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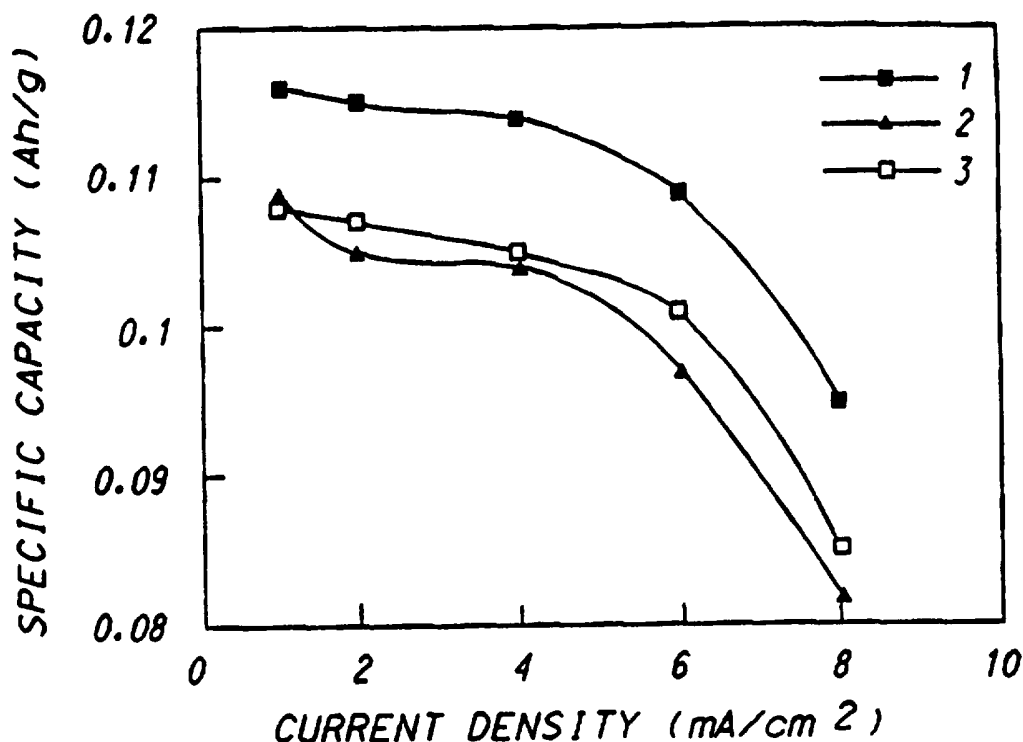
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(54) Title: LITHIUM MANGANESE OXIDE, METHOD OF PREPARATION AND USES THEREOF

(57) Abstract

A process for preparing a composition suitable for use as an electrode active material, comprises comminuting and heating intermingled particles of manganese dioxide and a lithium-containing compound, such manganese oxide particles having a median particle diameter after comminuting of about 10 microns or less, and reacting the manganese oxide particles with the lithium-containing compound by transporting lithium and optionally other elements across particle boundaries and releasing an oxygen containing gas from the particles whereby at least partial homogenization across particle boundaries produces product particles having a unit structure represented by the nominal general formula $\text{Li}_x\text{Mn}_2\text{O}_4$, where the heating is at a temperature below the melting point of the product.



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**LITHIUM MANGANESE OXIDE, METHOD
OF PREPARATION AND USES THEREOF**

5

Field of the Invention

This invention relates to a method of making an electrode active material and electrodes for electric current producing and storage cells and more particularly to a lithium metal oxide obtained through a new process of synthesis.

Background of the Invention

15

Cells and batteries based on transport of metal ions between an anode and cathode are known. Some cells and batteries are based on an alkali metal anode (negative electrode) and finely divided metal oxide cathode (positive electrode). An electrolyte provides transport between the electrodes. Particularly favored are such cells comprising a lithium-based anode active material of a thickness of about 75 microns, and an intercalation cathode layer of a similar thickness which contains finely divided transition metal oxide active material, electrically conductive carbon and solid electrolyte material. An electrolyte layer having a typical thickness of about 25 microns is positioned between the anode and cathode and is non-aqueous in view of the high chemical activity of alkali metal anodes such as lithium. The electrolyte layer separates the anode and cathode from one another while providing transport of ions between the anode and cathode. Typically, a current collector of conductive metal is positioned on the sides of both of the electrodes away from the electrolyte layer.

Processes for making electrochemical cells containing alkali metal active material and components of such cells are generally described in U.S. Patent No. 5,011,501 to Shackle and U.S. Patent No. 4,935,317 to Fauteux and Shackle. Each of these patents are
5 incorporated in its entirety herein.

The electrolyte is typically a solid or liquid electrolyte. Suitable liquid or solid electrolytes are known with polymer electrolytes presently being favored. A
10 variety of liquid, solid, and polymer electrolytes are described in U.S. Patent Nos. 4,009,052, 4,118,550, 4,792,504, 4,830,939, 4,990,413, 5,037,712, and 5,229,225 each of which is incorporated herein by reference in its entirety. One type of electrolyte is a solid organic
15 polymer matrix containing an ionically conducting powder or liquid with an alkali metal salt and the liquid is an aprotic polar solvent. Other electrolytes are liquid with dissolved metal salt usually used with a separator between the electrodes.

Several methods have been suggested for preparing
20 electrode active material including mixing precursor components containing lithium with a metal oxide component and then baking the mixture to cause formation of a molten product. Then it is necessary to cool and grind the
25 product into a powder. Such melt processes have certain disadvantages because it is difficult to handle high temperature molten products and significant mechanical energy is required to grind the cooled solidified product into a powder for inclusion in an electrode composition.
30 Despite these difficulties, typical melt processes as described in U.S. Patent No. 5,013,620 continue to be used. In view of such difficulties, U.S. Patent No. 5,135,732 describes synthesis of lithium manganese oxide prepared by mixing lithium hydroxide and a manganese acetate in an
35 aqueous reaction while including a base to establish a

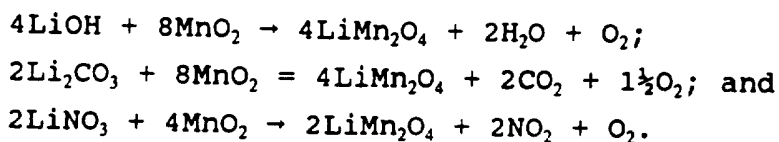
suitable solution pH to initiate formation of a gelatinous precipitate. Next, it is necessary to dry the precipitate to form a xerogel and then in a final step to anneal the xerogel in a preferred range of 200°C to 400°C for about 24 hours. This process is complex. U.S. Patent No. 5,110,696 describes preparing a very fine grain lithiated transition metal oxide by low temperature annealing of a stoichiometric thin film lithiated oxide layer deposited by reactive electron beam evaporation onto a suitable substrate from a bulk source of the oxide compound. In this very complex process, it is necessary to carefully control crystallite grain size during annealing; avoid epitaxial influence at the substrate surface by interposing an amorphous inert buffer layer between the substrate and the deposited film. This requires the use of an airtight enclosure in an atmosphere down to about 10^{-5} torr and very controlled temperatures. The complexity of this process and the control required are self-evident. Therefore, what is needed is a new process for preparing electrode active material which is economical, which does not require handling metal oxide constituents in a molten or xerogel state and which does not require highly controlled atmosphere and precise production conditions, and which is adaptable to commercial production processes and which achieves good conversion of the starting materials to the final desired product.

Summary of the Invention

In a preferred method, a lithium metal oxide, $\text{Li}_x\text{Mn}_y\text{O}_z$, composition is prepared having a unit structure characterized by the ability to insert lithium in an electrochemical reaction. Such compounds are referred to as intercalation compounds and they are transition metal chalcogen compounds having a reversible lithium insertion

ability. The preferred transition metal oxide product of the invention is represented by the nominal general formula LiMn_2O_4 ; $\text{Li}_x\text{Mn}_2\text{O}_4$, $0 \leq x \leq 2$; or $\text{Li}_{1-y}\text{Mn}_2\text{O}_4$, $0 \leq y \leq 1$ synthesized in discharged form. In use in a cell, during
5 charge, some lithium is removed from the structure according to $\text{LiMn}_2\text{O}_4 \rightarrow \text{Li}_{1-y}\text{Mn}_2\text{O}_4 + y\text{Li}^+ + y\text{e}^-$.

The process of the invention will be described with reference to the preparation of the active material, as synthesized, having the nominal general stoichiometric
10 formula $\text{Li}_x\text{Mn}_2\text{O}_4$ which has good energy, power and cycling capability. The $\text{Li}_x\text{Mn}_2\text{O}_4$, nominally LiMn_2O_4 , is prepared in a process which lithiates a precursor metal oxide, chemical manganese dioxide (CMD) in a reaction between intermingled particles of a lithium-containing compound and the CMD
15 metal oxide. The lithium-containing compound is preferably lithium carbonate (Li_2CO_3) or lithium hydroxide (LiOH). Other lithium-containing compounds such as LiNO_3 may also be used. The process is conducted by a sequence of steps, the first being forming a mixture comprising the
20 intermingled particles of the metal oxide and the lithium compound each in an amount sufficient to provide a stoichiometric amount of the lithium and the metal of the oxide in the final product. In the case of the preparation using LiOH , LiNO_3 , and Li_2CO_3 , the overall reactions may be
25 represented as follows:



30 As can be seen, the stoichiometric ratio of lithium and manganese in the product is 1:2 of Li:Mn. This corresponds to 1 mole equivalent of lithium carbonate for each 4 mole equivalent of chemical manganese dioxide (CMD); and 1 mole
35 equivalent of lithium hydroxide for each 2 mole equivalent

of CMD. The mixture may be in a stoichiometric ratio so that there is at least an approximate molar ratio of lithium to manganese of about 1:2. Optionally, there is a slight excess of either
5 starting material, the manganese oxide or the lithium-containing material. The excess of either of these starting materials may be such that the ratio of lithium to manganese in the starting material is 1:1.95 to 1:2.05, and preferably 1:1.98 to 1:2.02.
10 It is preferred that an excess amount of the lithium-containing compound be used. The particles are ground together to achieve a reduction in particle size; particularly, a reduction in size of the CMD particles.

15 The important performance advantages of the electrode material of the invention depend, at least in part, on the use of a manganese dioxide produced by a chemical method and designated chemical manganese dioxide (CMD). This is to distinguish it from the
20 less desirable electrochemical manganese dioxide (EMD).

Generally, a CMD should be selected to provide a BET surface area on the order of 90 to over 100 square meters per gram (m^2/g), desirably 95 to 105 m^2/g . Those having a surface area in the
25 range of 50 to 70 square meters per gram are less desirable. It is preferable to select a CMD having a BET surface area of at least about 100 square meters per gram. A CMD suitable for use in the invention will have a median particle diameter on
30 the order of 30 microns to 50 microns and typically on the order of 40 microns. It is desirable that the distribution of particle size in the starting chemical manganese dioxide be such that a major portion of the particles have a diameter on the
35 order of less than 50 microns.

