonate (Li_2CO_3), metal compound(s), for example, vanadium pentoxide (V_2O_5), iron oxide (Fe_2O_3), and/or manganese hydroxide, and a phosphoric acid derivative, preferably the phosphoric acid ammonium salt, diammonium hydrogen phosphate, $(NH_4)_2H(PO_4)$. Each of the precursor starting materials are available from a number of chemical outfits including Aldrich Chemical Company and Fluka. Using the method described herein, $LiFePO_4$ and $LiFe_{0.9}Mg_{0.1}PO_4$, $Li_3V_2(PO_4)_3$ were prepared with approximately a stoichiometric amount of Li_2CO_3, the respective metal compound, and $(NH_4)_2HPO_4$. Carbon powder was included with these precursor materials. The precursor materials were initially intimately mixed and dry ground for about 30 minutes. The intimately mixed compounds were then pressed into pellets. Reaction was conducted by heating in an oven at a preferred ramped heating rate to an elevated temperature, and held at such elevated temperature for several hours to complete formation of the reaction product. The entire reaction was conducted in a non-oxidizing atmosphere, under flowing pure argon gas. The flow rate will depend upon the size of the oven and the quantity needed to maintain the atmosphere. The oven was permitted to cool down at the end of the reaction period, where cooling occurred at a desired rate under argon. Exemplary and preferred ramp rates, elevated reaction temperatures and reaction times are described herein. In one aspect, a ramp rate of 2°/minute to an elevated temperature in a range of 750°C to 800°C was suitable along with a dwell (reaction time) of 8 hours. Refer to Reactions 1, 2, 3 and 4 herein. In another variation per Reaction 5, a reaction temperature of 600°C was used along with a dwell time of about one hour. In still another variation, as per Reaction 6, a two-stage heating was conducted, first to a temperature of 300°C and then to a temperature of 850°.

The general aspects of the above synthesis route are applicable to a variety of starting materials. Lithium-containing compounds include Li_2O (lithium oxide), LiH_2PO_4 (lithium hydrogen phosphate), $Li_2C_2O_4$(lithium oxalate), LiOH (lithium hydroxide), $LiOH.H_2O$ (lithium hydroxide monohydride), and $LiHCO_3$ (lithium hydrogen carbonate). The metal compounds(s) are reduced in the presence of the reducing agent, carbon. The same considerations apply to other lithium-metal- and phosphate-containing precursors. The thermodynamic considerations such as ease of reduction, of the selected precursors, the reaction kinetics, and the melting point of the salts will cause adjustment in the general procedure, such as, amount of carbon reducing agent, and the temperature of reaction.

Figures 1 through **21** which will be described more particularly below show characterization data and capacity in actual use for the cathode materials (positive electrodes) of the invention. Some tests were conducted in a cell comprising a lithium metal counter electrode (negative electrode) and other tests were conducted in cells having a carbonaceous counter electrode. All of the cells had an EC:DMC-$LiPF_6$ electrolyte.

Typical cell configurations will now be described with reference to **Figures 22 and 23**; and such battery or cell utilizes the novel active material of the invention. Note that the preferred cell arrangement described here is illustrative and the invention is not limited thereby. Experiments are often performed, based on full and half cell arrangements, as per the following description. For test purposes, test cells are often fabricated using lithium metal electrodes. When forming cells for use as batteries, it is preferred to use an insertion positive electrode as per the invention and a graphitic carbon negative electrode.

A typical laminated battery cell structure 10 is depicted in **Figure 22**. It comprises a negative electrode side 12, a positive electrode side 14, and an electrolyte/separator 16 there between. Negative electrode side 12 includes current collector 18, and positive electrode side 14 includes current collector 22. A copper collector foil 18, preferably in the form of an open mesh grid, upon which is laid a negative electrode membrane 20 comprising an insertion material such as carbon or graphite or low-voltage lithium insertion compound, dispersed in a polymeric binder matrix. An electrolyte/separator film 16 membrane is preferably a plasticized copolymer. This electrolyte/separator preferably comprises a polymeric separator and a suitable electrolyte for ion transport. The electrolyte/separator is positioned upon the electrode element and is covered with a positive electrode membrane 24 comprising a composition of a finely divided lithium insertion compound in a polymeric binder matrix. An aluminum collector foil or grid 22 completes the assembly. Protective bagging material 40 covers the cell and prevents infiltration of air and moisture.

In another embodiment, a multi-cell battery configuration as per **Figure 23** is prepared with copper current collector 51, negative electrode 53, electrolyte/separator 55, positive electrode 57, and aluminum current collector 59. Tabs 52 and 58 of the current collector elements form respective terminals for the battery structure. As used herein, the terms "cell" and "battery" refer to an individual cell comprising anode/electrolyte/cathode and also refer to a multi-cell arrangement in a stack.

The relative weight proportions of the components of the positive electrode are generally: 50-90% by weight active material; 5-30% carbon black as the electric conductive diluent; and 3-20% binder chosen to hold all particulate materials in contact with one another without degrading ionic conductivity. Stated ranges are not critical, and the amount of active material in an electrode may range from 25-95 weight percent. The negative electrode comprises about 50-95% by weight of a preferred graphite, with the balance constituted by the binder. A typical electrolyte separator film comprises approximately two parts polymer for every one part of a preferred fumed silica. The conductive solvent comprises any number of suitable solvents and salts. Desirable solvents and salts are described in U.S. Patent Nos. 5,643,695 and 5,418,091. One example is a mixture of EC:DMC:$LiPF_6$ in a weight ratio of about 60:30:10.

Solvents are selected to be used individually or in mixtures, and include dimethyl carbonate (DMC), diethylcarbonate (DEC), dipropylcarbonate (DPC), ethylmethylcarbonate (EMC), ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate, lactones, esters, glymes, sulfoxides, sulfolanes, etc. The preferred solvents are EC/DMC, EC/DEC, EC/DPC and EC/EMC. The salt content ranges from 5% to 65% by weight, preferably from 8% to 35% by weight.

Those skilled in the art will understand that any number of methods are used to form films from the casting solution using conventional meter bar or doctor blade apparatus. It is usually sufficient to air-dry the films at moderate temperature to yield self-supporting films of copolymer composition. Lamination of assembled cell structures is accomplished by conventional means by pressing between metal plates at a temperature of about 120-160°C. Subsequent to lamination, the battery cell material may be stored either with the retained plasticizer or as a dry sheet after extraction of the plasticizer with a selective low-boiling point solvent. The plasticizer extraction solvent is not critical, and methanol or ether are often used.

Separator membrane element 16 is generally polymeric and prepared from a composition comprising a copolymer. A preferred composition is the 75 to 92% vinylidene fluoride with 8 to 25% hexafluoropropylene copolymer (available commercially from Atochem North America as KYNAR FLEX®) and an organic solvent plasticizer. Such a copolymer composition is also preferred for the preparation of the electrode membrane elements, since subsequent laminate interface compatibility is ensured. The plasticizing solvent may be one of the various organic compounds commonly used as solvents for electrolyte salts, e.g., propylene carbonate or ethylene carbonate, as well as mixtures of these compounds. Higher-boiling plasticizer compounds such as dibutyl phthalate, dimethyl phthalate, diethyl phthalate, and tris butoxyethyl phosphate are particularly suitable. Inorganic filler adjuncts, such as fumed alumina or silanized fumed silica, may be used to enhance the physical strength and melt viscosity of a separator membrane and, in some compositions, to increase the subsequent level of electrolyte solution absorption.

In the construction of a lithium-ion battery, a current collector layer of aluminum foil or grid is overlaid with a positive electrode film, or membrane, separately prepared as a coated layer of a dispersion of insertion electrode composition. This is typically an insertion compound such as $LiMn_2O_4$ (LMO), $LiCoO_2$, or $LiNiO_2$, powder in a copolymer matrix solution, which is dried to form the positive electrode. An electrolyte/separator membrane is formed as a dried coating of a composition comprising a solution containing VdF:HFP copolymer and a plasticizer solvent is then overlaid on the positive electrode film. A negative electrode membrane formed as a dried coating of a powdered carbon or other negative electrode material dispersion in a VdF:HFP copolymer matrix solution is similarly overlaid on the separator membrane layer. A copper current collector foil or grid is laid upon the negative electrode layer to complete the cell assembly. Therefore, the VdF:HFP copolymer composition is used as a binder in all of the major cell components, positive electrode film, negative electrode film, and electrolyte/separator membrane. The assembled components are then heated under pressure to achieve heat-fusion bonding between the plasticized copolymer matrix electrode and electrolyte components, and to the collector grids, to thereby form an effective laminate of cell elements. This produces an essentially unitary and flexible battery cell structure.

Examples of forming cells containing metallic lithium anode, insertion electrodes, solid electrolytes and liquid electrolytes can be found in U.S. Patent Nos. 4,668,595; 4,830,939; 4,935,317; 4,990,413; 4,792,504; 5,037,712; 5,262,253; 5,300,373; 5,435,054; 5,463,179; 5,399,447; 5,482,795 and 5,411,820. Note that the older generation of cells contained organic polymeric and inorganic electrolyte matrix materials, with the polymeric being most preferred. The polyethylene oxide of 5,411,820 is an example. More modern examples are the VdF:HFP polymeric matrix. Examples of casting, lamination and formation of cells using VdF:HFP are as described in U.S. Patent Nos. 5,418,091; 5,460,904; 5,456,000; and 5,540,741; assigned to Bell Communications Research.

As described earlier, the electrochemical cell operated as per the invention, may be prepared in a variety of ways. In one embodiment, the negative electrode may be metallic lithium. In more desirable embodiments, the negative electrode is an insertion active material, such as, metal oxides and graphite. When a metal oxide active material is used, the components of the electrode are the metal oxide, electrically conductive carbon, and binder, in proportions similar to that described above for the positive electrode. In a preferred embodiment, the negative electrode active material is graphite particles. For test purposes, test cells are often fabricated using lithium metal electrodes. When forming cells for use as batteries, it is preferred to use an insertion metal oxide positive electrode and a graphitic carbon negative electrode. Various methods for fabricating electrochemical cells and batteries and for forming electrode components are described herein. The invention is not, however, limited by any particular fabrication method.

Formation of Active Materials

EXAMPLE I

Reaction 1(a). $LiFePO_4$ formed from $FePO_4$

$$FePO_4 + 0.5\ Li_2CO_3 + 0.5\ C \rightarrow LiFePO_4 + 0.5\ CO_2 + 0.5\ CO$$

(a) Pre-mix reactants in the following proportions using ball mill. Thus,

1 mol $FePO_4$	150.82g
0.5 mol Li_2CO_3	36.95g
0.5 mol carbon	6.0g

(but use <u>100%</u> excess carbon → 12.00g)

(b) Pelletize powder mixture

(c) Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°/minute under argon.

(e) Powderize pellet.

Note that at 750°C this is predominantly a CO reaction. This reaction is able to be conducted at a temperature in a range of about 700°C to about 950°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum.

EXAMPLE II

Reaction 1(b). $LiFePO_4$ formed from Fe_2O_3

$0.5\ Fe_2O_3 + 0.5\ Li_2CO_3 + (NH_4)_2HPO_4 + 0.5\ C \rightarrow LiFePO_4 + 0.5\ CO_2 + 2\ NH_3 + 3/2\ H_2O + 0.5\ CO$

(a) Premix powders in the following proportions

0.5 mol Fe_2O_3	79.85g
0.5 mol Li_2CO_3	36.95g
1 mol $(NH_4)_2HPO_4$	132.06g
0.5 mol carbon	6.00g

(use 100% excess carbon → 12.00g)

(b) Pelletize powder mixture

(c) Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°/minute under argon.

(e) Powderize

EXAMPLE III

Reaction 1(c). $LiFePO_4$ - from $Fe_3(PO_4)_2$

Two steps:

Part I. Carbothermal preparation of $Fe_3(PO_4)_2$

$3/2\ Fe_2O_3 + 2(NH_4)_2HPO_4 + 3/2\ C \rightarrow Fe_3(PO_4)_2 + 3/2\ CO + 4NH_3 + 5/2\ H_2O$

(a) Premix reactants in the following proportions

3/2 mol Fe_2O_3	239.54g

2 mol $(NH_4)_2HPO_4$	264.12g
3/2 mol carbon	18.00g

(use 100% excess carbon → 36.00g)

(b) Pelletize powder mixture

(c) Heat pellet to 800°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°C/minute under argon.

(e) Powderize pellet.

Part II. Preparation of $LiFePO_4$ from the $Fe_3(PO_4)_2$ of Part I.

$Li_3PO_4 + Fe(PO_4)_2 \rightarrow 3\ LiFePO_4$

(a) Premix reactants in the following proportions

1 mol Li_3PO_4	115.79g
1 mol $Fe_3(PO_4)_2$	357.48g

(b) Pelletize powder mixture

(c) Heat pellet to 750°C at a rate of 2°/minute in flowing inert atmosphere (e.g. argon). Dwell for 8 hours at 750°C under argon.

(d) Cool to room temperature at 2°C/minute under argon.

(e) Powderize pellet.

EXAMPLE IV

Reaction 2(a). $LiFe_{0.9}Mg_{0.1}PO_4$ ($LiFe_{1-y}Mg_yPO_4$) formed from $FePO_4$

$$0.5\ Li_2CO_3 + 0.9\ FePO_4 + 0.1\ Mg(OH)_2 + 0.1(NH_4)_2HPO_4 + 0.45C \rightarrow LiFe_{0.9}Mg_{0.1}PO_4 + 0.5CO_2 + 0.45CO + 0.2NH_3 + 0.25\ H_2O$$

(a) Pre-mix reactants in the following proportions

0.50 mol Li_2CO_3 = 36.95g
0.90 mol $FePO_4$ = 135.74g
0.10 mol $Mg(OH)_2$ = 5.83g
0.10 mol $(NH_4)_2HPO_4$ = 1.32g
0.45 mol carbon = 5.40g

(use 100% excess carbon → 10.80g)

(b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

EXAMPLE V

Reaction 2(b). $LiFe_{0.9}Mg_{0.1}PO4$ ($LiFe_{1-y}Mg_yPO_4$) formed from Fe_2O_3

$$0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.10\ Mg\ (OH)_2 + (NH_4)_2HPO_4 + 0.45C \rightarrow LiFe_{0.9}Mg_{0.1}PO_4 + 0.5\ CO_2 + 0.45\ CO + 2\ NH_3 + 1.6\ H_2O$$

(a) Pre-mix reactants in following ratio

0.50 mol Li_2CO_3 = 36.95g
0.45 mol Fe_2O_3 = 71.86g
0.10 mol $Mg(OH)_2$ = 5.83g
1.00 mol $(NH_4)_2HPO_4$ = 132.06g
0.45 mol carbon = 5.40g

(use 100% excess carbon → 10.80g)

(b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

EXAMPLE VI

Reaction 2(c). $LiFe_{0.9}Mg_{0.1}PO_4$ ($LiFe_{1-y}Mg_yPO_4$) formed from LiH_2PO_4

$$1.0\ LiH_2PO_4 + 0.45\ Fe_2O_3 + 0.10\ Mg(OH)_2 + 0.45C \rightarrow LiFe_{0.9}Mg_{0.1}PO_4 + 0.45\ CO + 1.1\ H_2O$$

(a) Pre-mix reactants in the following proportions

1.00 mol LiH_2PO_4 = 103.93g
0.45 mol Fe_2O_3 = 71.86g
0.10 mol $Mg(OH)_2$ - 5.83g
0.45 mol carbon = 5.40g

(use 100% excess carbon → 10.80g)

(b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

EXAMPLE VII

Reaction 3. Formation of $LiFe_{0.9}Ca_{0.1}PO_4$ ($LiFe_{1-y}Ca_yPO_4$) from Fe_2O_3

$$0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.1\ Ca(OH)_2 + (NH_4)_2HPO_4 + 0.45C \rightarrow LiFe_{0.9}Ca_{0.1}PO_4 + 0.5\ CO_2 + 0.45\ CO + 2\ NH_3 + 1.6\ H_2O$$

(a) Pre-mix reactants in the following proportions

0.50 mol Li_2CO_3 = 36.95g

0.45 mol Fe_2O_3 = 71.86g
0.10 mol $Ca(OH)_2$ = 7.41g
1.00 mol $(NH_4)_2HPO_4$ = 132.06g
0.45 mol carbon = 5.40g

(100% excess carbon → 10.80g)

(b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours' dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

EXAMPLE VIII

Reaction 4. Formation of $LiFe_{0.9}Zn_{0.1}PO_4$ ($LiFe_{1-y}Zn_yPO_4$) from Fe_2O_3.

$$0.50\ Li_2CO_3 + 0.45\ Fe_2O_3 + 0.033\ Zn_3\ (PO_4)_2 + 0.933(NH_4)_2HPO_4 + 0.45\ C \rightarrow LiFe_{0.9}Zn_{0.1}PO_4 + 0.50\ CO_2 + 0.45\ CO + 1.866\ NH_3 + 1.2\ H_2O$$

Pre-mix reactants in the following proportions

0.50 mol Li_2CO_3 = 36.95g
0.45 mol Fe_2O_3 = 71.86g
0.033 mol $Zn_3(PO_4)_2$ = 12.74g
0.933 mol $(NH_4)_2HPO_4$ = 123.21g
0.45 mol carbon = 5.40g

(100% excess carbon → 10.80g)

(b) Pelletize powder mixture

(c) Heat to 750°C at a rate of 2°/minute in argon. Hold for 8 hours dwell at 750°C in argon

(d) Cool at a rate of 2°/minute

(e) Powderize pellet.

EXAMPLE IX

Reaction 5. Formation of gamma-LiV_2O_5 (γ)

$$V_2O_5 + 0.5\ Li_2CO_3 + 0.25\ C \rightarrow LiV_2O_5 + 3/4\ CO_2$$

(a) Pre-mix alpha V_2O_5, Li_2CO_3 and Shiwinigan Black (carbon) using ball mix with suitable media. Use a 25% weight excess of carbon over the reaction amounts above. For example, according to reaction above:

Need:	1 mol V_2O_5	181.88g
	0.5 mol Li_2CO_3	36.95g
	0.25 mol carbon	3.00g

(but use 25% excess carbon → 3.75g)

(b) Pelletize powder mixture

(c) Heat pellet to 600°C in flowing argon (or other inert atmosphere) at a heat rate of approximately 2°/minute. Hold at 600°C for about 60 minutes.

(d) Allow to cool to room temperature in argon at cooling rate of about 2°/minute.

(e) Powderize pellet using mortar and pestle

This reaction is able to be conducted at a temperature in a range of about 400°C to about 650°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum. This reaction at this temperature range is primarily $C \rightarrow CO_2$. Note that the reaction $C \rightarrow CO$ primarily occurs at a temperature over about 650°C (HT, high temperature); and the reaction $C \rightarrow CO_2$ primarily occurs at a temperature of under about 650°C (LT, low temperature). The reference to about 650°C is approximate and the designation "primarily" refers to the predominant reaction thermodynamically favored although the alternate reaction may occur to some extent.