After grinding, the particle size will be reduced from its typical value of approximately 40 microns median particle diameter. After grinding, it is preferred that the particle size not exceed about 10 microns median particle diameter and preferably it should be on the order of 1 micron median particle diameter or less.

After particle size reduction, the ground particles are heated to an elevated temperature which is at or above the decomposition temperature of the CMD and below the melting point of the final lithium metal oxide product, LiMn_2O_4 . The LiMn_2O_4 product has a melting point of about 1200°C , and MnO_2 decomposes at about 500°C to 550°C and is thought to form Mn_2O_3 having a melting point greater than 1000°C . Desirably, the temperature of the process is less than 800°C and it is preferred that the temperature be even lower, that is, in a range of about 650°C to about 750°C .

When the ground particles are heated to an elevated temperature, diffusion of at least a portion of the elements, being one or more of manganese, lithium, and oxygen occurs across particle boundaries and release of effluent gas also occurs. The diffusion of one or more elements across particle boundaries causes at least partial homogenization or blending of such elements and concomitant release of effluent gas which provides the lithium-manganese-oxide product. Among the effluent gases are H_2O , CO_2 , O_2 , and NO_x . In a reaction in air, NO_2 is likely to be formed, and the LiNO_3 may be less desirable due to the release of NO_2 .

It is an object of the invention to provide a new method for preparing a lithium manganese oxide electrode active material for a lithium battery. Another object is to provide a lithium battery having good charge and discharge capacity. Another object is to provide an improved electrochemical battery based on lithium which maintains its integrity over prolonged life cycle as

compared to presently used batteries. Another object is to provide lithium manganese oxide active material having a relatively low amount of precursor materials and contaminates whereby the composition approaches 100 percent by weight $\text{Li}_x\text{Mn}_2\text{O}_4$. Another object is to provide good conversion of the starting materials to the $\text{Li}_x\text{Mn}_2\text{O}_4$ product.

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

Brief Description of the Drawings

Figure 1 is a graph of grain size expressed as median equivalent particle diameter of the chemical manganese dioxide used in the invention; such size distribution obtained by laser measurement with ultrasonics.

Figure 2 is a scanning electron micrograph (SEM) of untreated chemical MnO_2 (CMD-Table I). The white bars correspond to 10 microns (μm).

Figure 3 is a scanning electron micrograph of the MnO_2 of Figures 1, 2, and Table I after grinding for 16 hours in the presence of LiOH and water.

Figure 4 is an illustration of a cross section of a thin battery or cell embodying the invention.

Figure 5 shows curves of rate capability of lithium-manganese-oxide after about 10 cycles at 1 milliamp per square centimeter (mA/cm^2). Curve 1 is the product of the invention as described in Example 1 and curves 2 and 3, respectively, correspond to Comparative Examples 1 and 2.

Figure 6 shows cycling of lithium-manganese-oxide at $I_d = 6 \text{ mA}/\text{cm}^2$ and $I_c = 1 \text{ mA}/\text{cm}^2$. Curve 1 is the product of the invention as described in Example 1 and curves 2 and 3, respectively, correspond to Comparative Examples 1 and 2.

Figures 7 and 8 are scanning electron micrograph (SEM) pictures which show that the lithium-manganese-oxide of the invention (Figure 7) has smaller particles than the one obtained when starting from CMD ground alone (Figure 8) of the first Comparative Example.

Figure 9 is a typical first cycle of LiMn_2O_4 synthesized at 750°C . $I_c = 0.25 \text{ mA/cm}^2$, $I_d = 1 \text{ mA/cm}^2$.

Figures 10 and 11 are curves of EPS for LiMn_2O_4 - 750°C at the first and second cycle. Step: $10 \text{ mV}/0.5 \text{ h}$. The current values represent the average current of each step.

Figures 12 and 13 show EPS curves similar to Figures 10 and 11 but for LiMn_2O_4 prepared at 900°C .

Figures 14 (LiMn_2O_4 - 750°C) and 15 (LiMn_2O_4 - 900°C) show V and dx/dV vs. x curves obtained from EPS data.

Detailed Description of the Preferred Embodiments

Intercalation electrode of lithiated transition metal oxide is prepared having the nominal general formula LiMn_2O_4 (lithium manganese oxide) with small particle size (fine grain), high porosity, and high conversion of starting materials resulting in a low level of non-lithiated product materials. This material is prepared in the present invention by starting with a highly porous manganese dioxide having a relatively high surface area as more particularly described below and represented in Table I. The particle size is then reduced in the presence of solid particles of a lithiating agent which is a lithium compound such as lithium salt. In order to achieve the necessary high porosity, a chemical manganese dioxide (CMD) form of MnO_2 is prepared. The reduction of the particle size of the manganese dioxide is advantageously accomplished by grinding in a ball-mill in the presence of the lithiating agent.

It has conventionally been accepted that a reduction of the particle size of MnO_2 (manganese dioxide) is obtainable by just grinding it alone prior to preparation of a lithiated product. The present invention achieves a rather surprising result and improved advantages when the manganese dioxide particle size is reduced in the presence of a lithiating agent in the synthesis process of the invention. Both SEM and BET experiments described below confirm that the particle size of manganese dioxide (MnO_2) is rather only marginally reduced when ground alone in a ball-mill, and surprisingly, a more significant reduction in the particle size of MnO_2 is obtained by grinding in the presence of the lithiating agent. Satisfactory results have been achieved by starting with a highly porous manganese dioxide having a surface area of at least about 100 square meters per gram and then reducing its particle size from an original value of 40 microns in the ball-mill by mixing it intimately with a lithiating agent selected from the group of LiOH , LiNO_3 , or Li_2CO_3 . Preferably, the grinding occurs in a slurry. The solvent used in the slurry is not critical. Suitable solvents which act as dispersing agents are water or alcohol.

After grinding, the slurry is heated at a temperature sufficient to cause lithiation of the manganese dioxide in a reaction between the lithiating agent, which, at least initially, is in solid, particle form, and the manganese dioxide, also in solid, particle form. The reaction may be conducted over a relatively broad temperature range. It is suggested that the temperature be greater than 500°C and below 800°C in order to obtain the product having acceptable morphological properties. It is desirable that the reaction temperature be on the order of 650°C to about 800°C and preferably be in the range of about 700°C to about 750°C . Suitable results were achieved

by maintaining this reaction temperature over a 2 to 3 day period; shorter reaction times are thought to be suitable, also.

5 The lithium manganese oxide (LiMn_2O_4) material of the present invention is intended primarily for use as a positive electrode (cathode) in a rechargeable battery such as a lithium battery, with lithium metal or lithium intercalation negative electrodes. The basic elements of an exemplary battery wherein the lithium manganese oxide
10 (LiMn_2O_4), of the invention may be used, will be generally described later below.

The characteristics of the starting materials necessary to prepare the LiMn_2O_4 of the invention will now be described along with more specific details of its
15 preparation and comparative examples which demonstrate the unexpected and clear advantages of the invention.

Starting Materials

20 The important performance advantages of the electrode material of the invention depend, at least in part, on the use of a manganese dioxide produced by a chemical method and designated chemical manganese dioxide (CMD). This is to distinguish it from the less desirable
25 electrochemical manganese dioxide (EMD). The basic physical characteristics of the preferred CMD and a summary of its method of preparation will now be described. CMD may be purchased as it is produced commercially by M.M.M. Sedema, s.a., which has its headquarters in Brussels,
30 Belgium. Sedema's CMD is sold under the name Faradiser M. This material is also identified as IBA number 12 or IC number 12. The specifications for this product are listed in Table I.

TABLE I
CHEMICAL MANGANESE DIOXIDE*

GENERAL CHARACTERISTICS	
Formula	MnO ₂
Molecular Weight	86.94
Appearance	fine black powder
CAS No.	1313-13-9

TYPICAL SPECIFICATIONS			
(Dry basis)			
Mn	60.0	%	min
MnO ₂	90.0	%	min
H ₂ O (120°C)	3.5	%	max
Na ₂ O	0.3	%	max
Fe	0.05	%	max
SO ₄ ²⁻	0.50	%	max
Insol HCl	0.10	%	max
Co	10	ppm	max
Ni	10	ppm	max
Cu	5	ppm	max
O/Mn	1.94	-	-
<44μm	75	%	min
pH Water	4.5	-	min
Tapped Density	1.81	g/cc	-
Bulk Density	1.42	g/cc	-
SSA (BET)	105	m ² /g	-

* Typical specifications for battery grade Faradiser M brand sold by Sedema of Belgium. For particle size data see Figure 1; median diameter (grain size) 38 μm per laser measurement with ultrasonics. Some K₂O and CaO may also be present in 100 ppm to 1000 ppm quantities.

Generally, a CMD should be selected to provide a BET surface area on the order of 90 to over 100 square meters per gram (m^2/g), desirably 95 to 105 m^2/g . Those having a surface area in the range of 50 to 70 square meters per gram are less desirable. It is preferable to select a CMD having a BET surface area of at least about 100 square meters per gram. A CMD suitable for use in the invention will have a median particle diameter on the order of 30 microns to 50 microns and typically on the order of 40 microns. It is desirable that the distribution of particle size in the starting chemical manganese dioxide be such that a major portion of the particles have a diameter on the order of less than 50 microns. The distribution of the CMD particle size shown in Figure 1 shows that about 40 percent of the particles have a diameter of about 32 microns or less and about 78.7 percent of the particles have a diameter on the order 48 microns or less. Figure 2 shows a SEM of the CMD particles having the specification of Table I and the distribution of Figure 1.

After undergoing the mechanical grinding and lithiation process of the invention it is preferred that the particles of the product LiMn_2O_4 maintain a relatively high surface area typically greater than about 5 square meters per gram (m^2/g), desirably on the order of about 5 to about 10 or more m^2/g , and preferably on the order of about 8 to about 10 or more m^2/g . The reduction in surface area from the original starting material is a result of the lithiation process and by the method of the invention which causes some sintering. By the method of the invention, this reduction in surface area is held to an advantageously low level resulting in the superior performance of this material in a battery.

After grinding, the particle size is reduced from its typical value of approximately 40 microns median particle diameter. After grinding, it is desirable that the particle size not exceed about 10 microns median particle diameter. The duration of grinding should be sufficient to achieve particle size on the order of 5 microns. Lesser diameters on the order of 1 micron are possible but not thought necessary. Figure 3 shows a SEM of the CMD of Figure 2 after grinding with LiOH in H₂O for 16 hours.

If it is desired to prepare the manganese dioxide (MnO₂) starting material from the manganese ore the following process may be used. The manganese dioxide may be reduced in the presence of a hydrogen-carbon monoxide atmosphere which reduces the ore to MnO plus water and carbon dioxide. This material is then ground. The MnO (manganese oxide) is then treated with sulfuric acid (H₂SO₄) providing MnSO₄ in water. The pH is adjusted and MnSO₄ is collected. Next, a carbonate precipitation occurs with treatment with ammonium carbonate ((NH₄)₂CO₃) thereby forming MnCO₃. The MnCO₃ is then treated in a drying and oxidation step with hot air which converts a large portion of the MnCO₃ to the desired product MnO₂. To achieve higher conversion, the MnO₂/MnCO₃ mix is further treated with H₂SO₄ forming a mix of MnO₂ and MnSO₄. This mix is then treated with NaClO₃ whereby the MnSO₄ reacts with the NaClO₃ to provide further conversion to MnO₂. After washing and drying, a product equivalent to the Faradiser M having the properties described above is obtained.

The lithiating agents are lithium-containing compounds in solid form such as lithium salts: LiOH, LiNO₃, and Li₂CO₃. These lithium-containing compounds are widely known and available from a number of chemical supply houses including Fluka and Aldrich Chemical Co. Powder of lithium carbonate of a 99.997 percent purity is available

from Aldrich Chemical Co., Inc. of Milwaukee, Wisconsin. The material is in particle form, has a melting point of approximately 618°C, a specific gravity of approximately 2.1 grams per cc, a particle size of less than 200 mesh (about 70 microns) and has the appearance of a white powder. The chemical abstract (CAS) number for lithium carbonate is 554-13-2 and its synonyms are camcolit, carbonic acid dilithium salt, candamide, carbonic acid lithium salt and dilithium carbonate. Lithium hydroxide is a powder of essentially colorless crystals having a specific gravity of approximately 2.54 and a melting point of approximately 462° centigrade.

The physical characteristics of the dispersing agents, that is the solvent, are not critical. Water or alcohol may be used. Essentially, any solvent may be used so long as the solvent does not substantially dissolve the solid constituents and so long as the solvent provides the necessary dispersion of the solid materials during the mechanical process of comminution (reducing particle size). Suitable solvents are water and organic alcohols such as ethanol, methanol, and propanol. The amount of solvent used will mainly depend on the solubility of the lithiating agent. The solubility of Li_2CO_3 is poor and that of LiOH and LiNO_3 is relatively higher. It is undesirable to dissolve the lithiating agent during grinding since such grinding requires that particles of the lithiating agent be present. Some dissolution is tolerable but it should be limited so that the major portion of the lithiating agent remains in solid particle form with the CMD in the solvent dispersing agent.

The structure and surface of any manganese dioxide change upon heating as demonstrated by a Sedema heat-treated manganese dioxide which has a BET of only about 30 m^2/g . Such heat-treated material is usable in the method of the invention but would not be preferred since

the heat-treated form offers certain disadvantages. Accordingly, the step of heating to cause the lithiation reaction must be conducted within the temperature ranges described above as this prevents the BET surface area from reaching unacceptably low values.

It should be noted that the process of particle size reduction may be accomplished by a variety of means such as grinding, pulverizing, crushing, beating, and rubbing. In the examples below, grinding in a ball-mill is demonstrated but the invention is not limited to particle size reduction (comminution) by any particular means.

Example 1

Chemical manganese dioxide (CMD, MnO_2) was intimately mixed with a lithium hydroxide (LiOH) lithiating agent. Both the chemical MnO_2 and the LiOH were in particle form. The chemical MnO_2 was highly porous, having a surface area on the order of 100 square meters per gram. The particle size of the chemical MnO_2 in an initial condition was on the order of 40 microns. The chemical MnO_2 particles, in this condition, were intimately mixed with the LiOH particles and ground in a ball-mill. The grinding time was 15 hours. The grinding was done in a planetary micro-mill. Such micro-mills are known and basically constitute a steel jar containing some steel balls. The jar with the balls and the material desired to be ground is shaken and rotated so as to micronize, pulverize, or reduce the dimensions of the particles in the jar. Typically, the ball-mill contained stoichiometric amounts of the lithiating salt and the chemical manganese dioxide followed by addition of water in an amount sufficient to form a slurry and disperse the solids. The relative amounts of solids and dispersing agent are not critical. Good results were obtained using 2 to 10 milliliters of water for every

10 grams of the solids. Although a 15 hour milling time was used, a 3 hour milling time is also thought to be sufficient to obtain a slurry containing the chemical manganese dioxide with the desired reduced particle size. As stated earlier, it is desirable to reduce the particle size from about 40 microns median diameter to about 10 microns median diameter. Preferably, the median diameter is on the order of 1 micron or less.

After grinding, the slurry was heated at a temperature in the range of about 700°C to 750°C for 2 to 3 days. Shorter reaction times are thought to be sufficient. After this period of time, the LiMn_2O_4 product had a BET surface area of about 10 square meters per gram. This demonstrates that a synthesis temperature in a range of 700°C to 750°C is sufficiently high to cause diffusion or migration of the lithium and transformation of the manganese to the desired end product while at the same time avoiding excessively high temperatures which cause the formation of crystals which have less desired properties. The product of this example was in the form of small particles generally spherical in appearance in the form of individually distinguishable fluffy, generally spherical particles or grains having generally curved surfaces. The general shape of the final product particles (Figure 7) is similar to that shown after grinding (Figure 3). More elevated temperatures produce crystal products in the form of individual crystals distinguishable by sharp edges and angles. The product of the invention is distinguishable from other LiMn_2O_4 products prepared by other means. The method of the invention produces conversion of a majority portion of the starting material (CMD) to the final product. One can expect to have conversion of at least 90 percent of the CMD to the final product; conversion of over 95 percent and approaching about 100 percent yield is achieved.

Comparative Example 1

The method of the invention, as illustrated in the example above which produced the desired product, was followed except that the particle size of the chemical manganese dioxide was reduced without the presence of the lithiating agent. In this example, the chemical manganese dioxide was ground in the very same ball-mill (micro-mill) for the very same amount of grinding time, namely, 15 hours. The pre-ground chemical manganese dioxide was then intermingled with the lithiating agent, LiOH, and reacted at the same temperature as Example 1, namely, 700°C to 750°C for 2 to 3 days. The LiMn_2O_4 of this comparative example had a BET surface area of about 5 square meters per gram, considerably less than that of the method of the invention.

Comparative Example 2

In this last example, an experiment was conducted to determine whether a satisfactory LiMn_2O_4 product could be obtained when starting from electrochemical manganese dioxide (EMD) with sufficiently small particle size to avoid the grinding step. An EMD designated as IBA No. 21 with median particle diameter of 4 microns was selected. This 4 micron size is considerably less than the 40 micron size of the CMD of the examples earlier stated. The electrochemical manganese dioxide was combined with the lithiating agent at the temperatures described above to effect diffusion of lithium and transformation of the manganese dioxide to the desired product. The LiMn_2O_4 so obtained had a surface area of about 4 square meters per gram which is consistent with the original EMD having a relatively low porosity (surface area of approximately 40 square meters per gram).

The different manganese spinels obtained by the method of the invention (Example 1) and the comparative methods (Comparative Examples 1 and 2) were compared to determine their capacities and rate capabilities. Before describing the specific components of the test electrical chemical cells used to determine performance, the general configuration of an electrochemical cell will now be described.

Figure 4 shows an electrochemical cell or battery 10 which has a negative electrode (anode) side 12, a positive electrode (cathode) side 14, and an electrolyte or electrolyte/separator 16. In accordance with common usage, a battery may consist of one cell or multiple cells. The negative electrode is the anode during discharge, and the positive electrode is the cathode during discharge. The negative electrode side includes current collector 18, typically of nickel, stainless steel, and/or copper foil, and a body of negative electrode material 20. The negative electrode material 20 is sometimes simply referred to as the negative electrode or negative electrode composition. The negative electrode side 12 may consist of only a metallic electrode 20 without a separately distinguishable current collector 18. The positive electrode side 14 includes current collector 22, typically of aluminum, nickel, stainless steel, and/or copper foil, or such foils having a protective conducting coating foil, and a body of positive electrode material 24. The cathode composition 24 has a typical composition as set forth in Table II and includes the lithium-manganese-oxide the active material of the invention. The positive electrode material 24 is sometimes simply referred to as the positive electrode or positive electrode composition.

The electrolyte 16 is typically a solid or liquid electrolyte. Suitable liquid or solid electrolytes are known with polymer electrolytes presently being favored. A variety of liquid, solid and polymer electrolytes are described in U.S. Patent Nos. 4,009,052, 4,118,550, 4,792,504, 4,830,939, 4,990,413, 5,037,712, 5,229,225, 5,238,758, 5,262,253, 5,294,501, and 5,300,375 each of which is incorporated herein by reference in its entirety. One type of electrolyte is a solid organic polymer matrix containing an ionically conducting powder or liquid with an alkali metal salt and the liquid is an aprotic polar solvent. Other electrolytes are liquid with dissolved metal salt usually used with a separator between the electrodes. The preferred electrolyte 16 is prepared according to the present invention. It should be noted that the electrolyte/binder described herein is usable for the anode composition, the cathode composition, and for the electrolyte separator 16 disposed between the negative and positive electrode compositions 20 and 24. Accordingly, the properties of the electrolyte/binder (e/b) polymer are described with reference to all uses in various U.S. Patents Nos. 4,009,052 and 4,118,550 which show electrolytes in the form of flat porous mats made of microporous films or fibers with suitable solvents used for electrolyte. U.S. Patent Nos. 4,792,504, 4,830,939, 4,990,413, and 5,037,712 show solid polymeric electrolytes comprising a continuous network of cross-linked polymeric structure containing an ionically conducting liquid for use in electrochemical cells. Examples include polymers having repeating units containing at least 1 heteroatom such as an oxygen or nitrogen atom as described in these patents, incorporated by reference in their entirety. U.S. Patent No. 5,229,225 shows a solid electrolyte having solvent ligands and polymer ligands coordinated with metal ion. U.S. Patent No. 5,262,253 shows solid electrolytes

containing a solid polymeric matrix derived from vinyl sulfonate polyalkylene oxides. U.S. Patent No. 5,294,501 shows a single solid phase solvent containing electrolyte having recurring units derived from silane acrylate incorporated within the solid polymeric matrix of the solid electrolyte. U.S. Patent No. 5,238,758 shows an interpenetrating polymeric network containing a liquid electrolyte for use in a cell which comprises a suitable salt, various suitable organic and inorganic salts are also described in the other patents incorporated herein by reference, as well suitable solvents for the salts. U.S. Patent No. 5,300,375 describes a single phase solid solvent containing electrolyte having recurring units derived from a novel acrylic alkoxy substituted silane incorporated within the solid polymeric matrix of the solid electrolyte.

The electrolyte composition typically comprises from about 5 to 25 weight percent of an inorganic ion salt based on the total weight of the electrolyte; preferably, from about 10 to 20 weight percent; and even more preferably about 15 weight percent.