EXAMPLE X

Reaction 6. Formation of $Li_3V_2(PO_4)_3$

$$V_2O_5 + 3/2\ Li_2CO_3 + 3(NH_4)_2HPO_4 + C \rightarrow Li_3V_2(PO_4)_3 + 2\ CO + 3/2\ CO_2 + 6\ NH_3 + 9/2\ H_2O$$

(a) Pre-mix reactants above using ball mill with suitable media. Use a 25% weight excess of carbon. Thus,

1 mol V_2O_5	181.88g
3/2 mol Li_2CO_3	110.84g
3 mol $(NH_4)_2HPO_4$	396.18g
1 mol carbon	12.01g

(but use 25% excess carbon → 15.01g)

(b) Pelletize powder mixture

(c) Heat pellet at 2°/minute to 300°C to remove CO_2 (from Li_2CO_3) and to remove NH_3, H_2O. Heat in an inert atmosphere (e.g. argon). Cool to room temperature.

(d) Powderize and repelletize

(e) Heat pellet in inert atmosphere at a rate of 2°C/minute to 850°C. Dwell for 8 hours at 850°C

(f) Cool to room temperature at a rate of 2°/minute in argon.

(e) Powderize

This reaction is able to be conducted at a temperature in a range of about 700°C to about 950°C in argon as shown, and also under other inert atmospheres such as nitrogen or vacuum. A reaction temperature greater than about 670°C ensures C → CO reaction is primarily carried out.

Characterization of Active Materials and Formation and Testing of Cells

Referring to **Figure 1**, the final product $LiFePO_4$, prepared from Fe_2O_3 metal compound per Reaction 1(b), appeared brown/black in color. This olivine material product included carbon that remained after reaction. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 1**. The pattern evident in **Figure 1** is consistent with the single phase olivine phosphate, $LiFePO_4$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group SG = pnma (62) and the lattice parameters from XRD refinement are consistent with the olivine structure. The values are a = 10.2883A (0.0020), b = 5.9759 (0.0037), c = 4.6717A (0.0012) 0.0072, cell volume = 287.2264A^3 (0.0685). Density, p = 3.605 g/cc, zero = 0.452 (0.003). Peak at full width half maximum, PFWHM = 0.21. Crystallite size from XRD data = 704A.

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula $LiFePO_4$. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent, and that some portion of P may be substituted by Si, S or As; and some portion of O may be substituted by halogen, preferably F.

The $LiFePO_4$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 19.0mg of active material. The positive electrode contained, on a weight % basis, 85% active material, 10% carbon black, and 5% EPDM. The negative electrode was metallic lithium. The electrolyte was a 2:1 weight ratio mixture of ethylene carbonate and dimethyl carbonate within which was dissolved 1 molar $LiPF_6$. The cells were cycled between about 2.5 and about 4.0 volts with performance as shown in **Figures 2 and 3**.

Figure 2 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 19 milligrams of the $LiFePO_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFePO_4$. The lithium is extracted from the $LiFePO_4$ during charging of the cell. When fully charged, about 0.72 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to $Li_{1-x}FePO_4$ where x appears to be equal to about 0.72, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 19 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFePO_4$. The re-insertion corresponds to approximately 121 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative capacity demonstrated during the entire extraction-insertion cycle is 244mAh/g.

Figure 3 presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the $LiFePO_4$ versus lithium metal counter electrode between 2.5 and 4.0 volts. Data is shown for two temperatures, 23°C and 60°C. **Figure 3** shows the excellent rechargeability of the $LiFePO_4$ cell, and also shows good cycling and capacity of the cell. The performance shown after about 190 to 200 cycles is good and shows that electrode formulation is very desirable.

Referring to **Figure 4**, there is shown data for the final product $LiFe_{0.9}Mg_{0.1}PO_4$, prepared from the metal compounds Fe_2O_3 and $Mg(OH)_2 \rightarrow Mg(OH)_2$, per Reaction 2(b). Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 4**. The pattern evident in **Figure 4** is consistent with the single phase olivine phosphate compound, $LiFe_{0.9}Mg_{0.1}PO_4$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group SG = Pnma (62) and the lattice parameters from XRD refinement are consistent with the olivine structure. The values are a = 10.2688A (0.0069), b = 5.9709A (0.0072), c = 4.6762A (0.0054), cell volume = 286.7208A (0.04294), p = 3.617 g/cc, zero = 0.702 (0.003), PFWHM = 0.01, and crystallite = 950A.

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula $LiFe_{0.9}Mg_{0.1}PO_4$. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent, and that some substitution of P and O may be made while maintaining the basic olivine structure.

The $LiFe_{0.9}Mg_{0.1}PO_4$, prepared as described immediately above, was tested in an electrochemical cell. The positive electrode was prepared as described above, using 18.9mg of active materials. The positive electrode, negative electrode and electrolyte were prepared as described earlier and in connection with **Figure 1**. The cell was between about 2.5 and about 4.0 volts with performance as shown in **Figures 4, 5 and 6.**

Figure 5 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the $LiFe_{0.9}Mg_{0.1}PO_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.9}Mg_{0.1}PO_4$. The lithium is extracted from the $LiFe_{0.9}Mg_{0.1}PO_4$ during charging of the cell. When fully charged, about 0.87 units of lithium have been removed per formula unit.

Consequently, the positive electrode active material corresponds to $Li_{1-x}Fe_{0.9}Mg_{0.1}PO_4$ where x appears to be equal to about 0.87, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately 150 milliamp hours per gram corresponding to about 2.8 milliamp hours based on 18.9 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.9}Mg_{0.1}PO_4$. The re-insertion corresponds to approximately 146 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 296 mAhr/g. This material has a much better cycle profile than the $LiFePO_4$. **Figure 5** ($LiFe_{0.9}Mg_{0.1}PO_4$) shows a very well defined and sharp peak at about 150 mAh/g. In contrast, **Figure 2** ($LiFePO_4$) shows a very shallow slope leading to the peak at about 123 mAh/g. The Fe-phosphate **(Figure 2)** provides 123 mAh/g compared to its theoretical capacity of 170 mAh/g. This ratio of 123/170, 72% is relatively poor compared to the Fe/Mg-phosphate. The Fe/Mg-phosphate **(Figure 5)** provides 150 mAh/g compared to a theoretical capacity of 160, a ratio of 150/160 or 94%.

Figure 6 presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the $LiFe_{0.9}Mg_{0.1}PO_4$ versus lithium metal counter electrode between 2.5 and 4.0 volts. **Figure 6** shows the excellent rechargeability of the $Li/LiFe_{0.9}Mg_{0.1}PO_4$ cell, and also shows good cycling and capacity of the cell. The performance shown after about 150 to 160 cycles is very good and shows that electrode formulation $LiFe_{0.9}Mg_{0.1}PO_4$ performed significantly better than the $LiFePO_4$. Comparing **Figure 3** ($LiFePO_4$) to **Figure 6** ($LiFe_{0.9}Mg_{0.1}PO_4$) it can be seen that the Fe/Mg-phosphate maintains its capacity over prolonged cycling, whereas the Fe-phosphate capacity fades significantly.

Figure 7 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 16 milligrams of the $LiFe_{0.8}Mg_{0.2}PO_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Mg_{0.2}PO_4$. The lithium is extracted from the $LiFe_{0.8}Mg_{0.2}PO_4$ during charging of the cell. When fully charged, about 0.79 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $LiFe_{0.8}Mg_{0.2}PO_4$ where x appears to be equal to about 0.79, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction approximately 140 milliamp hours per gram corresponding to about 2.2 milliamp hours based on 16 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Mg_{0.2}PO_4$. The re-insertion corresponds to approximately 122 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total cumulative specific capacity over the entire cycle is 262 mAhr/g.

Referring to **Figure 8**, there is shown data for the final product $LiFe_{0.9}Ca_{0.1}PO_4$, prepared from Fe_2O_3 and $Ca(OH)_2$ by Reaction 3. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in Figure 8. The pattern evident in **Figure 8** is consistent with the single phase olivine phosphate compound, $LiFe_{0.9}Ca_{0.1}PO_4$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Here the space group SG = Pnma (62) and the lattice parameters from XRD refinement are consistent with olivine. The values are a = 10.3240A (0.0045), b = 6.0042A (0.0031), c = 4.6887A (0.0020), cell volume = 290.6370A (0.1807), zero = 0.702 (0.003), p = 3.62 g/cc, PFWHM = 0.18, and crystallite = 680A. The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula $LiFe_{0.9}Ca_{0.1}PO_4$.

Figure 9 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.5 milligrams of the $LiFe_{0.8}Ca_{0.2}PO_4$ active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Ca_{0.2}PO_4$. The lithium is extracted from the $LiFe_{0.8}Ca_{0.2}PO_4$ during charging of the cell. When fully charged, about 0.71 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $LiFe_{0.8}Ca_{0.2}PO_4$ where x appears to be equal to about 0.71, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately 123 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 18.5 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Ca_{0.2}PO_4$. The re-insertion corresponds to approximately 110 milliamp hours per gram proportional to the insertion of nearly all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts. The total specific cumulative capacity over the entire cycle is 233 mAhr/g.

Figure 10 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.5 and 4.0 volts based upon about 18.9 milligrams of the $LiFe_{0.8}Zn_{0.2}PO_4$ olivine active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is $LiFe_{0.8}Zn_{0.2}PO_4$, prepared from Fe_2O_3 and $Zn_3(PO_4)_2$ by Reaction 4. The lithium is extracted from the $LiFe_{0.8}Zn_{0.2}PO_4$ during charging of the cell. When fully charged, about 0.74 units of lithium have been removed per formula unit. Consequently, the positive electrode active material corresponds to $Li_{1-x}Fe0.8Zn0.2PO4$ where x appears to be equal to about 0.74, when the cathode material is at 4.0 volts versus Li/Li^+. The extraction represents approximately 124 milliamp hours per gram corresponding to about 2.3 milliamp hours based on 18.9 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the $LiFe_{0.8}Zn_{0.2}PO_4$. The re-insertion corresponds to approximately 108 milliamp hours per gram proportional to the insertion of nearly all of the lithium. The bottom of the curve corresponds to approximately 2.5 volts.

Referring to **Figure 11**, the final product LiV_2O_5, prepared by Reaction 5, appeared black in color. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 11**. The pattern evident in **Figure 11** is consistent with a single oxide compound gamma-LiV_2O_5. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed.

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula gamma-LiV_2O_5. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent.

The LiV_2O_5 prepared as described immediately above, was tested in an electrochemical cell. The cell was prepared as described above and cycled with performance as shown in **Figures 12 and 13.**

Figure 12 shows the results of the first constant current cycling at 0.2 milliamps per square centimeter between about 2.8 and 3.8 volts based upon about 15.0 milligrams of the LiV_2O_5 active material in the cathode (positive electrode). In an as prepared, as assembled, initial condition, the positive electrode active material is LiV_2O_5. The lithium is extracted from the LiV_2O_5 during charging of the cell. When fully charged, about 0.93 unit of lithium had been removed per formula unit. Consequently, the positive electrode active material corresponds to $Li_{1-x}V_2O_5$ where x appears to be equal to about 0.93, when the cathode material is at 3.8 volts versus Li/Li^+. The extraction represents approximately 132 milliamp hours per gram corresponding to about 2.0 milliamp hours based on 15.0 milligrams active material. Next, the cell is discharged whereupon a quantity of lithium is re-inserted into the LiV_2O_5. The re-insertion corresponds to approximately 130 milliamp hours per gram proportional to the insertion of essentially all of the lithium. The bottom of the curve corresponds to approximately 2.8 volts.

Figure 13 presents data obtained by multiple constant current cycling at 0.4 milliamp hours per square centimeter (C/2 rate)of the LiV_2O_5 versus lithium metal counter electrode between 3.0 and 3.75 volts. Data for two temperature conditions are shown, 23°C and 60°C. **Figure 13** is a two part graph with **Figure 13A** showing the excellent rechargeability of the LiV_2O_5. **Figure 13B** shows good cycling and capacity of the cell. The performance shown up to about 300 cycles is good.

Referring to **Figure 14**, the final product $Li_3V_2(PO_4)_3$, prepared by Reaction 6, appeared green/black in color. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 14**. The pattern evident in **Figure 14** is consistent with a single phosphate compound $Li_3V_2(PO_4)_3$ of the monoclinic, Nasicon phase. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed.

The x-ray pattern demonstrates that the product of the invention was indeed the nominal formula $Li_3V_2(PO_4)_3$. The term "nominal formula" refers to the fact that the relative proportion of atomic species may vary slightly on the order of 2 percent to 5 percent, or more typically, 1 percent to 3 percent; and that substitution of P and O may occur.

The $Li_3V_2(PO_4)_3$ prepared as described immediately above, was tested in an electrochemical cell. The cell was prepared as described above, using 13.8mg of active material. The cell was prepared as described above and cycled between about 3.0 and about 4.2 volts using the EVS technique with performance as shown in **Figures 16 and 17**. **Figure 16** shows specific capacity versus electrode potential against Li. **Figure 17** shows differential capacity versus electrode potential against Li.

A comparative method was used to form $Li_3V_2(PO_4)_3$. Such method was reaction without carbon and under H_2-reducing gas as described in U.S. Patent No. 5,871,866. The final product, prepared as per U.S. Patent No. 5,871,866, appeared green in color. Its CuKα x-ray diffraction pattern contained all of the peaks expected for this material as shown in **Figure 15**. The pattern evident in **Figure 15** is consistent with a monoclinic Nasicon single phase phosphate compound $Li_3V_2(PO_4)_3$. This is evidenced by the position of the peaks in terms of the scattering angle 2 θ (theta), x axis. The x-ray pattern showed no peaks due to the presence of precursor oxides indicating that the solid state reaction is essentially entirely completed. Chemical analysis for lithium and vanadium by atomic absorption spectroscopy showed, on a percent by weight basis, 5.17 percent lithium and 26 percent vanadium. This is close to the expected result of 5.11 percent lithium and 25 percent vanadium.

The chemical analysis and x-ray patterns of **Figures 14 and 15** demonstrate that the product of **Figure 14** was the same as that of **Figure 15.** The product of **Figure 14** was prepared without the undesirable H_2 atmosphere and was prepared by the novel carbothermal solid state synthesis of the invention.

Figure 16 shows a voltage profile of the test cell, based on the $Li_3V_2(PO_4)_3$ positive electrode active material made by the process of the invention and as characterized in **Figure 14.** It was cycled against a lithium metal counter electrode. The data shown in **Figure 16** is based on the Electrochemical Voltage Spectroscopy (EVS) technique. Electrochemical and kinetic data were recorded using the Electrochemical Voltage Spectroscopy (EVS) technique. Such technique is known in the art as described by J. Barker in Synth, Met 28, D217 (1989); Synth. Met. 32, 43 (1989); J. Power Sources, 52, 185 (1994); and Electrochemica Acta, Vol. 40, No. 11, at 1603 (1995). **Figure 16** clearly shows and highlights the reversibility of the product. The positive electrode contained about 13.8 milligrams of the $Li_3V_2(PO_4)_3$ active material. The positive electrode showed a performance of about 133 milliamp hours per gram on the first discharge. In **Figure 16**, the capacity in, and the capacity out are essentially the same, resulting in essentially no capacity loss. **Figure 17** is an EVS differential capacity plot based on **Figure 16**. As can be seen from **Figure 17**, the relatively symmetrical nature of peaks indicates good electrical reversibility, there are small peak separations (charge/discharge), and good correspondence between peaks above and below the zero axis. There are essentially no peaks that can be related to irreversible reactions, since all peaks above the axis (cell charge) have corresponding peaks below the axis (cell discharge), and there is essentially no separation between the peaks above and below the axis. This shows that the carbothermal method of the invention produces high quality electrode material.

Figure 18 presents data obtained by multiple constant current cycling at 0.2 milliamp hours per square centimeter of the $LiFe_{0.8}Mg_{0.2}PO_4$ versus lithium metal counter electrode between 2.5 and 4.0 volts. **Figure 18** shows the excellent rechargeability of the $Li/LiFe_{0.8}Mg_{0.2}PO_4$ cell, and also shows good cycling and capacity of the cell. The performance shown after about 110 to 120 cycles at 23°C is very good and shows that electrode formulation $LiFe_{0.8}Mg_{0.2}PO_4$ performed significantly better than the $LiFePO_4$. The cell cycling test at 60°C was started after the 23°C test and was ongoing. Comparing **Figure 3** ($LiFePO_4$) to **Figure 18** ($LiFe_{0.8}Mg_{0.2}PO_4$), it can be seen that the Fe/Mg-phosphate maintains its capacity over prolonged cycling, whereas the Fe-phosphate capacity fades significantly.

In addition to the above cell tests, the active materials of the invention were also cycled against insertion anodes in non-metallic, lithium ion, rocking chair cells.

The lithium mixed metal phosphate and the lithium metal oxide were used to formulate a cathode electrode. The electrode was fabricated by solvent casting a slurry of the treated, enriched lithium manganese oxide, conductive carbon, binder, plasticizer and solvent. The conductive carbon used was Super P (MMM Carbon). Kynar Flex 2801® was used as the binder and electronic grade acetone was used as a solvent. The preferred plasticizer was dibutyl phthalate (DPB). The slurry was cast onto glass and a free-standing electrode was formed as the solvent was evaporated. In this example, the cathode had 23.1mg $LiFe_{0.9}Mg_{0.1}PO_4$ active material. Thus, the proportions are as follows on a percent weight basis: 80% active material; 8% Super P carbon; and 12% Kynar binder.

A graphite counter electrode was prepared for use with the aforesaid cathode. The graphite counter electrode served as the anode in the electrochemical cell. The anode had 10.8 mg of the MCMB graphite active material. The graphite electrode was fabricated by solvent casting a slurry of MCMB2528 graphite, binder, and casting solvent. MCMB2528 is a mesocarbon microbead material supplied by Alumina Trading, which is the U.S. distributor for the supplier, Osaka Gas Company of Japan. This material has a density of about 2.24 grams per cubic centimeter; a particle size maximum for at least 95% by weight of the particles of 37 microns; median size of about 22.5 microns and an interlayer distance of about 0.336. As in the case of the cathode, the binder was a copolymer of polyvinylidene difluoride (PVdF) and hexafluoropropylene (HFP) in a wt. ratio of PVdF to HFP of 88:12. This binder is sold under the designation of Kynar Flex 2801®, showing it's a registered trademark. Kynar Flex is available from Atochem Corporation. An electronic grade solvent was used. The slurry was cast onto glass and a free standing electrode was formed as the casting solvent evaporated. The electrode composition was approximately as follows on a dry weight basis: 85% graphite; 12% binder; and 3% conductive carbon.

A rocking chair battery was prepared comprising the anode, the cathode, and an electrolyte. The ratio of the active cathode mass to the active anode mass was about 2.14:1. The two electrode layers were arranged with an electrolyte layer in between, and the layers were laminated together using heat and pressure as per the Bell Comm. Res. patents. In a preferred method, the cell is activated with EC/DMC solvent in a weight ratio of 2:1 in a solution containing 1 M $LiPF_6$ salt.