Cell 10 is preferably a laminar thin-cell type including a lithium anode (negative electrode 20). Laminar thin-cell batteries containing lithium anodes are known in the art, and it will be appreciated that the cell can include various constructions such as bi-faced or bi-polar cell designs. Examples of cell constructions include a "jelly roll" or a fan folded laminate strip design as described in U.S. Patent No. 4,879,190 incorporated herein by reference in its entirety. Cell 10 also includes a protective covering (40) which functions to prevent water and air from contacting the reactive layers of the cell 10.

The anode is typically comprised of a compatible anodic material which is any material which functions as an anode in a solid electrolytic cell. Such compatible anodic materials are well known in the art and include, by way of

example, lithium, lithium alloys such as alloys of lithium with aluminum, mercury, tin, zinc, and the like, and intercalation based anodes such as carbon, chalcogen intercalation materials, transition-metal oxides or sulfides, conductive polymers such as polypyrrole, and the like. These are known in the art and are discussed in U.S. Patent Nos. 4,517,265, 5,028,500, 5,238,758, 4,812,376, and 4,987,042 each of which is incorporated by reference herein in its entirety. Most preferred are light weight electropositive materials such as alkali metals and particularly lithium and sodium.

In one embodiment, a cathode composition 24, containing the electrolyte of the invention is formed on the current collector 22 of the cell 10 of Figure 4. The current collector 22 may be a sheet of metal foil, an electrically conductive screen, grid, expanded metal, etched foil, electrodeposited film, woven or non-woven conductive fabric. In practice, it is preferred to use as the current collector a thin metal foil having a metal, preferably the same metal, electrodeposited on the surface thereof which will contact the cathode layer. A preferred metal is known as surface-treated nickel. A microroughened or etched surface on the current collector 22 enables better adherence of the cathode composition 24 to the current collector. (Figure 4)

In practice, the thickness of current collector 22 ranges from about 1 micron to about 25 microns. Preferably, the current collector is as thin as practicable. Alternatively, the current collector can take the form of a thin polymeric film having coated thereon an electrically conductive metal. The advantage of this current collector is that it is extremely light-weight and can be utilized in extremely thin layers. An example of such a material is a polyethylene terephthalate substrate having electrodeposited thereon a first layer of copper and a second layer of nickel.

The cathode composition is typically a highly viscous paste or gel applied onto the microroughened surface of current collector 22. In one embodiment, cathode composition 24 is paste-like in consistency and typically includes the active cathodic material; and an electrically conductive filler or an electrically conductive polymer such as polypyrrole, polyacetylene, polyaniline, etc.; and an ionically-conductive electrolyte. The electrically conductive filler is usually graphite, acetylene black, carbon black, carbon powder, or carbon particles generally referred to as carbonaceous material; metallic powders may also be used. One example of carbon powder is Shawinigan Black brand sold by Chevron Chemical Company having a BET surface area of about 100 square meters per gram (m^2/g).

In one embodiment, LiMn_2O_4 comprises between 25 and 85 percent by weight of the entire cathode composition, desirably between 35 and 75 percent by weight, and preferably between 45 and 65 percent by weight. The conductive agent (e.g., carbon) constitutes about 1 to about 20 weight percent, the solvent, e.g., propylene carbonate (PC), constitutes about 20 to 40 weight percent, a binding polymer, e.g., polyethylene oxide PEO (number average molecular weight of at least 100,000) constitutes about 0 to about 20 weight percent, the matrix forming monomer or partial monomer (acrylate) constitutes about 5 to about 30 weight percent.

TABLE II

TYPICAL CATHODE COMPOSITION	PERCENT WEIGHT
ACTIVE MATERIAL	45.0
CARBON	10.0
PC**	33.0
POLYETHYLENE OXIDE (PEO)	1.0
POLYETHYLENEGLYCOLDI- ACRYLATE (PEGDA)	9.0
TRIMETHYLPOLYETHYLENE OXIDE TRIACRYLATE (TMPEOTA)	2.0

** Commonly used are PC (propylene carbonate); EC (ethylene carbonate); gamma-butyrolactone; dioxolane; DME (dimethoxyethane); DMC (dimethylcarbonate); and DEC (diethylcarbonate). See patents regarding electrolytes previously incorporated by reference.

The cathode half element is obtained by coating a foil member such a nickel foil with the aforesaid composition in a thickness of about 10 to 100 microns and preferably about 30 to 60 microns, and curing. The cathode composition may be coated by any of the techniques discussed previously, but it is particularly desirable to design an extrudable cathode composition. The radiation curable composition used in the present invention functions as a dispersing medium for the cathode materials.

The materials prepared by the examples described above were used as active materials in cathodes to test their performance in a cell. The cathodes to be used with liquid electrolytes were also prepared with additives. Since LiMn_2O_4 is a semi-conductor (conductivity of about 10^6 ohm cm), a sufficient amount of an electronic conductor was

added to limit the voltage drop. It was ascertained that a properly prepared mixture of carbon black and polytetrafluoroethylene, mixed with the active material by dry or wet technique is effective in reducing the initial resistance to acceptably low values. It was determined that cathodes of the invention must contain a sufficient amount of the carbonaceous material electronic conductor. On the basis of weight percents of the constituents of the cathode, namely, (a) LiMn_2O_4 , active material, (b) carbon, and (c) binder, the following indicative proportions could be followed: 70 percent, 20 percent, and 10 percent, respectively. The anode material was constituted by a lithium foil. Figure 5 shows the characteristics of the three LiMn_2O_4 materials prepared as mentioned above. The material made by the method of the invention in Example 1 is designated as 1 and by blackened or filled in squares; and the Comparative Examples 1 and 2 are designated as 2 (or blackened or filled in triangles), and 3 (open squares). It is clear that the material prepared by the method of the invention as demonstrated by the curves of filled in squares has much better performance. The rate capability of the material of the invention after 10 cycles at 1 milliamp per centimeter squared is consistently higher than that of the Comparative Examples demonstrated by the curves of open squares and filled in triangles. As can be seen from Figure 5, the results of tests at different current densities show that the chemical manganese dioxide pre-ground in the presence of the lithiating agent (obtained by grinding in a slurry) has a higher capacity and an excellent rate capability far above that of the Comparative Examples.

In Figure 6, the high rate characteristics of the LiMn_2O_4 of the invention, prepared according to the method of the invention, is shown as compared to the Comparative Examples described earlier. The current density of 6

milliamps per centimeter squared of Figure 6 corresponds to 3.5 C, that is, to a 0.3 hour rate. Accordingly, the cycling behavior of LiMn_2O_4 is illustrated by the closed squares in Figure 6 at I_a equals 6 mA/cm square and I_c equals 1 mA/cm square. Further demonstrating the difference between the product prepared by the method of the invention and the Comparative Examples, there is shown in Figures 7 and 8 scanning electron micrographs which show that the LiMn_2O_4 of the invention (Figure 7) has smaller particles than the one obtained when starting from the CMD ground alone (Figure 8) as in the first Comparative Example. Although, in both cases the grinding time was the same and the reaction conditions were the same, the product of the invention as shown in Figure 7 has a BET surface of 10 square meters per gram while the value for the LiMn_2O_4 of Comparative Example 1 as in Figure 8 is only about 5 square meters per gram. If one were to compare the product of the invention to LiMn_2O_4 prepared at reaction temperatures which are considerably elevated from that recommended above, one would find formation of small crystals having a surface area of less than 1 square meter per gram which is unsuitable for cycling at high rates; such small crystals have clearly defined sharp edges which is completely different from the relatively spherical, particles of the product of the invention.

In summary, the method of the invention produces a $\text{Li}_x\text{Mn}_2\text{O}_4$ product suitable for use as a cathode (positive electrode) and provides high rate lithium and lithium-ion batteries. The good performance of such cathodes is achieved by the small particle size, high surface area, and high rate of conversion of the starting materials to the desired cathode product, and correspondingly low amount of unreacted manganese dioxide. The method of the invention is thought to be the only one effective for obtaining such results and these surprising advantages are achieved by

grinding the lithiating agent with MnO_2 of high porosity for several hours in the presence of a dispersing liquid, followed by heating at moderate temperatures. The performance of this product contrasts considerably with an LiMn_2O_4 product obtained by conventional means, which is ground after its synthesis, as is typical. Although grinding the product after formation, rather than before, increases the surface area, problems remain since the conversion of starting materials to the desired product is incomplete. A considerable amount of the starting material (MnO_2) exists in the product and must be separated or else it becomes part of the cathode material and reduces the performance. The advantages of the method of the invention are striking in that the LiMn_2O_4 of the invention has characteristics which allow it to be cycled at high rates on the order of up to 5 C, i.e., a 0.2 hour rate with a reduced capacity loss. This is an especially important advantage essential to achieving lithium-ion cells which can be charged in a very short time.

Without being bound to any particular theory, the electrodes of the present invention need not necessarily be stoichiometric compounds in their final formulation so that they are generally represented by the nominal general formula $\text{Li}_x\text{Mn}_2\text{O}_4$. For example, electrodes may be synthesized in which defects are created by varying the quantity of lithium-ions at various sites to generate a lithium deficient product with slightly less than 1 mole of lithium for every 2 moles of manganese. Alternatively, electrodes may be synthesized in which defects are created by varying the quantity of manganese ions in the structure of the product. When the $\text{Li}_x\text{Mn}_2\text{O}_4$ product of the present invention is assembled into a cell as a cathode with a suitable anode counter electrode, charging will involve a reduction of the value of x to a theoretical minimum value of approaching zero in the fully charged state. It is also possible in

principle to discharge such cells further than a partially discharged state in which the value of x achieves a theoretical maximum value of x equal to 2. Although x values in excess of 1.5 are possible, the electrochemical reaction when x exceeds 1.5 is not desirable. In practice, the value of x will be controlled between operating values such as $x = 0$ in the nominally fully charged state and a value of $x = 1$ in the nominally fully discharged state.

It is believed that an advantage of the present invention arises from the relatively less developed crystallinity and high surface area of the final $\text{Li}_x\text{Mn}_2\text{O}_4$ product as contrasted with conventionally well developed crystallinity obtained by other means and as per the Comparative Examples.

This product has been found to exhibit a high degree of electrochemical activity in electrochemical cells of the type described above, and has been found to operate reversibly which makes it attractive as a cathode material. This results in exceptionally utility for use as a reversible cathode in electrochemical cells due to the reversible behavior of the cathode with regard to insertion and extraction of lithium-ions during discharging and charging. This reversibility is believed to arise from the exceptionally high surface area and relatively less perfect but yet good crystallinity of the product of the present invention as compared to conventional products.

The conventional products are prepared from conventional lower surface area CMD and EMD, without grinding, and at various temperatures. The effect of temperature, proportion of carbonaceous material, and type of electrolyte are also thought to contribute to performance. These added factors were observed for LiMn_2O_4 and $\text{LiCr}_{0.2}\text{Mn}_{1.8}\text{O}_4$ prepared with conventional starting materials, having lower surface area and without grinding. It was observed that spinels prepared at 700°C to 750°C

have electrochemical features different from those of the spinels made at 800°C to 900°C. In particular, Li⁺ is more easily extracted from the former in a process which seems to create Li⁺ ordering for $x = 2/3$ and $x = 1/3$ in $\text{Li}_x\text{Mn}_2\text{O}_4$. It has been determined that the self-discharge characteristics of fully oxidized spinels in different electrolytes differ. The proportion of carbon in the electrode is also a factor.

The LiMn_2O_4 is a hopping semiconductor ($\sigma = 2 \times 10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$) and so is $\lambda\text{-MnO}_2$ (3×10^{-6}) obtained by full delithiation. A semiconductor-metal transition is not observed by Li⁺ extraction, because the critical Mn-Mn distance for this transition (2.743 Å) is shorter than those observed for $\lambda\text{-MnO}_2$ and LiMn_2O_4 (2.803 Å and 2.913 Å, respectively). However, upon Li⁺ removal the charge transfer resistance of the spinel decreases, perhaps as a consequence of an easier Li⁺ crossing of the electrolyte/cathode interface. A full charge/discharge cycle does not allow to reinsert the same amount of Li⁺ extracted as a consequence of a structural alteration. The abrupt voltage drop at the end of the cycle coincides with a unit cell parameter ~8.24 Å, for which the Jahn-Teller distortion elongating the MnO_6 octahedra reduces the symmetry from cubic to tetragonal.

In evaluation of these features, the spinel was admixed with 30 percent teflonized acetylene black (TAB) when working with liquid electrolytes. Button cells were prepared. A solution commonly used was 1M $\text{LiClO}_4\text{-EC/DMC/DEC}$ (2:2:1). For storage tests, the following solutions were also used: $\text{LiAsF}_6\text{-EC/PC}$, $\text{LiPF}_6\text{-EC/DMC}$, $\text{LiClO}_4\text{-PC/DME}$, $\text{LiPF}_6\text{-PC/DEC}$, and $\text{LiPF}_6\text{-EC/DMC/DEC}$.

Oxidation brings about a sudden voltage jump followed by a more gradual increase (Figure 9). The curve has a step at $x \sim 0.5$, reaches a minimum x ($0 < x < \sim 0.2$) depending on the synthesis conditions, and, upon discharge, never again attains, whatever the discharge rate, the initial $x = 1$ at potentials above 3 V.

Indeed, a sudden voltage drop occurs (Figure 9) for $x < 1$, i.e., for such compositions as $\text{Li}_{0.8}[\text{Mn}^{+4}\sim 0.8 \text{Mn}^{+3}]\text{O}_4$, that is $x = 0.8$. In this respect, it is noted the impossibility to fully relithiate LiMn_2O_4 , following its electrochemical oxidation. Cubic symmetry is maintained in a large x interval as a consequence of the fact that the MnO_6 octahedra are sufficiently regular. It seems that only when a critical elongation of the octahedron is reached, its symmetry changes and the overall unit cell symmetry has also to change from cubic to tetragonal. In the latter configuration, the octahedron has 4 Mn-O distances at 1.937 Å and 2 at 2.286 Å. The distortion (c/a) is then 1.18. So, it may be concluded that for $a > \sim 8.24$ Å, the octahedron cannot stand the Jahn-Teller distortion and a tetragonal phase is created which determines the sharp voltage drop (~ 1 V).

It has already been stressed that spinels prepared at 700°C to 750°C outperform those prepared at 800°C to 900°C in terms of capacity and cyclability. It is though that this stems from morphological and structural factors more favorable for the lower-temperature spinels. This has been verified by EPS experiments. In Figures 10 through 13, the I-V curves at the 1st (Figures 10 and 12) and 2nd cycle (Figures 11 and 13) for both spinels are shown. The curve defined by squares pertains to the left scale (V/volts) and the curve of triangles to the right scale (dx/dv). To better understand the differences, some significant parameters have been calculated and reported in Table III.

TABLE III
PARAMETERS DERIVATED FROM THE EPS
EXPERIMENTS OF FIGURES 8 AND 9

1ST CYCLE					
Spinel	V_2V_1	ΔV_1	ΔV_2	i_{pa1}	i_{pa2}
$\text{LiMn}_2\text{O}_4\text{-750}$	0.13	0.04	0.05	0.153	0.197
$\text{LiMn}_2\text{O}_4\text{-900}$	0.14	0.06	0.07	0.134	0.132
2ND CYCLE					
Spinel	V_2V_1	ΔV_1	ΔV_2	i_{pa1}	i_{pa2}
$\text{LiMn}_2\text{O}_4\text{-750}$	0.12	0.03	0.03	0.15	0.24
$\text{LiMn}_2\text{O}_4\text{-900}$	0.15	0.06	0.07	0.073	0.098
$V_1 = V$ of the 1st anodic peak; $V_2 = V$ of the 2nd anodic peak; $\Delta V_1 =$ anodic/cathodic V separation of the 1st peak; $\Delta V_2 =$ anodic/cathodic V separation of the 2nd peak; $i_{pa1} =$ height of the 1st anodic peak; $i_{pa2} =$ height of the 2nd anodic peak					

All data are in favor of the spinel synthesized at the lower temperature; 1st peak/2nd peak separation, anodic/cathodic peak separations, peak's heights and their variations from the 1st to the 2nd cycle. In particular, the peaks corresponding to the 2 oxidation steps are considerably shortened in $\text{LiMn}_2\text{O}_4\text{-900}$, this indicating a more problematic reversibility. In Figures 14 and 15, the potentiostatic 1st oxidation of the 2 spinels is shown. Again, the larger Li^+ removal in $\text{LiMn}_2\text{O}_4\text{-750}$ (Figure 14) is evident. But, another feature may be of interest. If dx/dV is plotted vs. x , one may notice, for $\text{LiMn}_2\text{O}_4\text{-750}$, minima at $x \sim 2/3$ and $\sim 1/3$. It seems that Li^+ is removed from the tetrahedra in such a way as to create Li^+ ordering at these preferential compositions. Such a behavior would be very similar to that observed during Li^+ intercalation

in some chalcogenides, e.g., TiS_2 . Ordering in a tridimensional compounds has never been reported. As for LiMn_2O_4 -900 (Figure 15), the minima in dx/dV vs. x appear shifted to higher values.

5 It has been found that the 2 spinels have a slightly different a parameter, 8.227 Å for LiMn_2O_4 -750 vs. 8.240 Å for LiMn_2O_4 -900, and that the changes in a are not the same upon Li^+ extraction. For the former, a decreases monotonously, while for the latter splitting of the main
10 peaks at $2\theta \sim 36^\circ$ and $\sim 44^\circ$ has been observed in the final oxidation stages. So, in LiMn_2O_4 -750 either a single cubic phase is also present for $x < 0.5$ or 2 cubic phases with very similar a coexist. Instead, for LiMn_2O_4 -900 the appearance of 2 cubic phases with $a_1 = 8.15$ Å and $a_2 = 8.06$
15 Å is evidenced.

 It is really remarkable that minor differences in the cubic a parameter may bring about so large differences in the electrochemical behavior. Apart from the features stressed above, LiMn_2O_4 -750 may long be cycled with limited
20 capacity losses. The higher surface area of the former certainly helps in this respect, but one should remember that LiMn_2O_4 -450, whose surface area is obviously even higher, cannot be cycled satisfactorily.

 During the course of this study, it was found
25 that the type of electrolyte solution influences the self-discharge. It was also found that the self-discharge rates of fully charged $\text{Li}/\text{LiMn}_2\text{O}_4$ cells appears to be related to the amount of carbon since carbon plays a role in the decomposition of the electrolyte due to its high active
30 area. Some cathodes containing 20 percent acetylene black were used, whereas in other experiments only a 3 percent carbon was used. This point was found to be relevant in the construction of real cells, since lesser carbon resulted in lower self-discharge rates.

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.

5

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

CLAIMS:

1.

A process for preparing lithium manganese oxide by the steps comprising:

- 5 a. providing chemical manganese dioxide having a median particle diameter less than about 40 microns and a BET surface area of at least about 90 m²/g;
- 10 b. reducing the particle size of the chemical manganese dioxide in the presence of a solid lithiating agent and a dispersing agent; and
- 15 c. heating the product of step (b) to an elevated temperature to react the chemical manganese dioxide with the lithiating agent to produce a product of the nominal general formula Li_xMn₂O₄.

2.

The process according to claim 1 wherein step (c) is conducted by heating the particles to an elevated temperature which is below the melting point of Li_xMn₂O₄ to
5 cause a diffusion of one or more of the lithium-manganese and oxygen elements across particle boundaries and a release of an oxygen containing by product gas.

3.

The process according to claim 1 wherein step (b) is conducted to reduce the median particle size to less than about 10 microns.

4.

The process according to claim 3 wherein the median particle size is reduced to a size of about 1 micron to about 5 microns.

5.

The process according to claim 1 wherein step (c) is conducted by heating to a temperature of at least about 650°C and less than about 750°C.

6.

The process according to claim 5 wherein the step of heating occurs for at least about 40 hours.

7.

5 A process for preparing a composition suitable for use as an electrode active material, comprising comminuting and heating intermingled particles of chemical manganese dioxide and a lithium-containing compound and reacting the manganese oxide particles with the lithium-containing compound by transporting lithium and optionally other elements across particle boundaries and releasing an oxygen containing gas from the particles whereby at least partial homogenization across particle boundaries produces product particles having a unit structure represented by the nominal general formula $\text{Li}_x\text{Mn}_2\text{O}_4$, where the heating is at a temperature below the melting point of the product.

10

8.

The process according to claim 7 wherein the comminuting is conducted to achieve a median particle size of about 10 microns or less.

9.

The process according to claim 7 wherein the comminuting is conducted to achieve a median particle size of about 5 microns or less.

10.

The process according to claim 7 wherein the comminuting is conducted by grinding in a ball-mill.

11.

The process according to claim 7 wherein step of heating is conducted by heating to a temperature of at least about 650°C and less than about 750°C.

12.

The process according to claim 7 wherein the oxygen-containing gas comprises a gas selected from the group consisting of oxygen (O₂), carbon dioxide (CO₂), water (H₂O), and nitrogen dioxide (NO₂).

13.

A process for preparing lithium manganese oxide by the steps comprising:

- a. providing chemical manganese dioxide particles having a BET surface area of at least about 90 m²/g;
- b. comminuting the chemical manganese dioxide particles in the presence of particles of a lithiating agent; and
- c. heating the product of step (b) to an elevated temperature to react the chemical manganese dioxide with the lithiating agent to produce a product of the nominal general formula Li_xMn₂O₄.

14.

The process according to claim 13 wherein the comminuting is conducted to achieve a median particle size of about 10 microns or less.

15.

The process according to claim 13 wherein the comminuting is conducted to achieve a median particle size of about 5 microns or less.

16.

The process according to claim 13 wherein the comminuting is conducted by grinding in a ball-mill.

17.

The process according to claim 13 wherein step of heating is conducted by heating to a temperature of at least about 650°C and less than about 750°C.

18.

The process according to claim 17 wherein the step of heating occurs for at least about 40 hours.