Figures 19 and **20** show data for the first four complete cycles of the lithium ion cell having the $LiFe_{0.9}Mg_{0.1}PO_4$ cathode and the MCMB2528 anode. The cell comprised 23.1mg active $LiFe_{0.9}Mg_{0.1}PO_4$ and 10.8mg active MCMB2528 for a cathode to anode mass ratio of 2.14. The cell was charged and discharged at 23°C at an approximate C/10 (10 hour) rate between voltage limits of 2.50 V and 3.60 V. The voltage profile plot (**Figure 19**) shows the variation in cell voltage versus time for the $LiFe_{0.9}Mg_{0.1}PO_4$/MCMB2528 lithium ion cell. The symmetrical nature of the charge-discharge is clearly evident. The small degree of voltage hysteresis between the charge and discharge processes is evidence for the low overvoltage in the system, which is very good. **Figure 20** shows the variation of $LiFe_{0.9}Mg_{0.1}PO_4$ specific capacity with cycle number. Clearly, over the cycles shown, the material demonstrates good cycling stability.

Figure 21 shows data for the first three complete cycles of the lithium ion cell having the gamma-LiV_2O_5 cathode and the MCMB2528 anode. The cell prepared was a rocking chair, lithium ion cell as described above.

The cell comprised 29.1mg gamma-LiV_2O_5 cathode active material and 12.2mg MCMB2528 anode active material, for a cathode to anode mass ratio of 2.39. As stated earlier, the liquid electrolyte used was EC/DMC (2:1) and 1M $LiPF_6$. The cell was charged and discharged at 23°C at an approximate C/10 (10 hour) rate between voltage limits of 2.50 V and 3.65 V. The voltage profile plot **(Figure 21)** shows the variation in cell voltage versus time for the LiV_2O_5/MCMB2528 lithium ion cell. The symmetrical nature of the charge-discharge is clearly evident. The small degree of voltage hysteresis between the charge and discharge processes is evidence for the low overvoltage in the system, which is very good.

In summary, the invention provides new compounds $Li_aMI_bMII_c(PO_4)_d$ and gamma-LiV_2O_5 by new methods which are adaptable to commercial scale production. The $Li_1MI_{1-y}MII_yPO_4$ compounds are isostructural olivine compounds as demonstrated by XRD analysis. Substituted compounds, such as $LiFe_{1-y}Mg_yPO_4$ show better performance than $LiFePO_4$ unsubstituted compounds when used as electrode active materials. The method of the invention utilizes the reducing capabilities of carbon along with selected precursors and reaction conditions to produce high quality products suitable as electrode active materials or as ion conductors. The reduction capability of carbon over a broad temperature range is selectively applied along with thermodynamic and kinetic considerations to provide an energy-efficient, economical and convenient process to produce compounds of a desired composition and structure. This is in contrast to known methods.

Principles of carbothermal reduction have been applied to produce pure metal from metal oxides by removal of oxygen. See, for example, U.S. Patent Nos. 2,580,878, 2,570,232, 4,177,060, and 5,803,974.

Principles of carbothermal and thermal reduction have also been used to form carbides. See, for example, U.S. Patent Nos. 3,865,745 and 5,384,291; and non-oxide ceramics (see U.S. Patent No. 5,607,297). Such methods are not known to have been applied to form lithiated products or to form products without oxygen abstraction from the precursor. The methods described with respect to the present invention provide high quality products which are prepared from precursors which are lithiated during the reaction without oxygen abstraction. This is a surprising result. The new methods of the invention also provide new compounds not known to have been made before.

For example, alpha-V_2O_5 is conventionally lithiated electrochemically against metallic lithium. Thus, alpha-V_2O_5 is not suitable as a source of lithium for a cell. As a result, alpha-V_2O_5 is not used in an ion cell. In the present invention, alpha-V_2O_5 is lithiated by carbothermal reduction using a simple lithium-containing compound and the reducing capability of carbon to form a gamma-LiV_2O_5. The single phase compound, gamma-LiV_2O_5 is not known to have been directly and independently prepared before. There is not known to be a direct synthesis route. Attempts to form it as a single phase resulted in a mixed phase product containing one or more beta phases and having the formula $Li_xV_2O_5$ with $0 < x \leq 0.49$. This is far different from the present single phase gamma-$Li_xV_2O_5$ with x equal to one, or very close to one. The flexibility of the process of the present invention is such that it can be conducted over a wide temperature range. The higher the temperature, the more quickly the reaction proceeds. For example, at 650°C, conversion of alpha-V_2O_5 to gamma-LiV_2O_5 occurs in about one hour, and at 500° it takes about 8 hours. Here, about one quarter (1/4) atomic unit of carbon is used to reduce one atomic unit of vanadium, that is, $V^{+5}V^{+5}$ to $V^{+5}V^{+4}$. The predominate reaction is C to CO_2

where for each atomic unit of carbon at ground state zero, a plus 4 oxidation state results. Correspondingly, for each 1/4 atomic unit of carbon, one atomic unit of vanadium is reduced from V^{+5} to V^{+4}. (See Reaction 5). The new product, gamma-LiV_2O_5 is air-stable and suitable as an electrode material for an ion cell or rocking chair battery.

The convenience and energy efficiency of the present process can also be contrasted to known methods for forming products under reducing atmosphere such as H_2 which is difficult to control, and from complex and expensive precursors. In the present invention, carbon is the reducing agent, and simple, inexpensive and even naturally occurring precursors are useable. For example, it is possible to produce $LiFePO_4$ from Fe_2O_3, a simple common oxide. (See Reaction 1b). The production of $LiFePO_4$ provides a good example of the thermodynamic and kinetic features of the method. Iron phosphate is reduced by carbon and lithiated over a broad temperature range. At about 600°C, the C to CO_2 reaction predominates and takes about a week to complete. At about 750°C, the C to CO reaction predominates and takes about 8 hours to complete. The C to CO_2 reaction requires less carbon reductant but takes longer due to the low temperature kinetics. The C to CO reaction requires about twice as much carbon, but due to the high temperature reaction kinetics, it proceeds relatively fast. In both cases, the Fe in the precursor Fe_2O_3 has oxidation state +3 and is reduced to oxidation (valence) state +2 in the product $LiFePO_4$. The C to CO reaction requires that ½ atomic unit of carbon be used for each atomic unit of Fe reduced by one valence state. The CO to CO_2 reaction requires that 1/4 atomic unit of carbon be used for each atomic unit of Fe reduced by one valence state.

The active materials of the invention are also characterized by being stable in an as-prepared condition, in the presence of air and particularly humid air. This is a striking advantage, because it facilitates preparation of and assembly of battery cathodes and cells, without the requirement for controlled atmosphere. This feature is particularly important, as those skilled in the art will recognize that air stability, that is, lack of degradation on exposure to air, is very important for commercial processing. Air-stability is known in the art to more specifically indicate that a material does not hydrolyze in presence of moist air. Generally, air-stable materials are also characterized by Li being extracted therefrom above about 3.0 volts versus lithium. The higher the extraction potential, the more tightly bound the lithium ions are to the host lattice. This tightly bound property generally confers air stability on the material. The air-stability of the materials of the invention is consistent with the stability demonstrated by cycling at the conditions stated herein. This is in contrast to materials which insert Li at lower voltages, below about 3.0 volts versus lithium, and which are not air-stable, and which hydrolyze in moist air.

While this invention has been described in terms of certain embodiments thereof, it is not intended that it be limited to the above description, but rather only to the extent set forth in the following claims.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined in the following claims.

CLAIMS:

1. A method for synthesis of a Li metal compound of the formula

$Li_aMI_{1-y}MII_y(XO_4)_d$

wherein a is greater than 0 but less than or equal to 3, and y is greater than or equal to 0 and less than or equal to 1, d is greater than 0 and less than or equal to 3, X is P, S or Si, MI is a transition metal or a mixture of transition metals, selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Ti, and Cr, and MII is an element with fixed valency selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof, by forming a mixture containing at least one precursor of:

a) a source of the element MI, at least part of said transition metal or metals that constitute MI being in an oxidation state greater than that of the metal in the compound of the above formula;

b) a source of the element MII when said compound includes the element MII;

c) a compound that is a source of the element lithium, and,

d) a compound that is a source of the XO_4 if the element X is not present in another compound or source;

said at least one precursor of said sources (a) to (d) being present in the mixture in proportions required to form the lithium metal compound, and said at least one precursor having one or more additional elements other than the elements of (a) to (d), and wherein said mixture contains at least one other component comprising a binder which is decomposable to form a carbon residue,

said method comprising effecting a reaction under elevated temperatures to decompose said binder and to reduce the valency of the transition metal or metals whereby the oxidation state of at least one metal ion of the precursor or precursors is reduced to form the compound of said formula.

2. The method according to claim 1, in which the source of carbon generates a gaseous reducing atmosphere by thermal decomposition thereof.

3. The method according to claim 2, wherein the gaseous atmosphere includes carbon monoxide or a mixture of carbon dioxide and carbon monoxide.

4. The method according to any one of claims 1 to 3, in which at least one of the following conditions apply: the source of MI is also the source of X; the source of MII is also the source of X; and the source of lithium is also the source of X; and the source of X is also the source of lithium.

5. The method according to any one of claims 1 to 4, in which the mixture of precursors a) to d) is formed by providing an intimate or homogeneous mixture of source compounds.

6. The method according to any one of claims 1 to 5, in which the compound which is the source of MI is iron (III) oxide or magnetite, manganese dioxide, di-vanadium pentoxide, a ferric phosphate, or a mixture of the compounds.

7. The method according to claim 6, wherein the ferric phosphate is trivalent ferric phosphate.

8. The method according to any one of claims 1 to 7, in which the compound that is the source of lithium is chosen from the group constituted by lithium oxide, lithium carbonate, lithium phosphate, the acid phosphate LiH_2PO_4, lithium acetate, lithium nitrate, lithium oxalate, lithium vanadate, and mixtures thereof.

9. The method according to claim 8, in which the lithium source compound is lithium carbonate of the formula Li_2CO_3.

10. The method according to claim 1 or 9, the synthesis being carried out in a reducing or neutral gas atmosphere.

11. The method according to any one of claims 1 to 10, in which the compound of said formula are obtained in the form of particles.

12. The method according to any one of claims 1 to 11, in which the source of carbon or carbon residue is present in the synthesis in an amount so as to leave a residual amount of carbon in the reaction product.

13. The method according to any one of claims 1 to 12, in which the compound of said formula has an olivine or Nasicon structure, including a monoclinic form.

14. The method according to any one of claims 1 to 13, in which the synthesis is carried out in a two step reaction.

15. The method according to claim 1 or 2, in which the reaction between the source compounds a) to d) is carried out during heating and degradation of the binder.

16. The method according to any one of claims 1 to 15, in which the sources a) to d) are in the form of compressed pellets prior to the thermal synthesis being carried out.

17. The method according to claim 14 or 15, wherein the polymer is the source of carbon.

18. The method according to claim 10, said synthesis being carried out in the presence of reducing atmosphere wherein the reducing atmosphere contains a neutral gas.

19. The method according to any one of claims 1 to 18, said synthesis being carried out in the presence of the reducing atmosphere wherein the reducing atmosphere contains nitrogen or argon.

20. The method according to any one of claims 1 to 5, or 15, in which the transition metal or metals

comprise a metal selected from the group consisting of iron, manganese, cobalt, nickel, vanadium, titanium, chromium, copper and a mixture thereof.

21. The method according to any one of claims 1 to 5, in which the compound that is the source of MI has an oxidation state that varies from 3 to 7.

22. The method according to any one of claims 1 to 21, wherein MI is Fe, MII is Mg or Ca, X is PO_4 and y is greater than 0 and less than 1.

23. The method according to any one of claims 1 to 3, in which the source of X is selected from the group consisting of sulfuric acid, lithium sulfate, phosphoric acid, phosphoric acid esters, the neutral phosphate Li_3PO_4, the acid phosphate LiH_2PO_4, the monoammonium phosphates, diammonium phosphates, trivalent ferric phosphate, manganese ammonium phosphate (NH_4MnPO_4), silica, lithium silicates, alkoxysilanes, alkoxysilane partial hydrolysis products and mixtures of the alkoxysilanes.

24. The method according to claim 23, in which the precursor compound for the source of element X is ferric phosphate.

25. The method according to any one of claims 1 to 24, wherein the synthesis temperature is up to 1200°C, and the time of reaction is up to 8 hours.

26. The method according to claim 25, wherein said temperature is between about 500 to about 800°C.

27. The method according to any one of claims 1 to 26, in which the particles of the compound obtained are substantially constituted by said compound of said formula, and in which the compound obtained includes an amount of carbon in association with said particles.

28. The method according to any one of claims 1 to 27, wherein, in the metal compound, MI is Fe, MII is Mg, X is PO_4 and y is greater than 0 and less than 1.

29. The method according to any one of claims 1 to 28, in which the method is carried out above a minimum temperature at which the reaction reduces the transition element or elements to their oxidation state required in the compound of said formula and under reaction conditions leading to a reduction of the transition element or elements without full reduction to a metallic state.

30. A method for the synthesis of a Li metal compound having electrical conductivity and having the formula

$$Li_aMI_{1-y}MII_y(XO_4)_d$$

wherein a is greater than 0 and less than or equal to 3, and y is greater than or equal to 0 and less than or equal to 1, d is greater than 0 and less than or equal to 3, X is P, S or Si, MI is a transition metal or a mixture of transition metals selected from the group consisting of Fe, Co, Ni, Mn, Cu, V, Ti, and Cr, and MII is an element with fixed valency selected from the group consisting of Mg, Ca, Zn, Sr, Pb, Cd, Sn, Ba, Be, and mixtures thereof, by the steps of

1) forming a mixture for a thermal synthesis in which the mixture contains at least one precursor of

   a) a source of the element MI, at least part of said transition metal or metals that constitute MI being in an oxidation state greater than that of the metal in the compound of the above formula;

   b) a source of the element MII when said compound includes MII;

   c) when said compound includes the element Li, a compound that is a source of the element lithium;

   d) a compound that is a source of the element X if the element X is not present in another compound or source; and

   e) a source of carbon,

   said at least one precursor of said sources (a) to (e) being present in the mixture in proportions required to form said Li metal compound, and said at least one precursor having one or more additional elements other than the elements of (a) to (d), and

2) reducing the valency of the transition metal or metals in the mixture to the desired valency, by subjecting the mixture to a thermal synthesis reaction between said precursors of said mixture under a gaseous atmosphere, said thermal synthesis reaction including the step of subjecting said source of carbon to a temperature sufficient to decompose or degrade the same, to thereby obtain said Li metal compound having electrical conductivity, and wherein, during the reducing

step, the composition of the gaseous atmosphere, the temperature of the reaction and the relative amount of the source of lithium proportionately to the sources of (a), (b) and (d) are controlled.

31. The method according to any one of claims 2, 3 and 30, in which the synthesis between the source compounds a) to d) is carried out simultaneously with heating and degradation of the source compound e).

32. The method according to claim 30, in which the synthesis is carried out in a two step reaction.

33. The method according to claim 30, 31 or 32, the synthesis being carried out in a reducing or neutral gas atmosphere.

34. The method according to any one of claims 30 to 33, in which the compounds of said formula are obtained in the form of particles.

35. The method according to any one of claims 30 to 34, in which the source of carbon is present in the synthesis in an amount so as to be present in a residual amount in the reaction product to thereby coat particles of the compound obtained.

36. The method according to any one of claims 30 to 35, in which the amount of the source of carbon in the reaction medium is such so as to be nucleated or bound to particles of the compound of said formula.

37. The method according to any one of claims 30 to 36, in which the mixture of at least one precursor has a form comprising pellets.

38. The method according to any one of claims 30 to 37, in which the source of the carbon is carbon or a precursor thereof.

39. The method according to any one of claims 30 to 37, in which the source of carbon contains a source of oxygen and hydrogen which are chemically bound.

40. The method according to any one of claims 30 to 37, in which the source of carbon comprises at least one carbon source which degrades said carbon source compound being a polymer or a mineral oil.

41. The method according to any one of claims 30 to 37, in which the source of carbon comprises a polymer.

42. The method according to any one of claims 30 to 37, in which the carbon source is present as part of the mixture.

43. The method according to claim 37, wherein the source of carbon forms part of said compressed pellets.

44. The method according to any one of claims 30 to 43, said synthesis being carried out at a temperature of up to 650 - 800° C, and for a dwell time of up to 8 hours.

45. The method according to any one of claims 30 to 44, said synthesis being carried out in the presence of a reducing atmosphere and wherein the valency of the elements of the source compounds is reduced to the valency of the elements of a compound of said formula.

46. The method according to any one of claims 30 to 45, said synthesis being carried out in the presence of the reducing atmosphere wherein the reducing atmosphere contains a neutral gas.

47. The method according to claim 46, wherein said neutral gas is nitrogen or argon.

48. The method according to any one of claims 30 to 47, the synthesis temperature being up to 1200°C, and the reaction time mixture being up to 8 hours.

49. The method according to claim 48, wherein said temperature is between about 500 to about 800°C.

50. The method according to any one of claims 30 to 49, in which the reducing atmosphere is obtained by thermal decomposition of said source of carbon, the synthesis being carried out to react the source compounds to obtain a compound of said formula.

51. The method according to any one of claims 30 to 50, in which the amount of the carbon source, present in the reactants, is below about 9% based on the total weight of the reaction mixture.

52. The method according to claim 51, wherein said amount of the carbon source is below about 1.6%.

53. The method according to claim 50, in which the gaseous reducing atmosphere is obtained by partial oxidation of oxygen or air, and of the source of carbon, said synthesis being carried out at an elevated temperature.

54. The method according to claim 53, in which the synthesis is carried out at a temperature of between 400 - 1200°C.

55. The method according to any one of claims 30 to 54, in which the dwell time of the source compounds in the thermal processing step is up to 8 hours.

56. The method according to any one of claims 30 to 55, in which at least one of the following conditions apply: the source of MI is also the source of X; the source of MII is also the source of X; and the source of lithium is also the source of X; and the source of X is also the source of lithium.

57. The method according to any one of claims 30 to 56, in which the mixture of precursors a) to d) is formed by forming an intimate or homogeneous mixture of the source compounds.

58. The method according to any one of claims 30 to 57, in which the transition metal or metals comprise a metal selected from the group consisting of iron, manganese, cobalt, nickel, vanadium, titanium, chromium, copper and a mixture thereof.

59. The method according to any one of claims 30 to 57, in which the compound that is the source of MI has an oxidation state that varies from 3 to 7.

60. The method according to any one of claims 30 to 57, in which the compound which is the source of MI is iron (III) oxide, magnetite, manganese dioxide, di-vanadium pentoxide, a ferric phosphate, or a mixture of the compounds.

61. The method according to claim 60, wherein the ferric phosphate is trivalent ferric phosphate.

62. The method according to any one of claims 30 to 61, in which the compound that is the source of lithium is chosen from the group constituted by lithium oxide, lithium carbonate, lithium phosphate, the acid phosphate LiH_2PO_4, lithium acetate, lithium nitrate, lithium oxalate, lithium vanadate, and mixtures thereof.

63. The method according to claim 62, in which the lithium source compound is lithium carbonate of the formula Li_2CO_3.

64. The method according to any one of claims 30 to 57, in which the source of X is selected from the group consisting of sulfuric acid, lithium sulfate, phosphoric acid, phosphoric acid esters, the neutral phosphate Li_3PO_4, the acid phosphate LiH_2PO_4, the monoammonium phosphates, diammonium phosphates, trivalent ferric phosphate, manganese ammonium phosphate (NH_4MnPO_4), silica, lithium

silicates, alkoxysilanes, alkoxysilane partial hydrolysis products and mixtures of the alkoxysilanes.

65. The method according to claim 64, in which the precursor compound for the source of element X is ferric phosphate.

66. The method according to any one of claims 30 to 60, wherein MI is Fe, MII is Mg or Ca, X is PO_4 and y is greater than 0 and less than 1.

67. The method according to any one of claims 30 to 60, wherein MI is Fe, MII is Mg, X is PO_4 and y is greater than 0 and less than 1.

68. The method of synthesis according to any one of claims 30 to 60, in which the compound of said formula is a compound of the formula $C\text{-}Li_xMI_{1-y}MII_y(XO_4)_n$ and in which the reaction product includes carbon remaining after the reaction is completed.

69. The method of synthesis according to any one of claims 30 to 60, in which the particles of the compound obtained are substantially constituted by said compound of said formula, and in which the compound obtained includes an amount of carbon in association with said particles.

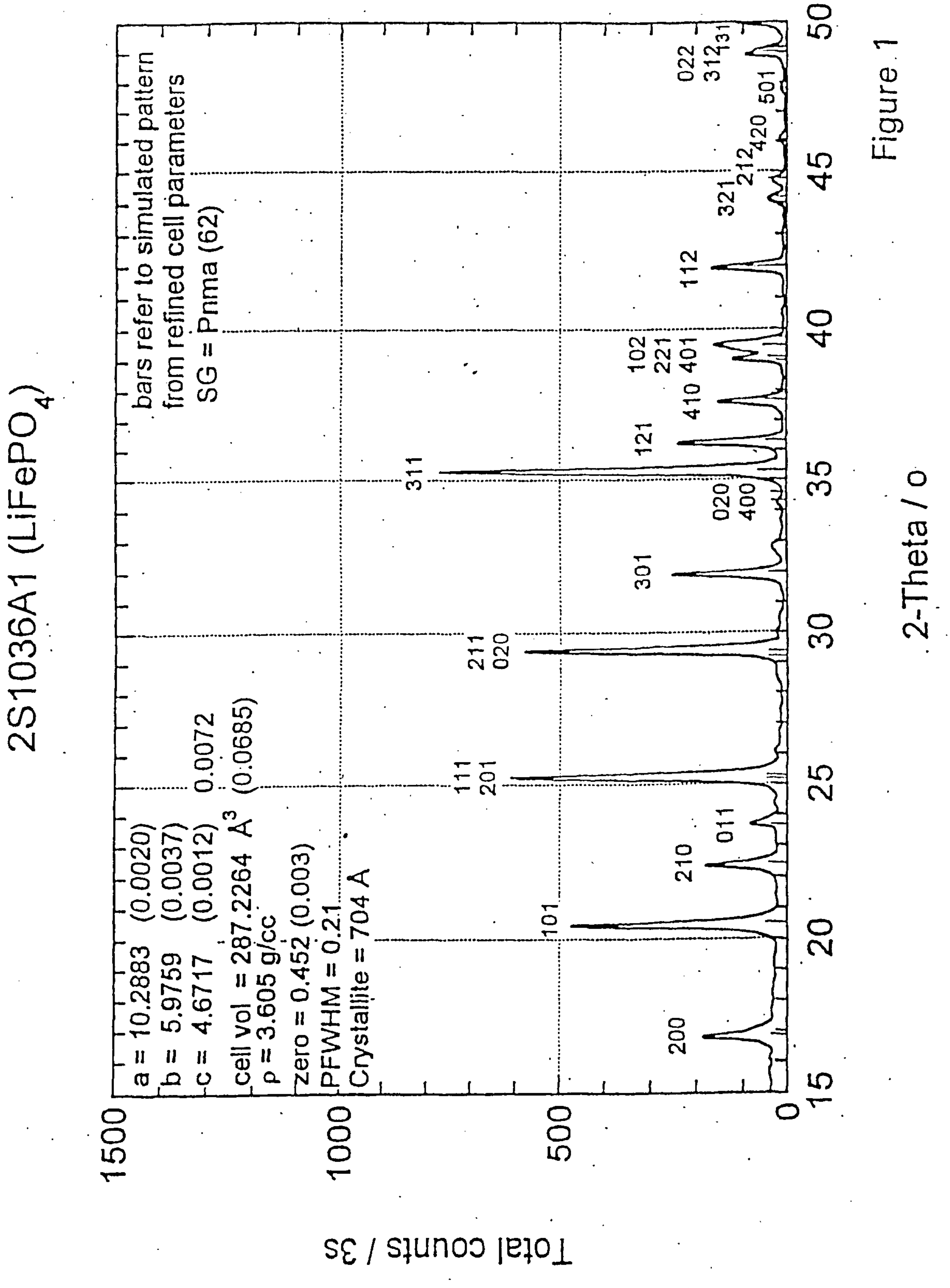

2S1036A1 (LiFePO$_4$)
a = 10.2883 (0.0020)
b = 5.9759 (0.0037)
c = 4.6717 (0.0012) 0.0072
cell vol = 287.2264 Å^3 (0.0685)
ρ = 3.605 g/cc
zero = 0.452 (0.003)
PFWHM = 0.21
Crystallite = 704 Å
bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)
200
101
210
011
111
201
211
020
301
020
400
311
121
410
102
221
401
112
321
212
420
501
022
312
131
Total counts / 3s
0
500
1000
1500
2-Theta / o
15
20
25
30
35
40
45
50

Figure 1

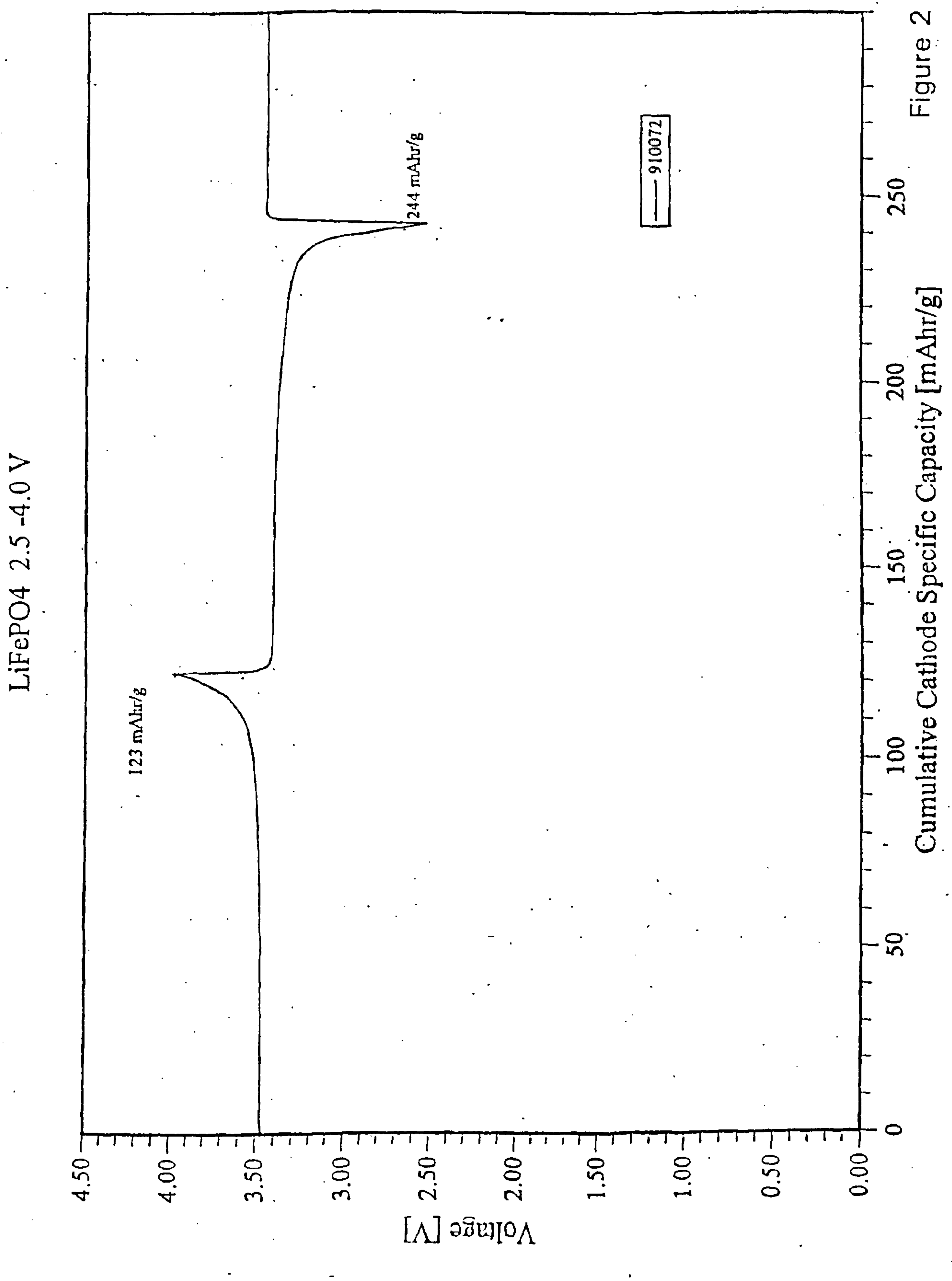

LiFePO4 2.5 -4.0 V
123 mAhr/g
244 mAhr/g
910072
Voltage [V]
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Cumulative Cathode Specific Capacity [mAhr/g]
0
50
100
150
200
250

Figure 2

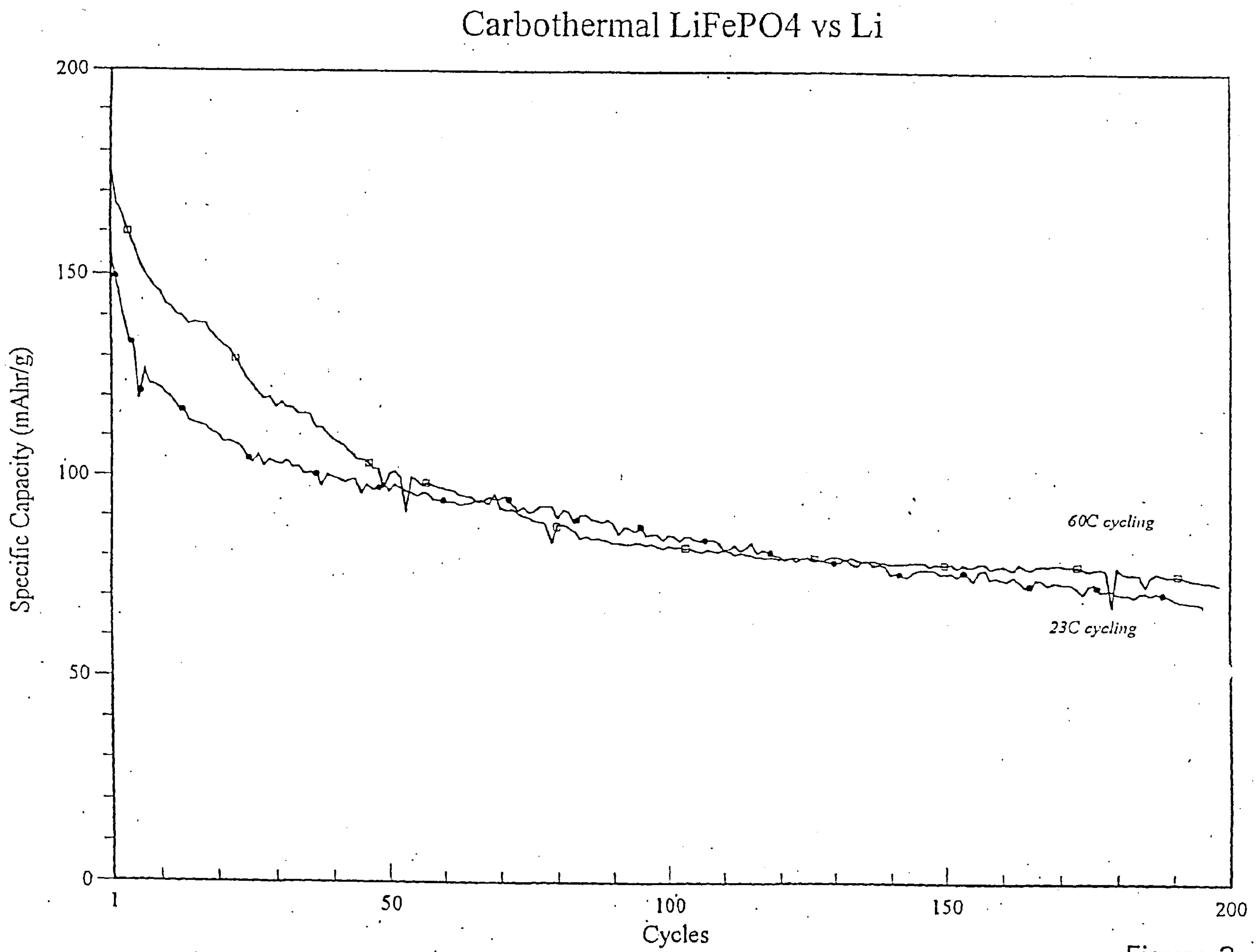

Carbothermal LiFePO4 vs Li
Specific Capacity (mAhr/g)
200
150
100
50
0
1
50
100
150
200
Cycles
60C cycling
23C cycling

Figure 3

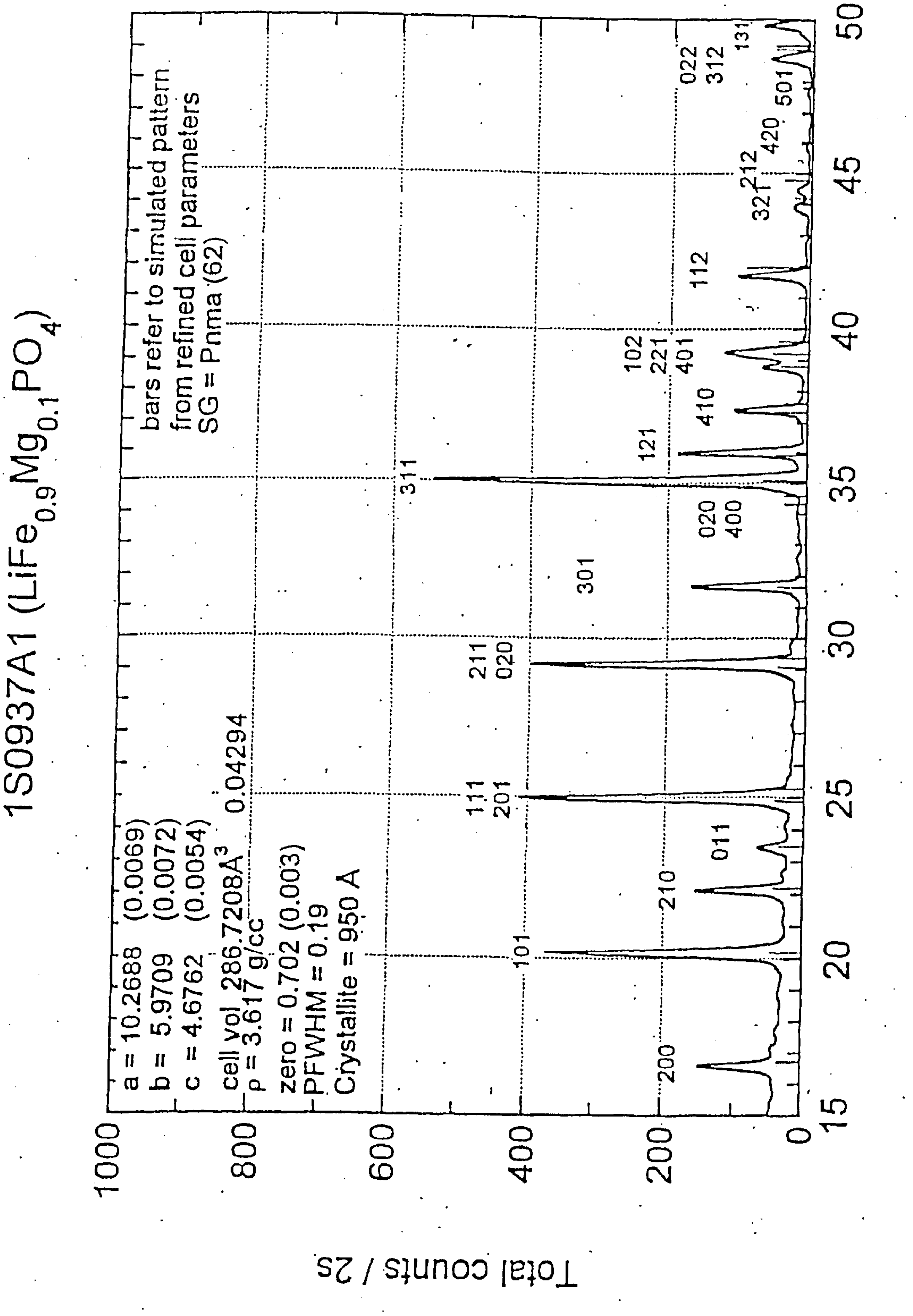

1S0937A1 (LiFe$_{0.9}$Mg$_{0.1}$PO$_4$)
a = 10.2688 (0.0069)
b = 5.9709 (0.0072)
c = 4.6762 (0.0054)
cell vol. 286.7208Å^3 0.04294
ρ = 3.617 g/cc
zero = 0.702 (0.003)
PFWHM = 0.19
Crystallite = 950 A
bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)
200
101
210
011
111
201
211
020
301
020
400
311
121
410
102
221
401
112
321
212
420
501
022
312
131
Total counts / 2s
0
200
400
600
800
1000
2-Theta / (°)
15
20
25
30
35
40
45
50