19.

5 A battery or cell comprising an electrode having a current collector and an active material layer on said current collector, said active material layer comprising
10 lithium-manganese-oxide active material formed from comminuted, heated, and lithiated particles of chemical manganese dioxide, said chemical manganese dioxide particles being comminuted in the presence of a lithiating agent which is in particle form, heated in the presence of said agent, and lithiated by diffusion of lithium into the chemical manganese dioxide particles from said lithiating agent.

20.

A composition comprising lithiated chemical manganese oxide in the form of individually distinguishable generally spherical particles having a surface area of at
5 least about 5 square meters per gram (m^2/g).

21.

The composition according to claim 20 having a surface area of about 5 to about 10 m^2/g .

22.

The composition according to claim 20 wherein said particles have substantially continuously curved surfaces.

1/9

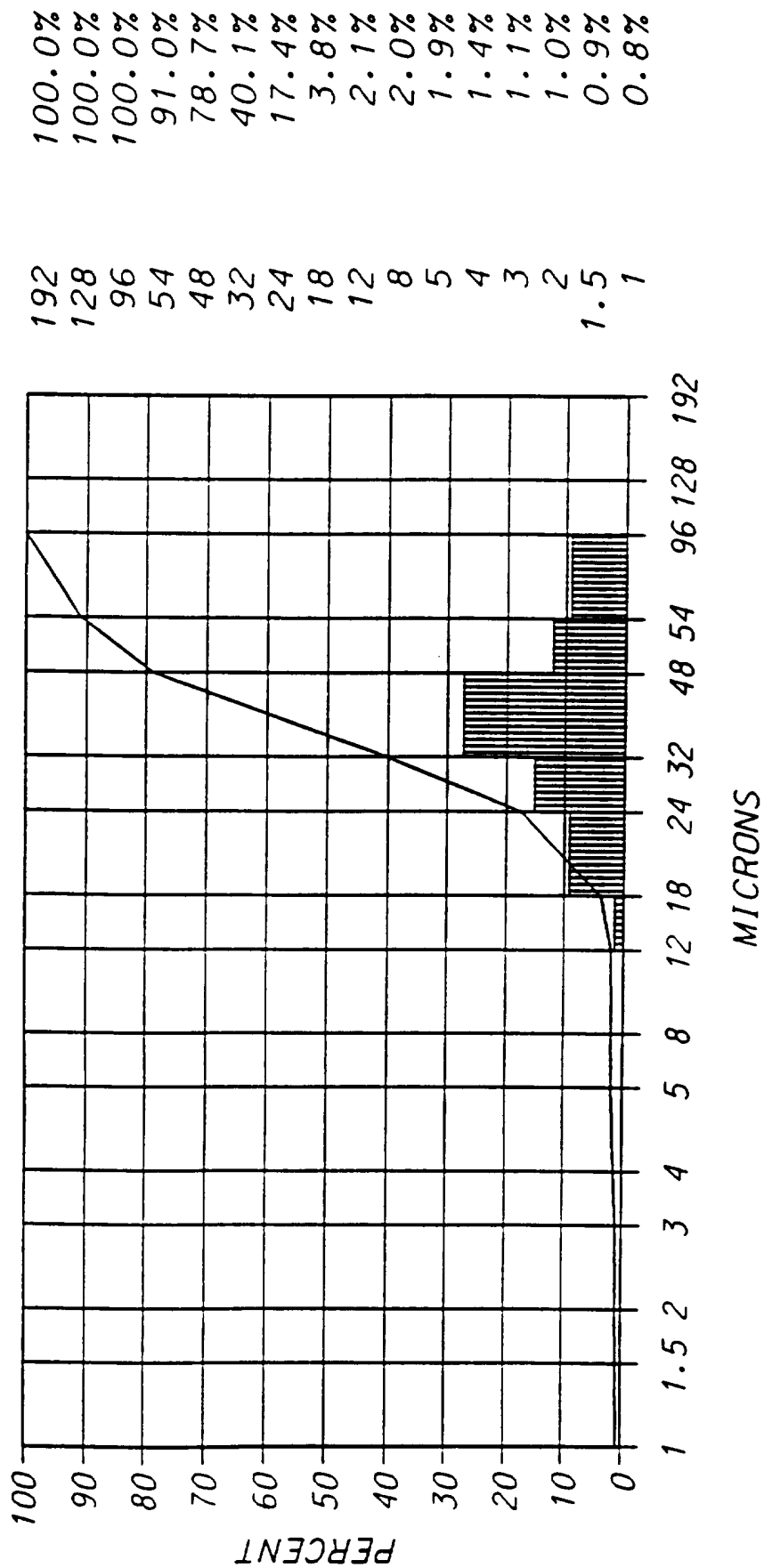


Fig. 1

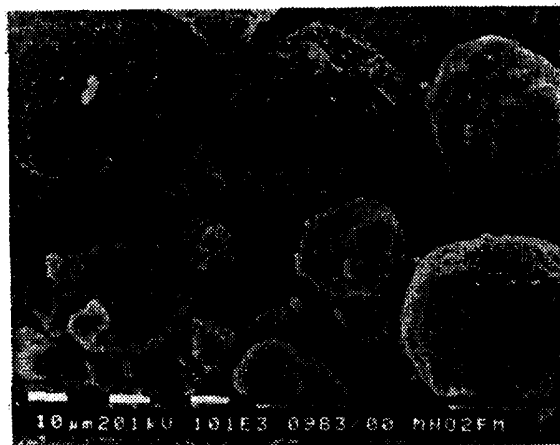


Fig. 2

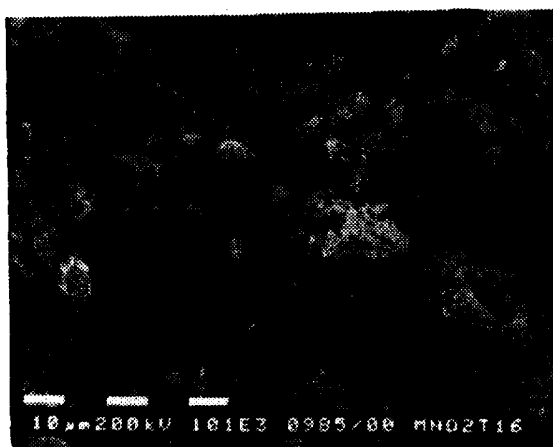


Fig. 3

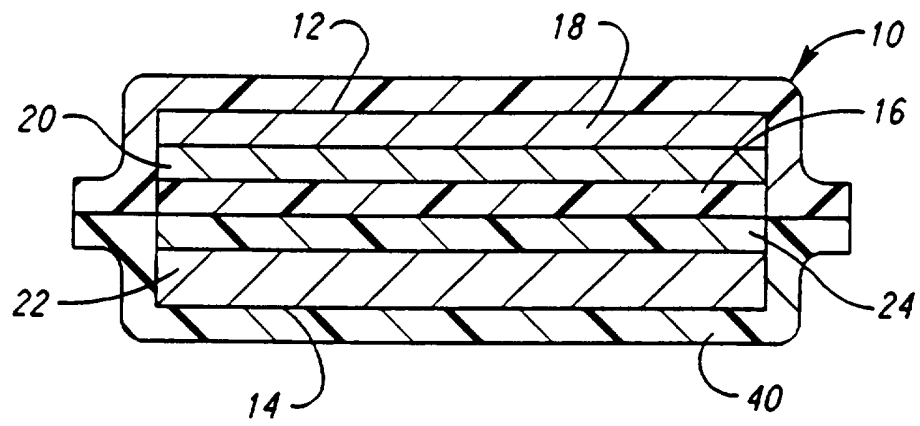


Fig. 4

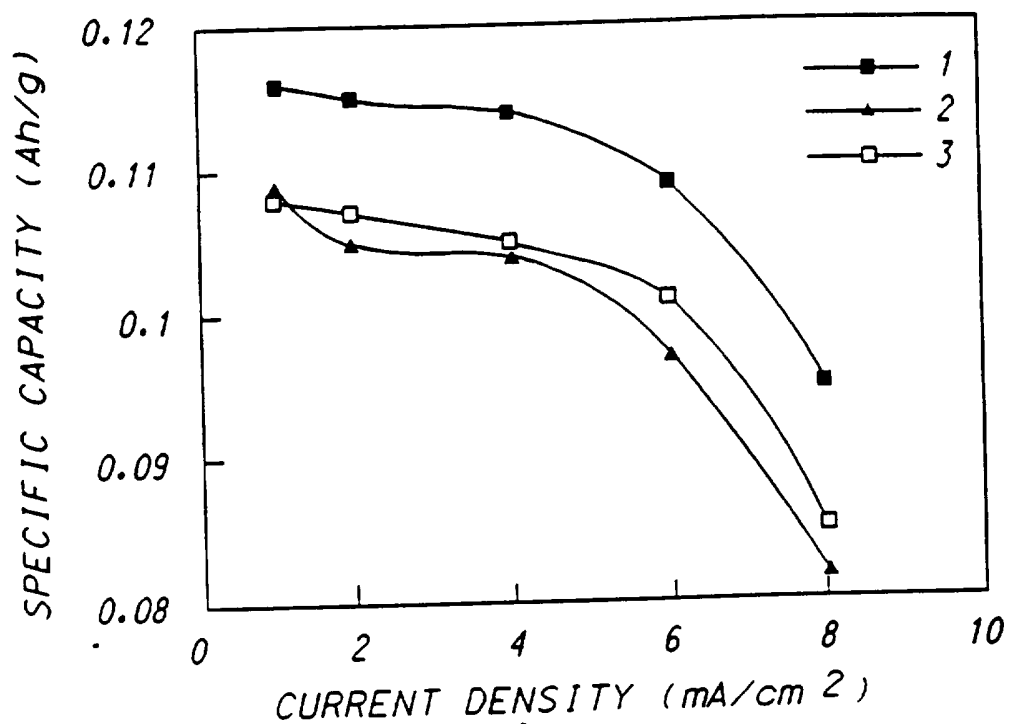


Fig. 5

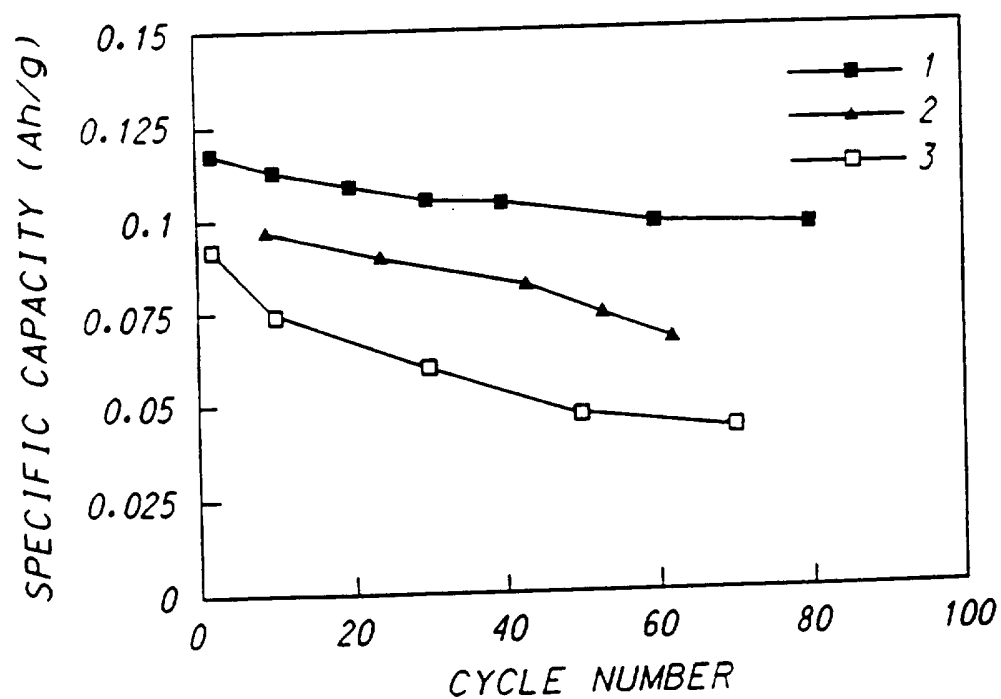


Fig. 6

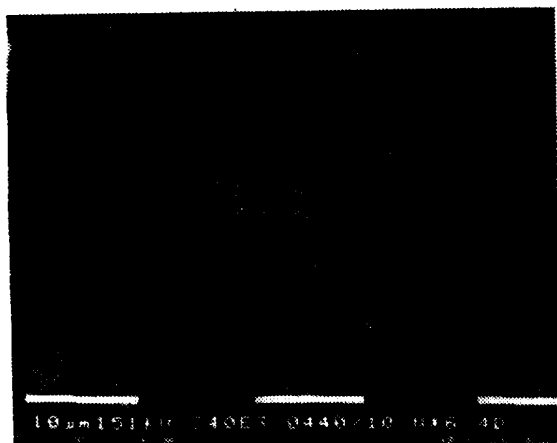


Fig. 7

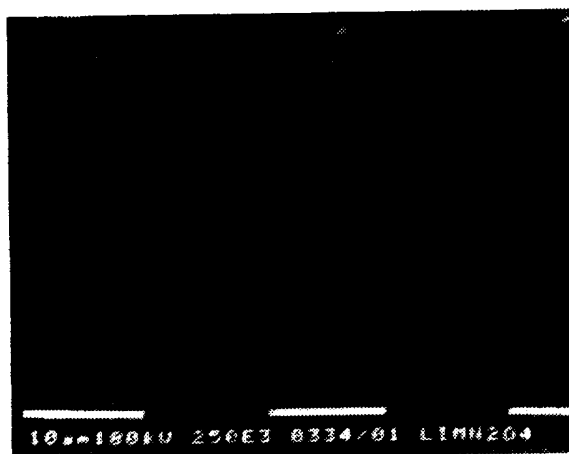


Fig. 8

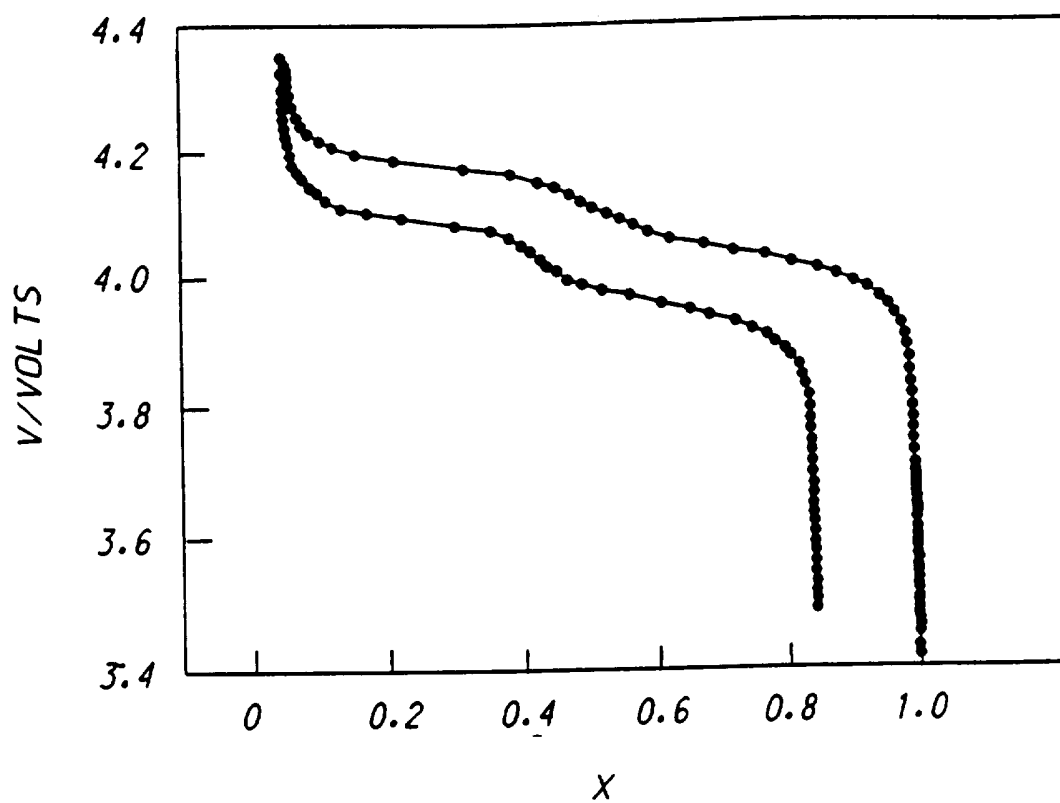


Fig. 9

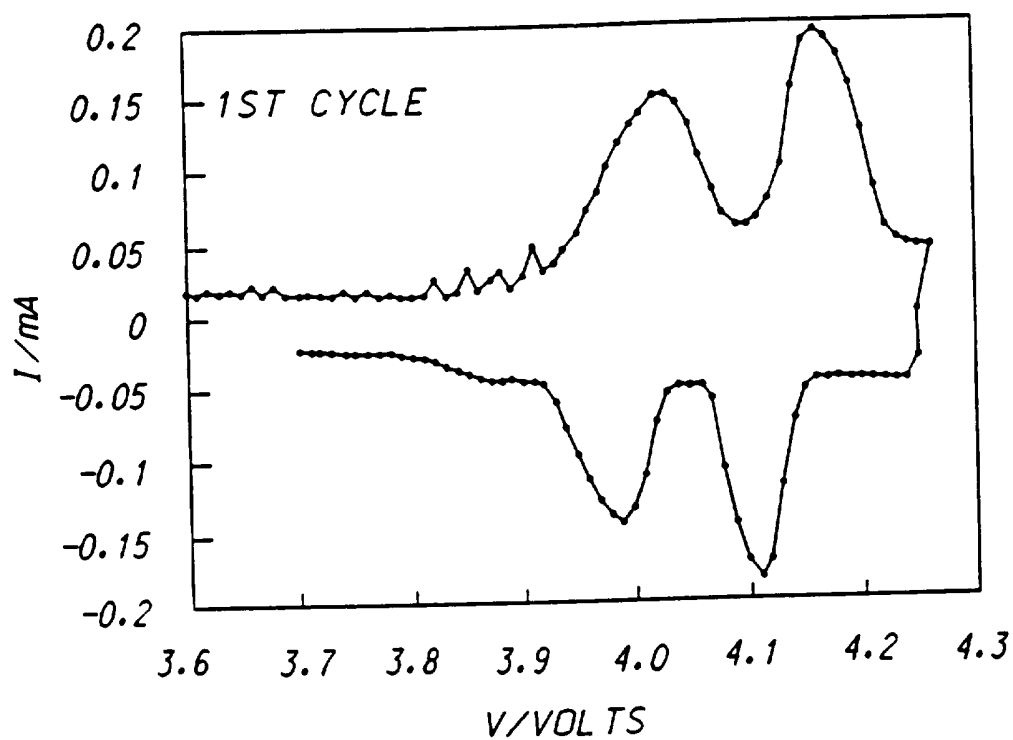


Fig. 10

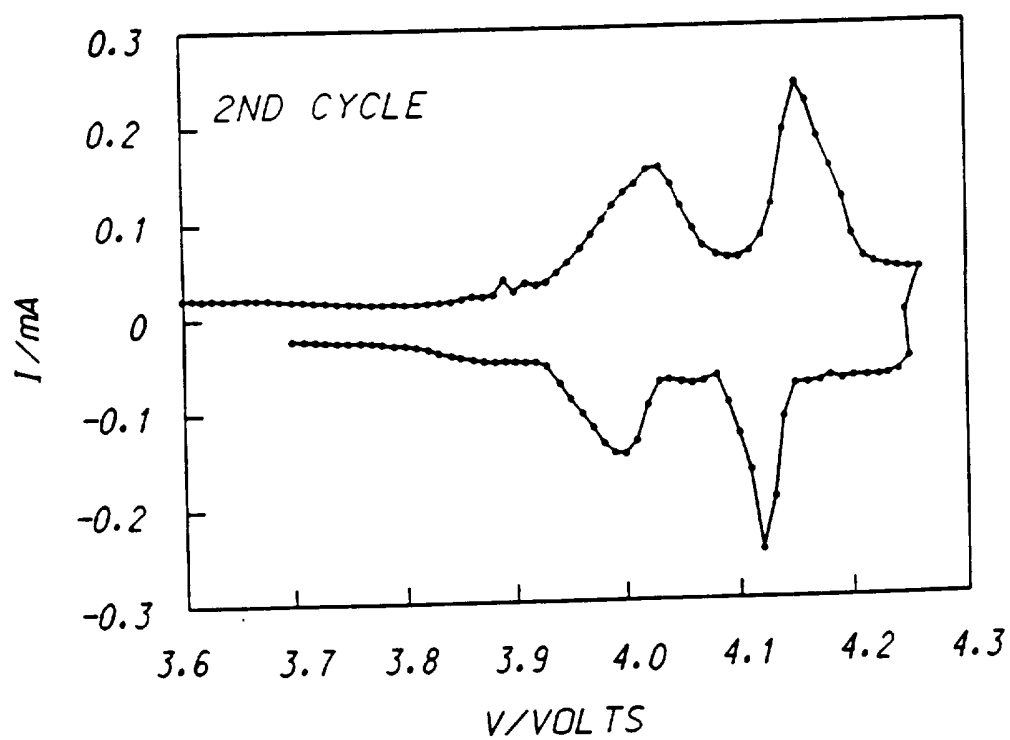


Fig. 11

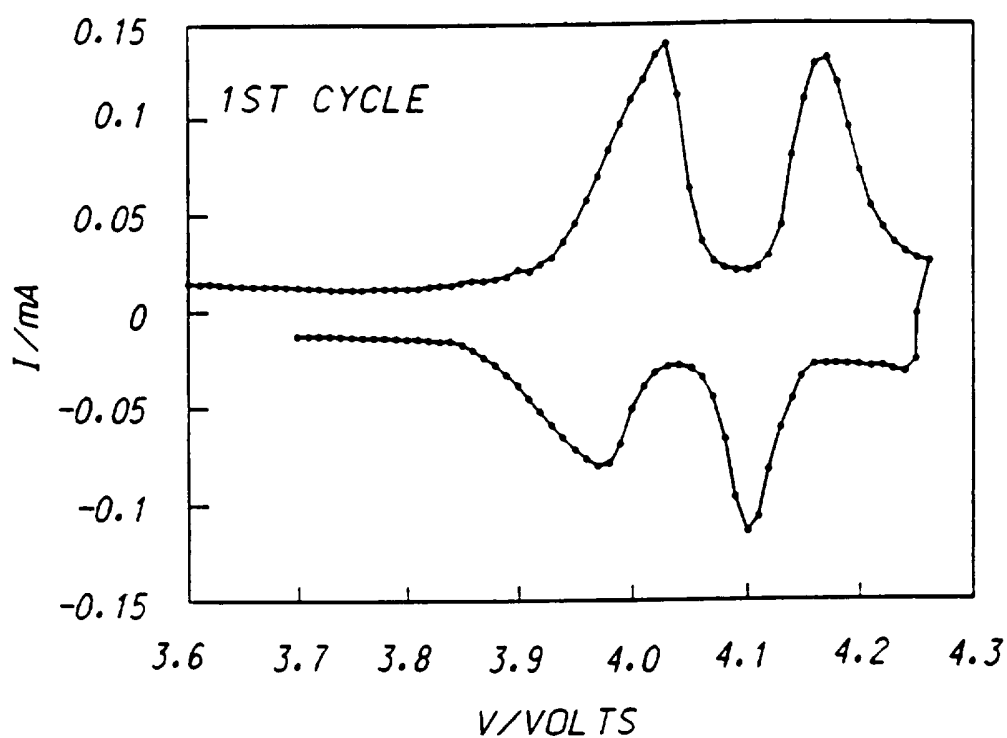


Fig. 12

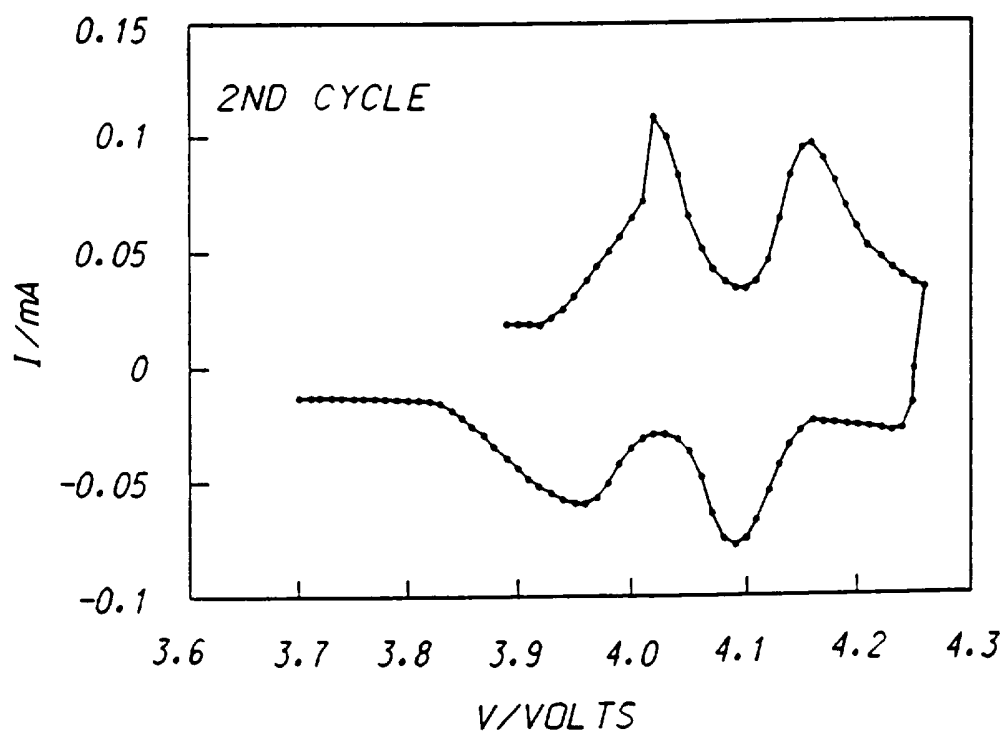


Fig. 13

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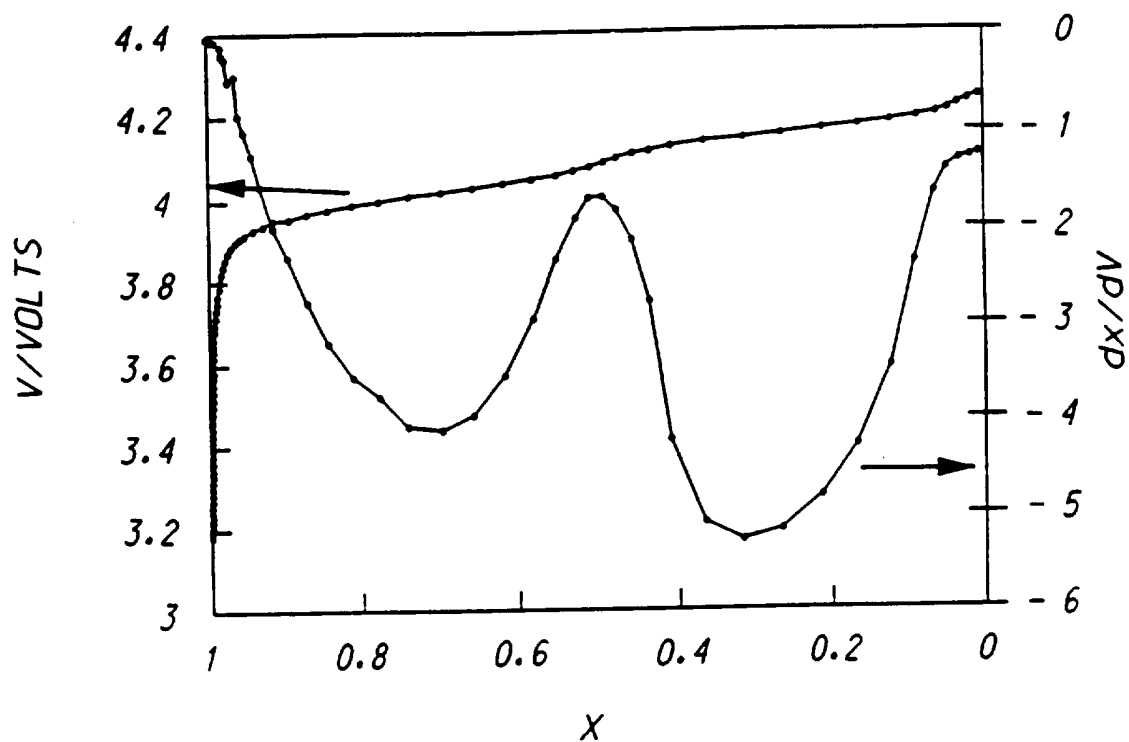


Fig. 14

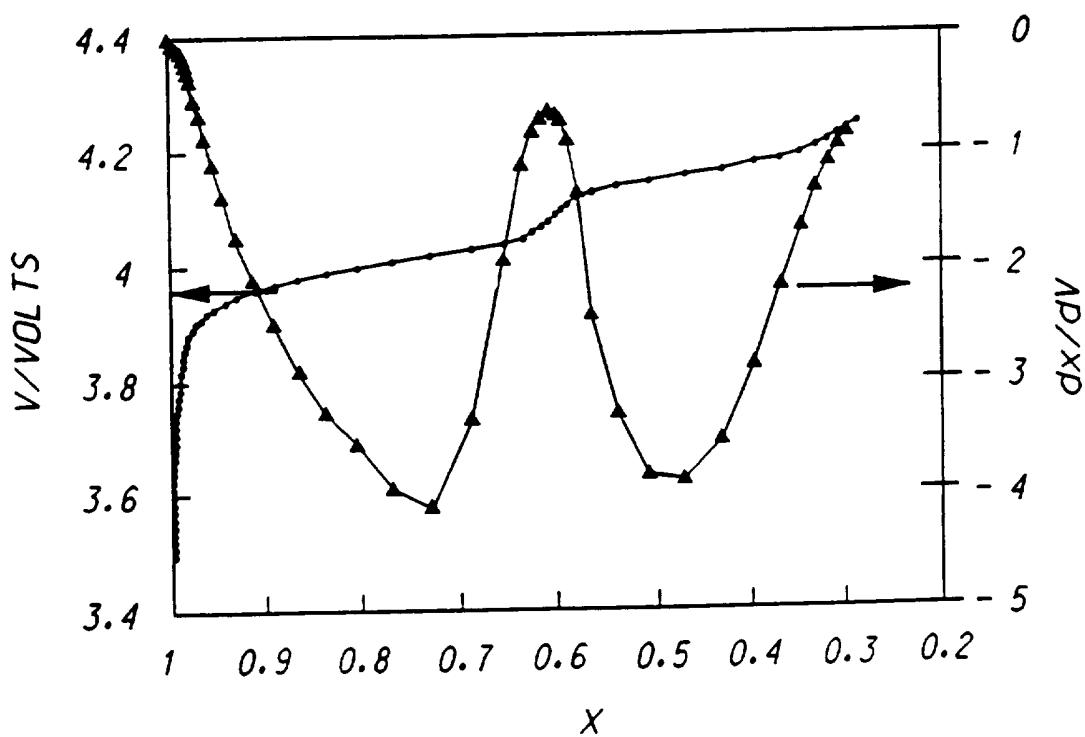


Fig. 15

INTERNATIONAL SEARCH REPORT

Inter. Appl. No.
PCT/US 95/13106

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C01G45/00 H01M4/50

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 C01G H01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 221 213 (CSIR) 31 January 1990 see the whole document ---	1,2
A	EP,A,0 413 313 (SANYO ELECTRIC CO) 20 February 1991 see page 4 ---	1,7
A	PATENT ABSTRACTS OF JAPAN vol. 018 no. 324 (E-1564) ,20 June 1994 & JP,A,06 076824 (NIPPONDENSO CO LTD) 18 March 1994, see abstract -----	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search

21 February 1996

Date of mailing of the international search report

6 March 1996 (6.03.96)

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter. Appl. Application No
PCT/US 95/13106

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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EP-A-413313	20-02-91	CA-A, C 2022898 DE-D- 69014168 DE-T- 69014168 US-A- 5294499 JP-A- 3250563	16-02-91 22-12-94 20-04-95 15-03-94 08-11-91