Figure 4

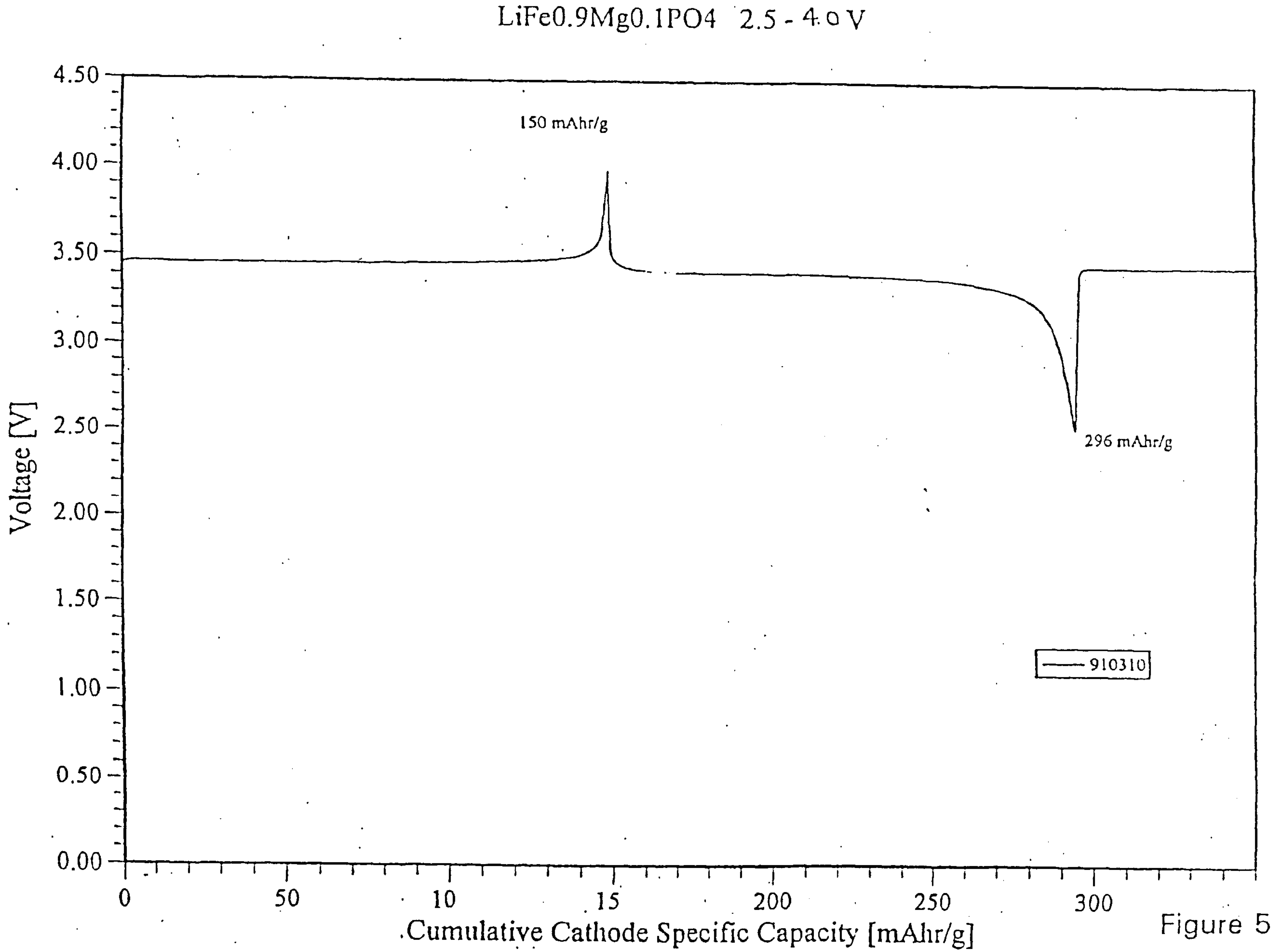

LiFe0.9Mg0.1PO4 2.5 - 4.0 V
150 mAhr/g
296 mAhr/g
910310
Voltage [V]
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
50
10
15
200
250
300
Cumulative Cathode Specific Capacity [mAhr/g]

Figure 5

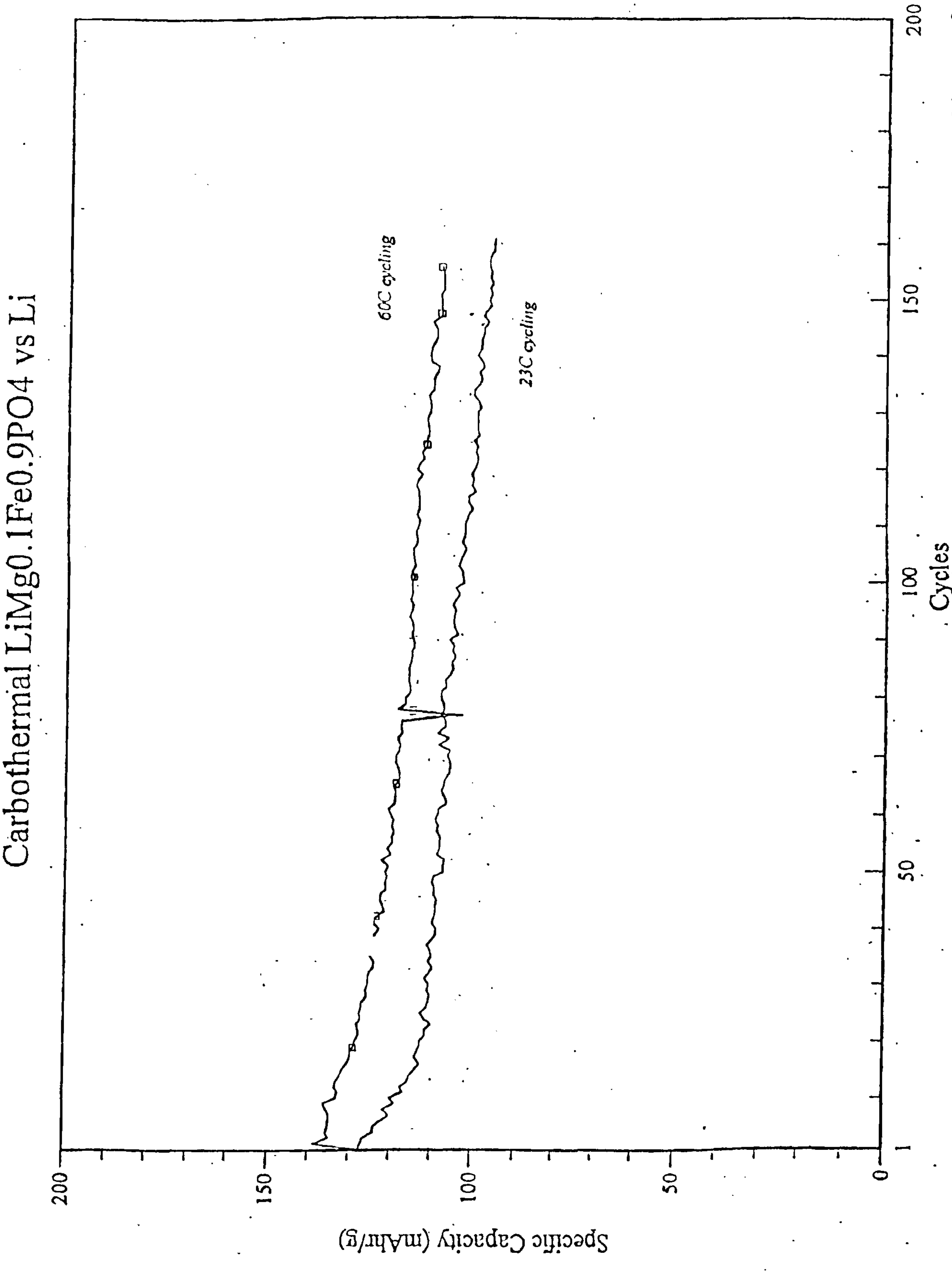

Carbothermal LiMg0.1Fe0.9PO4 vs Li
60C cycling
23C cycling
Specific Capacity (mAhr/g)
200
150
100
50
0
Cycles
1
50
100
150
200

Figure 6

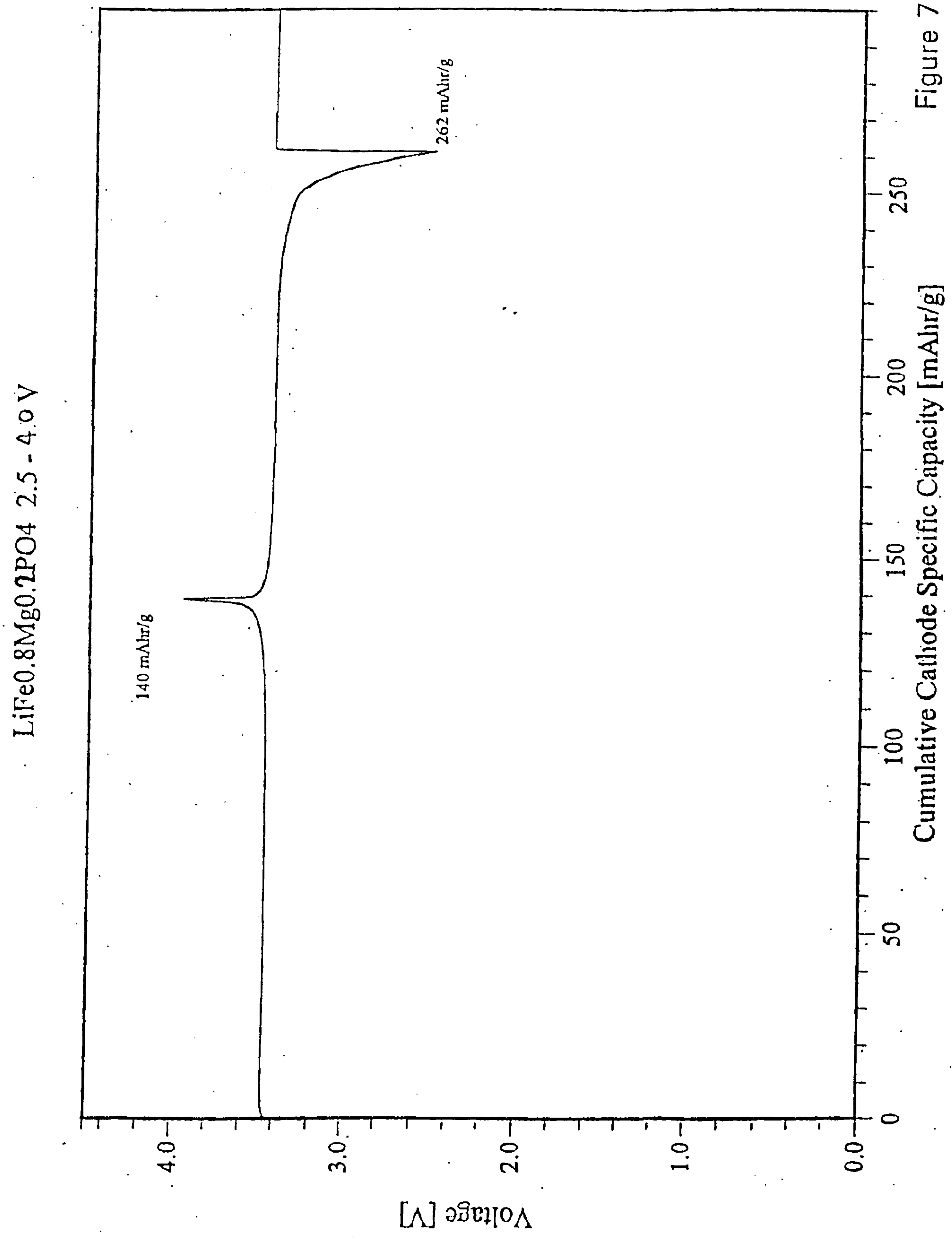

LiFe0.8Mg0.2PO4 2.5 - 4.0 V
140 mAhr/g
262 mAhr/g
Voltage [V]
4.0
3.0
2.0
1.0
0.0
Cumulative Cathode Specific Capacity [mAhr/g]
0
50
100
150
200
250

Figure 7

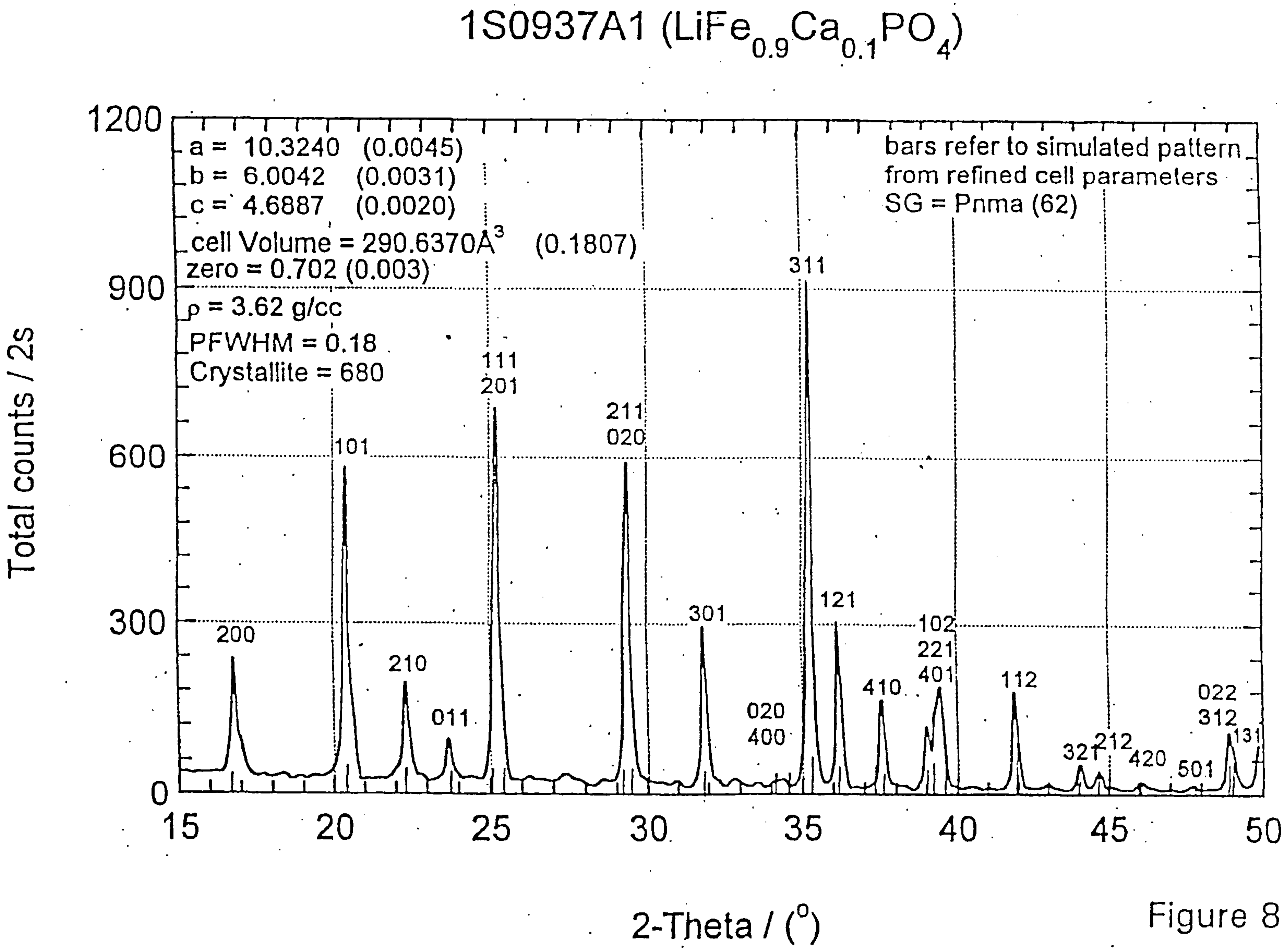

1S0937A1 ($LiFe_{0.9}Ca_{0.1}PO_4$)
a = 10.3240 (0.0045)
b = 6.0042 (0.0031)
c = 4.6887 (0.0020)
cell Volume = 290.6370Å^3 (0.1807)
zero = 0.702 (0.003)
ρ = 3.62 g/cc
PFWHM = 0.18
Crystallite = 680
bars refer to simulated pattern
from refined cell parameters
SG = Pnma (62)
200
101
210
011
111
201
211
020
301
020
400
311
121
410
102
221
401
112
321
212
420
501
022
312
131
Total counts / 2s
1200
900
600
300
0
15
20
25
30
35
40
45
50
2-Theta / (°)

Figure 8

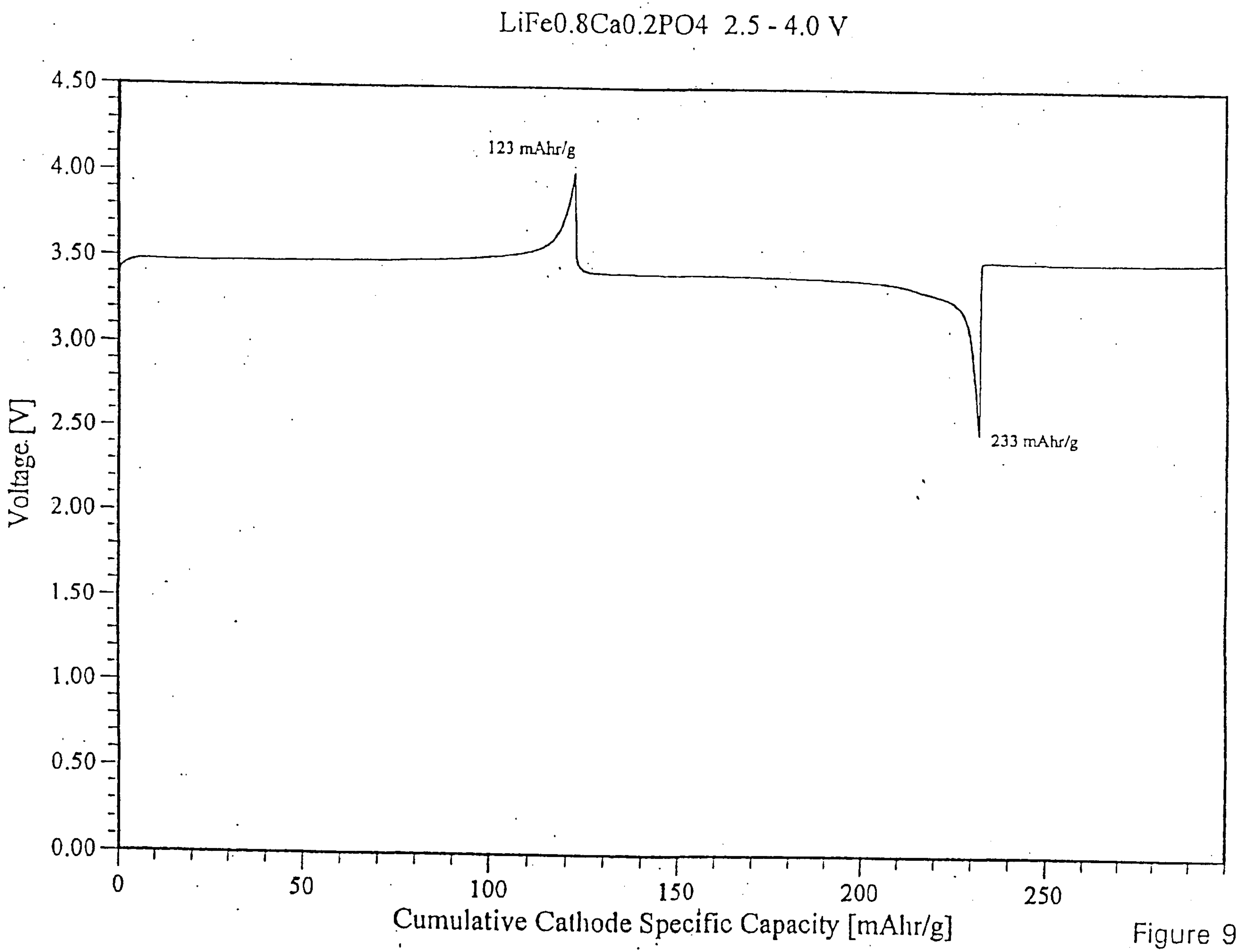

LiFe0.8Ca0.2PO4 2.5 - 4.0 V
123 mAhr/g
233 mAhr/g
Voltage [V]
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
0
50
100
150
200
250
Cumulative Cathode Specific Capacity [mAhr/g]

Figure 9

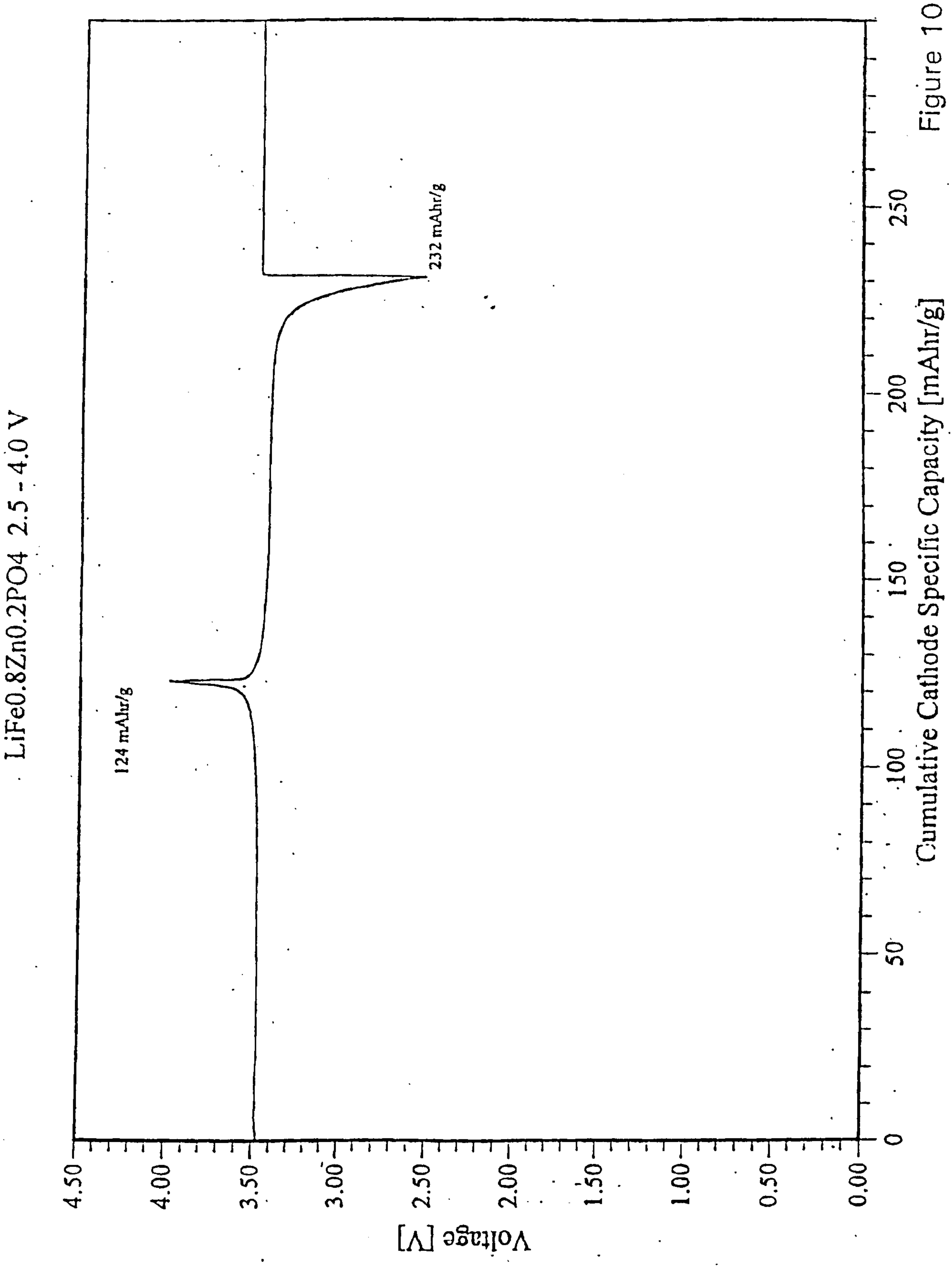

LiFe0.8Zn0.2PO4 2.5 - 4.0 V
124 mAhr/g
232 mAhr/g
Voltage [V]
4.50
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
Cumulative Cathode Specific Capacity [mAhr/g]
0
50
100
150
200
250

Figure 10

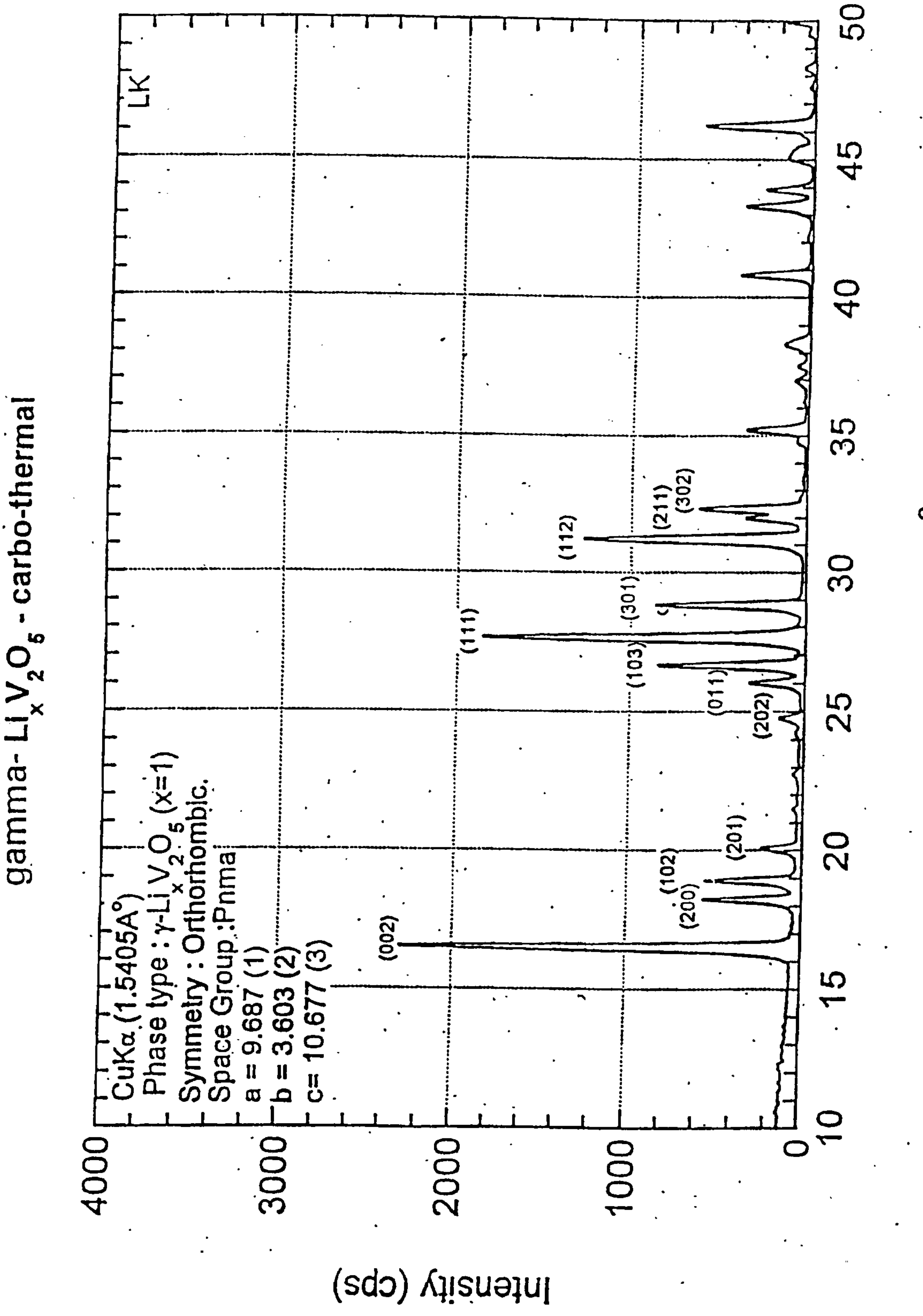

gamma- $Li_xV_2O_5$ - carbo-thermal
CuKα (1.5405A°)
Phase type : γ-$Li_xV_2O_5$ (x=1)
Symmetry : Orthorhombic.
Space Group :Pnma
a = 9.687 (1)
b = 3.603 (2)
c= 10.677 (3)
LK
(002)
(200)
(102)
(201)
(202)
(011)
(103)
(111)
(301)
(112)
(211)
(302)
Intensity (cps)
0
1000
2000
3000
4000
2-theta (°)
10
15
20
25
30
35
40
45
50

Figure 11

gamma-LiV2O5 Synthesized by Carbothermal Reduction Method

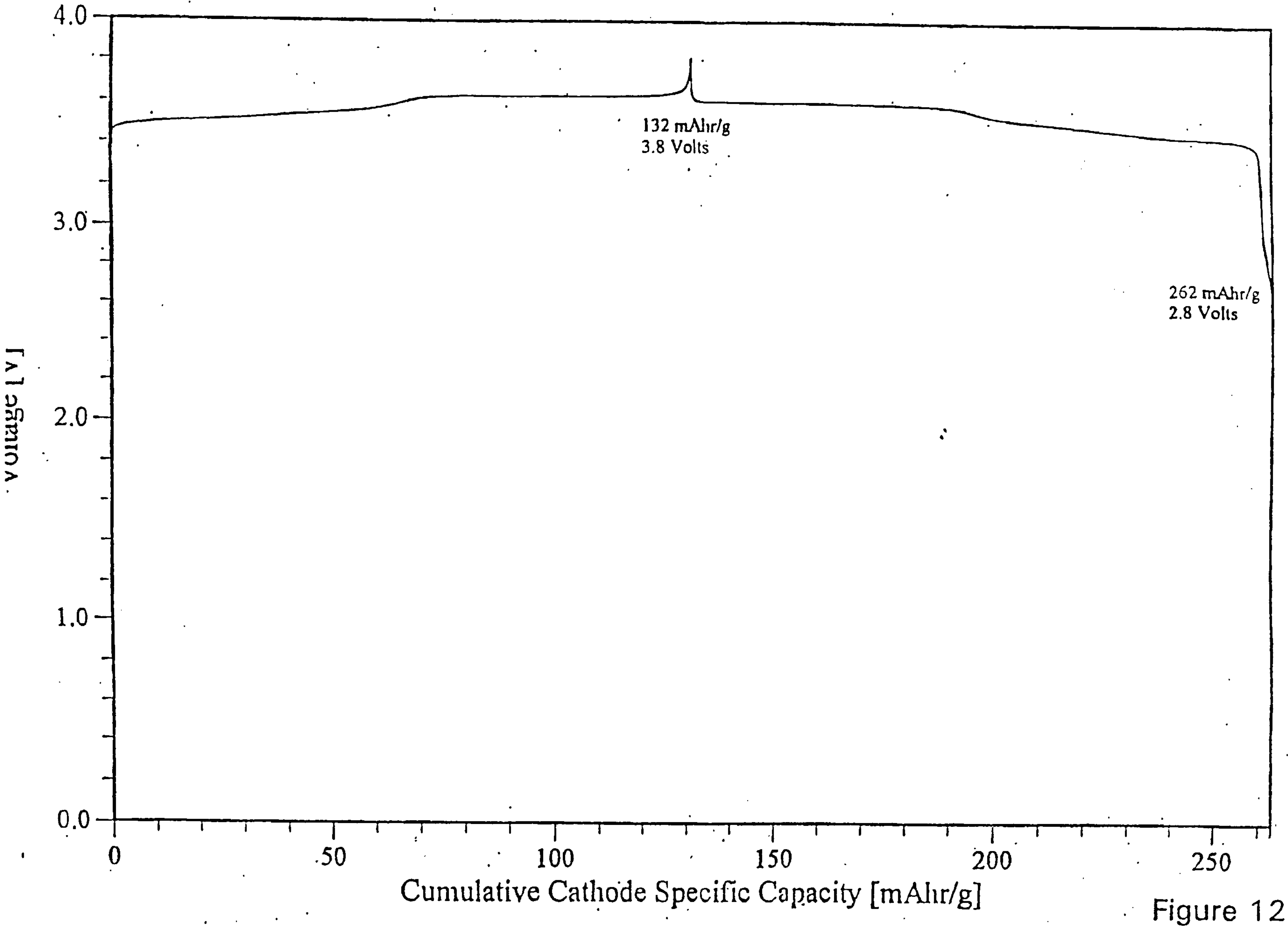


Figure 12

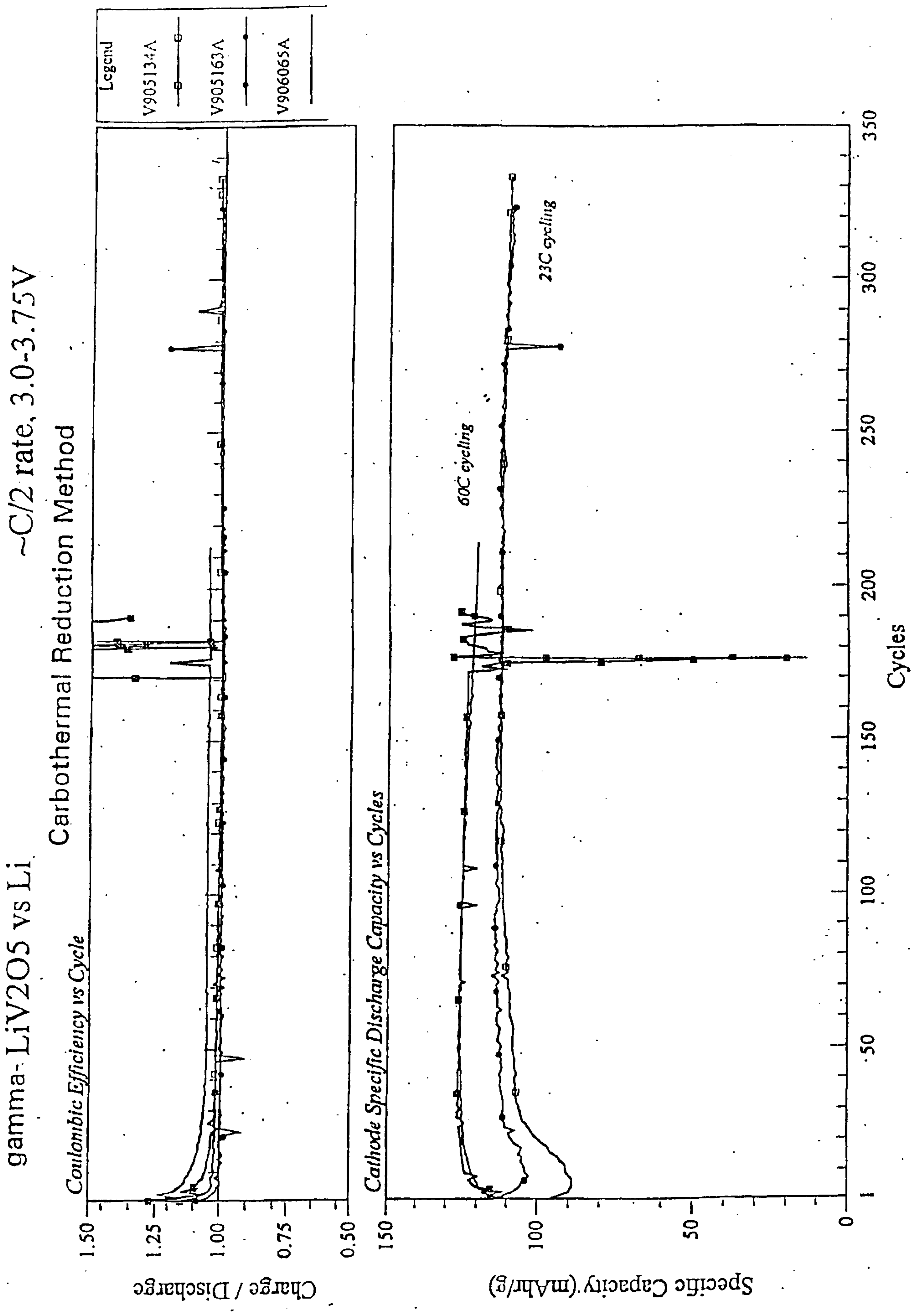

gamma-LiV2O5 vs Li
~C/2 rate, 3.0-3.75V
Carbothermal Reduction Method
Legend
V905134A
V905163A
V906065A
Coulombic Efficiency vs Cycle
Charge / Discharge
1.50
1.25
1.00
0.75
0.50
Cathode Specific Discharge Capacity vs Cycles
Specific Capacity (mAhr/g)
150
100
50
0
60C cycling
23C cycling
Cycles
1
50
100
150
200
250
300
350

Figure 13

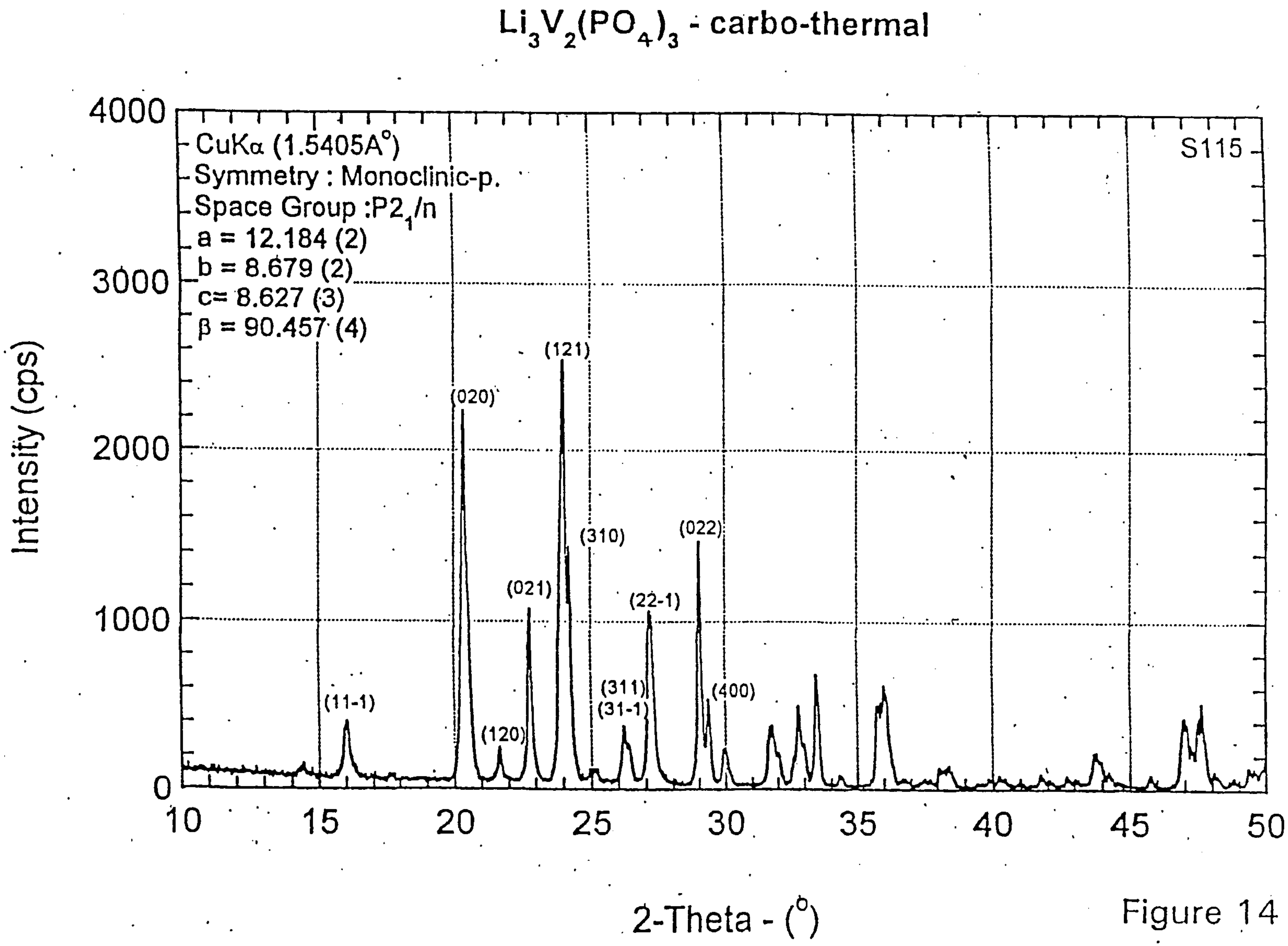

Li$_3$V$_2$(PO$_4$)$_3$ - carbo-thermal
CuKα (1.5405A°)
Symmetry : Monoclinic-p.
Space Group :P2$_1$/n
a = 12.184 (2)
b = 8.679 (2)
c= 8.627 (3)
β = 90.457 (4)
S115
(11-1)
(020)
(120)
(021)
(121)
(310)
(311)
(31-1)
(22-1)
(022)
(400)
Intensity (cps)
4000
3000
2000
1000
0
10
15
20
25
30
35
40
45
50
2-Theta - (°)

Figure 14

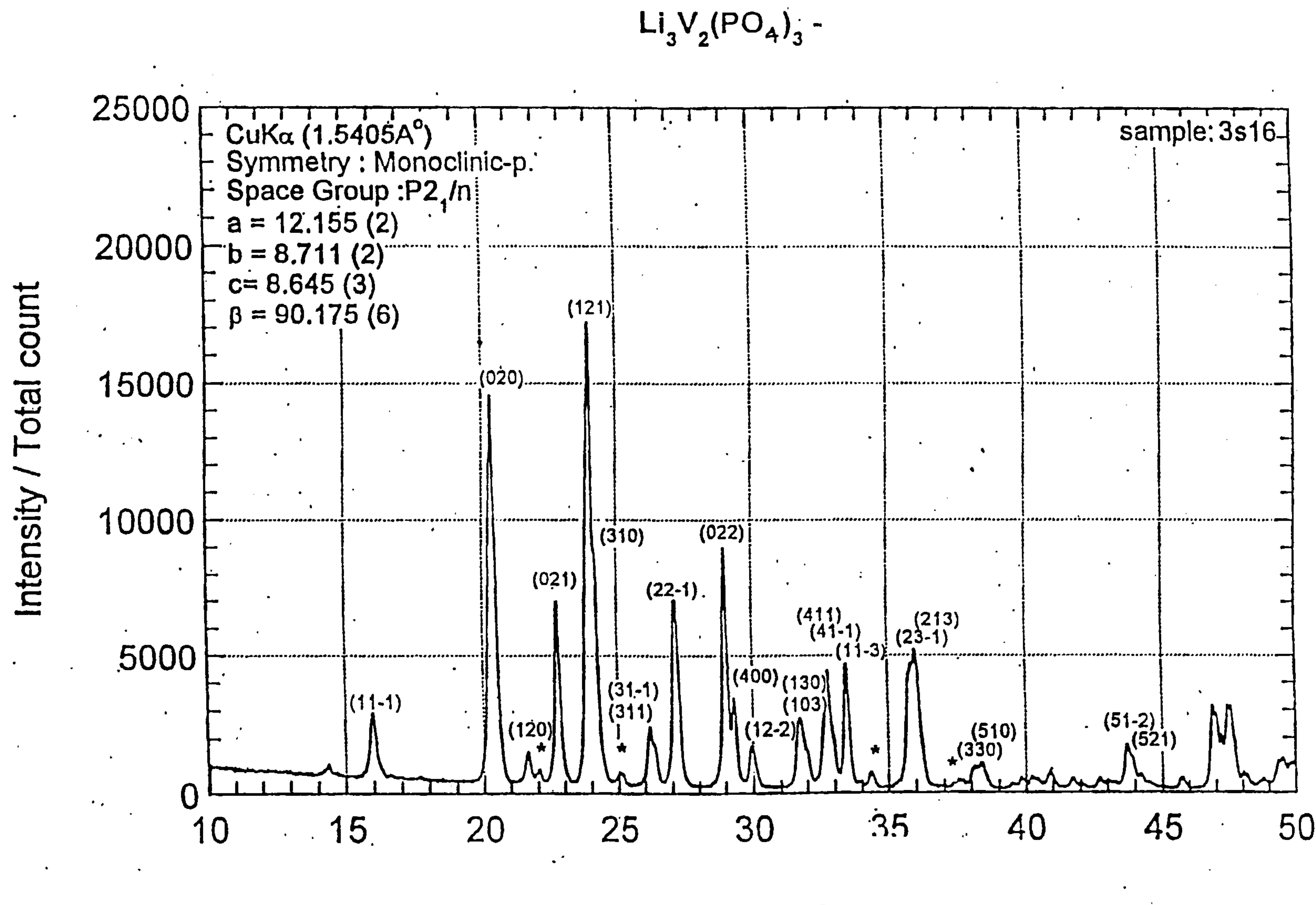
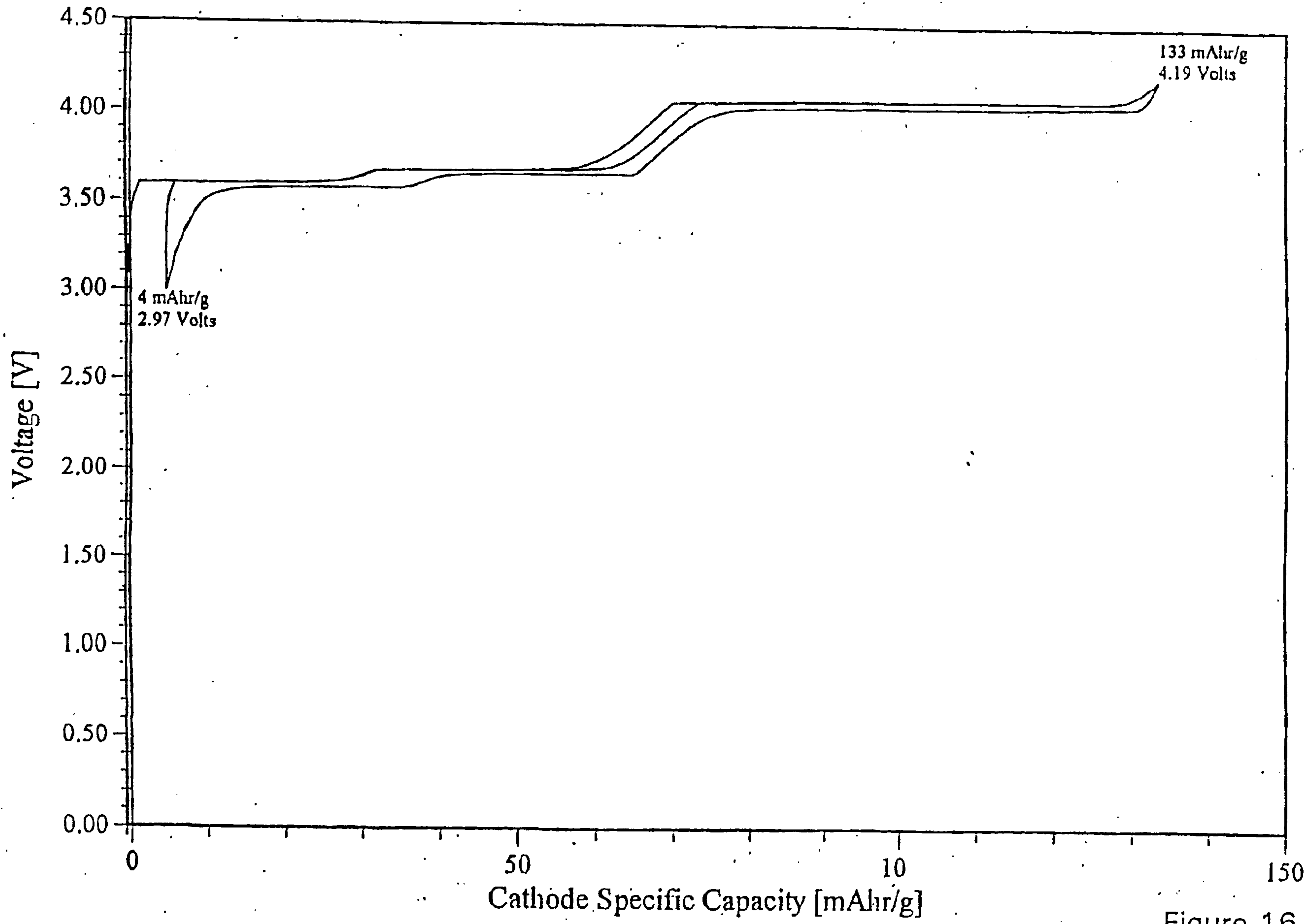

$Li_3V_2(PO_4)_3$ -
CuKα (1.5405A°)
Symmetry : Monoclinic-p.
Space Group :P2_1/n
a = 12.155 (2)
b = 8.711 (2)
c= 8.645 (3)
β = 90.175 (6)
sample: 3s16
Intensity / Total count
0
5000
10000
15000
20000
25000
10
15
20
25
30
35
40
45
50
2-Theta (°)
(11-1)
(020)
(120)
*
(021)
(121)
(310)
(31-1)
(311)
*
(22-1)
(022)
(400)
(12-2)
(130)
(103)
(411)
(41-1)
(11-3)
*
(213)
(23-1)
*
(330)
(510)
(51-2)
(521)

Figure 15



Li3V2(PO4)3 Synthesis by Carbothermal Reduction Method 13.8 mg active

Figure 16

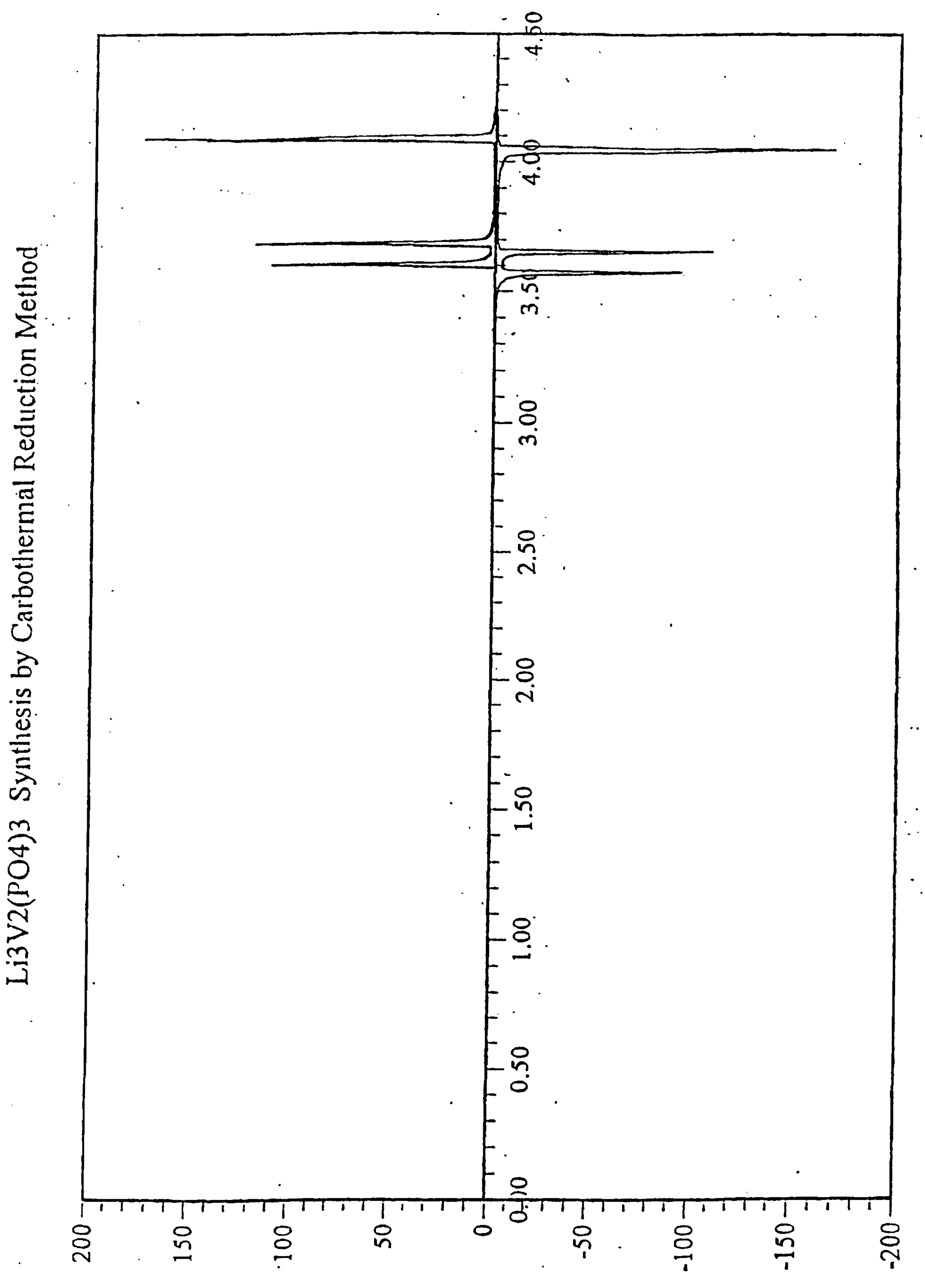

Li3V2(PO4)3 Synthesis by Carbothermal Reduction Method
Voltage [V]
0.00
0.50
1.00
1.50
2.00
2.50
3.00
3.50
4.00
4.50
200
150
100
50
0
-50
-100
-150
-200

Figure 17

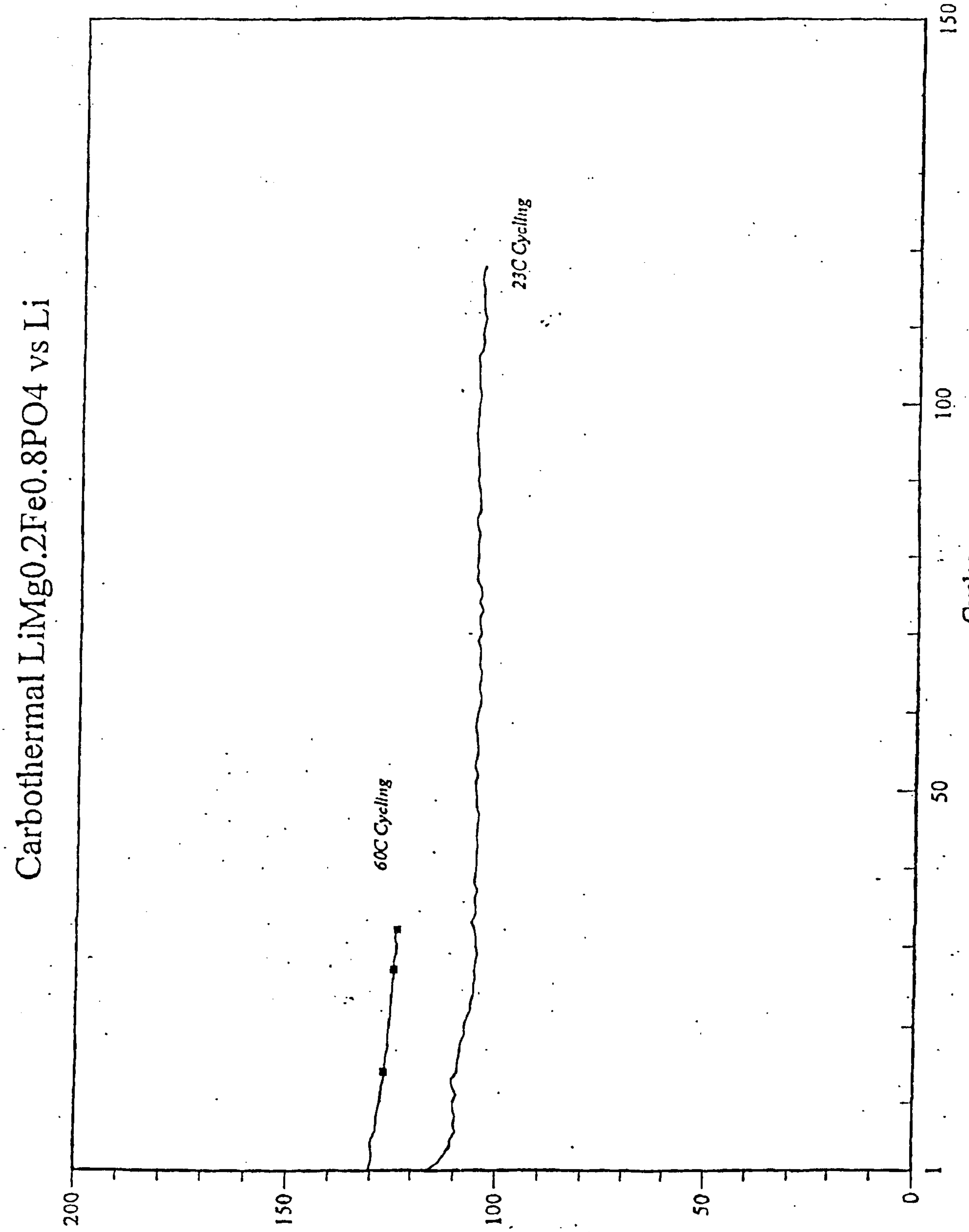

Carbothermal LiMg0.2Fe0.8PO4 vs Li
Specific Capacity (mAhr/g)
200
150
100
50
0
Cycles
1
50
100
150
60C Cycling
23C Cycling

Figure 18

Voltage Profile for LiMg0.1Fe0.9PO4 vs MCMB

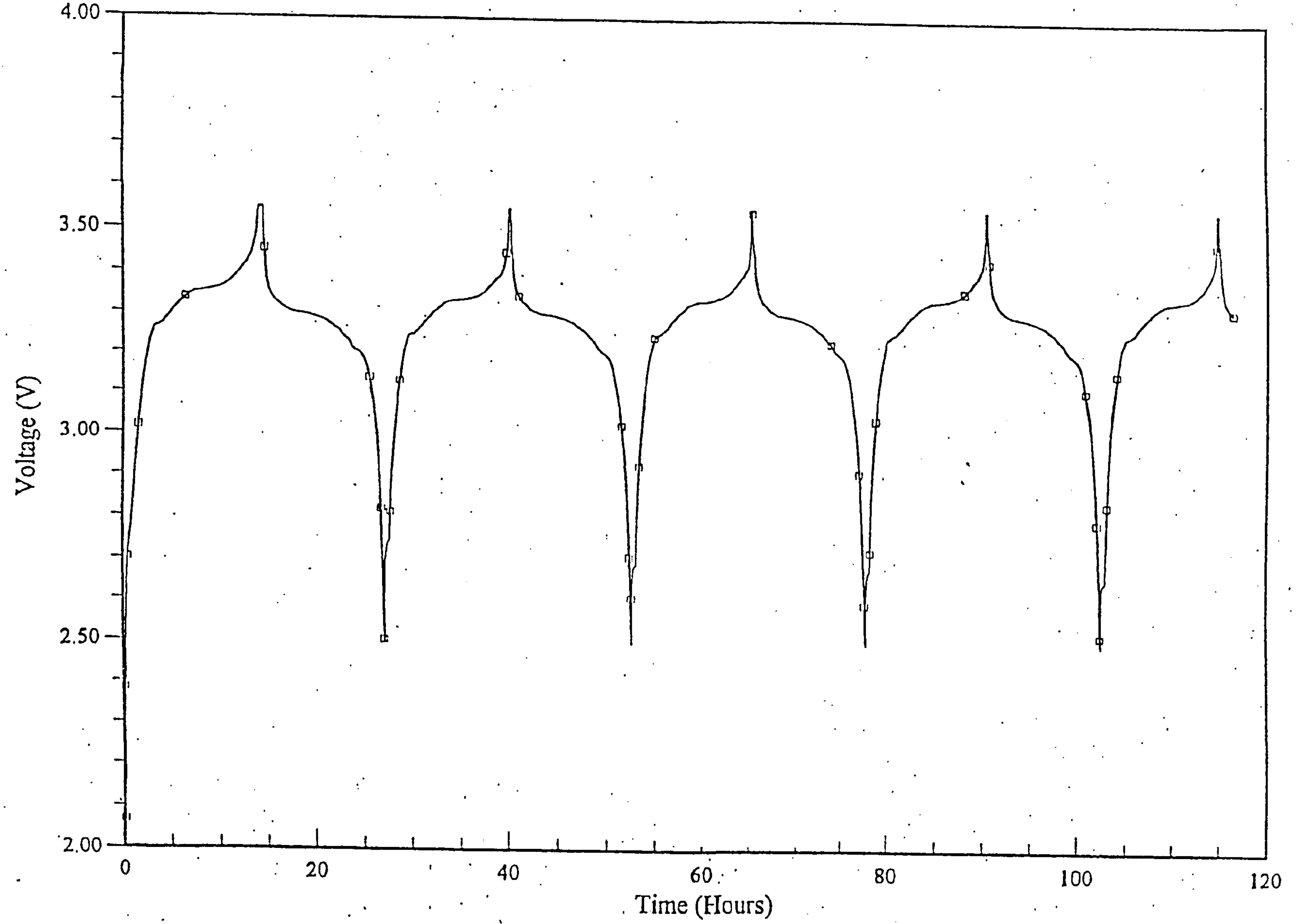


Figure 19

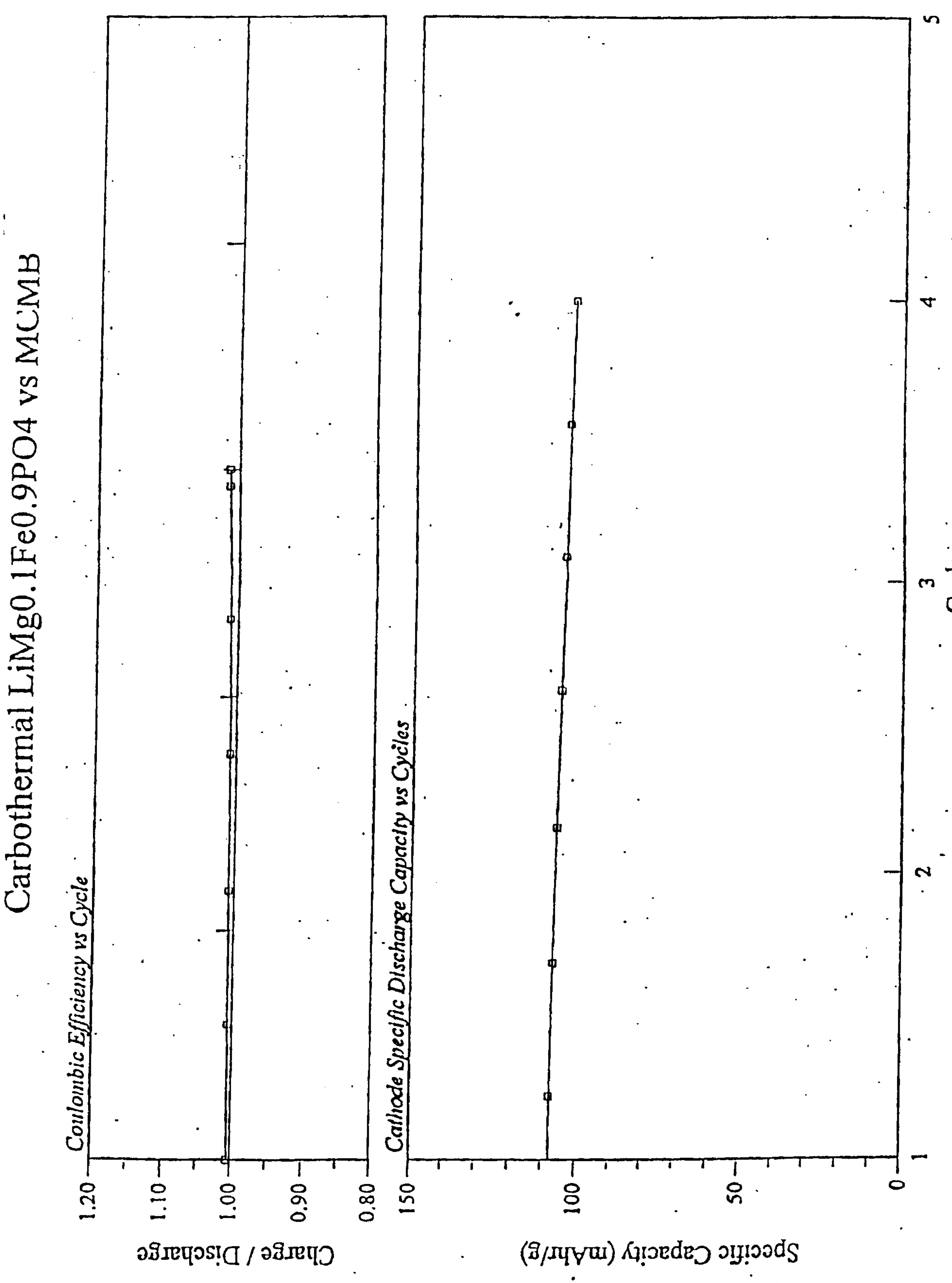

Carbothermal LiMg0.1Fe0.9PO4 vs MCMB
Coulombic Efficiency vs Cycle
Charge / Discharge
1.20
1.10
1.00
0.90
0.80
Cathode Specific Discharge Capacity vs Cycles
Specific Capacity (mAhr/g)
150
100
50
0
1
2
3
4
5
Cycles

Figure 20

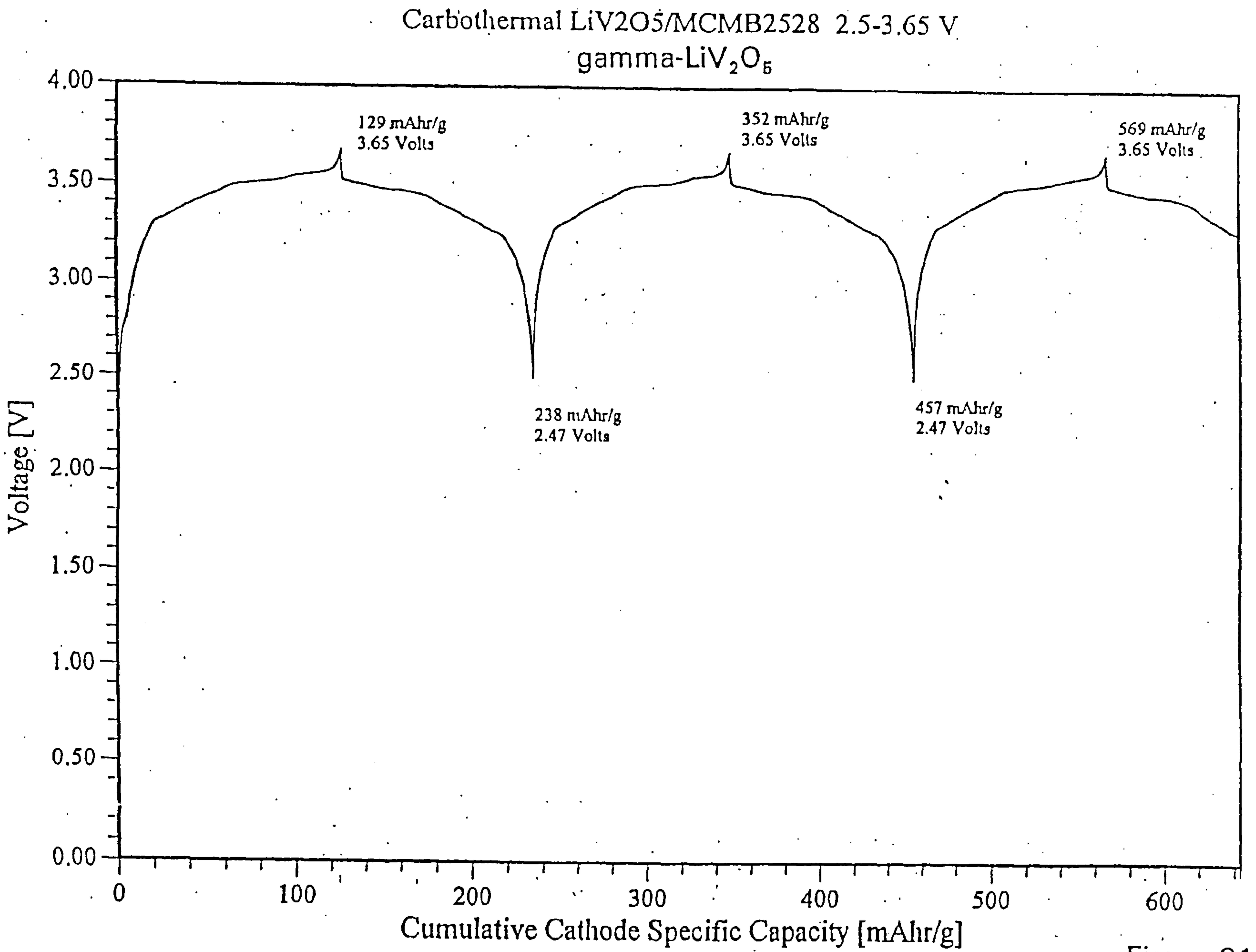

Carbothermal LiV2O5/MCMB2528 2.5-3.65 V
gamma-LiV_2O_5
Voltage [V]
4.00
3.50
3.00
2.50
2.00
1.50
1.00
0.50
0.00
129 mAhr/g
3.65 Volts
238 mAhr/g
2.47 Volts
352 mAhr/g
3.65 Volts
457 mAhr/g
2.47 Volts
569 mAhr/g
3.65 Volts
0
100
200
300
400
500
600
Cumulative Cathode Specific Capacity [mAhr/g]

Figure 21

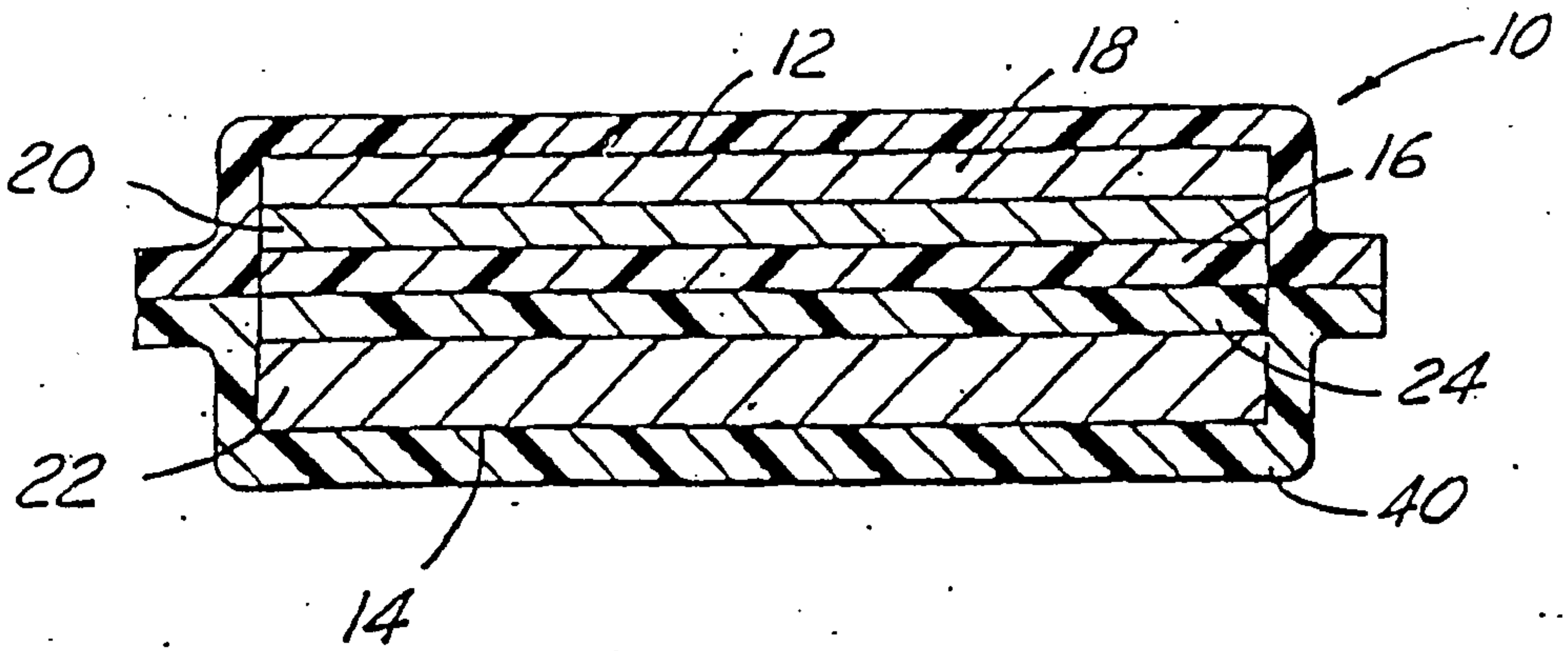


Figure 22

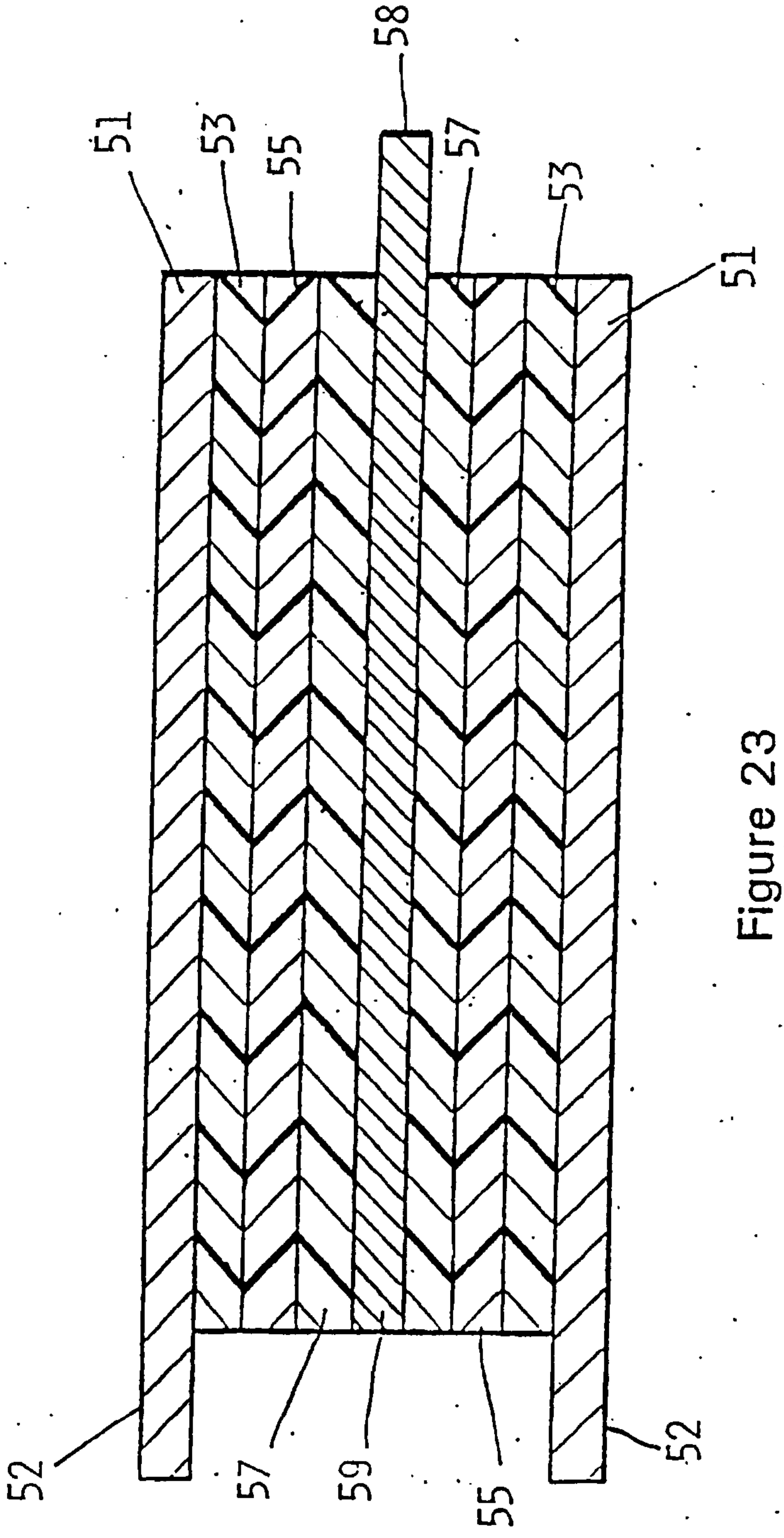


Figure 23