

APPARATUS AND METHOD FOR *IN SITU* X-RAY
STUDY OF ELECTROCHEMICAL CELLS

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BACKGROUND OF THE INVENTION

The present invention relates to an apparatus and method
10 for monitoring structural changes of an electrode in a
rechargeable battery, and, more particularly, to an apparatus
and method utilizing an *in situ* x-ray electrochemical cell
having rechargeable battery structure and orientation which
eliminates corrosion of the beryllium window of the x-ray cell.
15 Even more particularly, the invention relates to a rechargeable
battery structure for use in an *in situ* x-ray electrochemical
cell.

The battery-monitoring apparatus of the present invention
20 generally includes an electrolytic cell comprising polymeric
film composition electrodes and separator membranes. In
particular, the apparatus includes a rechargeable battery cell
comprising an intermediate separator element containing an
electrolyte solution through which ions from a source electrode
25 material move between cell electrodes during the charge/
discharge cycles of the cell. The invention is particularly
useful for studying the operation of such cells in which one or
both of the electrodes comprises a material capable of
intercalating mobile ions, e.g., of sodium, potassium, and
30 particularly lithium, and the separator membrane comprises a
polymeric matrix made ionically conductive by the incorporation

of an organic solution of a dissociable salt which provides ion mobility. Electrolytic battery cells of this type are generally described in U.S. Patent Nos. 5,192,629 and 5,296,318, the disclosures of which are incorporated herein by reference, and
5 in U.S. Pat. Application Ser. No. 08/160,018, filed 30 November 1993, each of which is assigned to the assignee of this application,

The rechargeable battery industry is rapidly promoting
10 the use of rechargeable Li-ion technology. In the Li-ion cell, the positive and negative electrodes comprise lithium intercalation compounds which can be viewed as host structures able to reversibly accept guest lithium ions. The structure of the host compound normally includes vacant sites which
15 determine the number of lithium ions that the material can reversibly accept. The more such vacant sites, the greater the capacity (ampere/gram) of a battery cell using such an intercalation electrode. Thus, it is important for researchers working in the rechargeable battery field to have means for
20 determining the factors limiting the number of lithium ions in an intercalation compound, for instance, the structural changes in the host material induced by intercalation or deintercalation of lithium during charge/discharge cycling.

25 With a technique that provides this information, one may monitor structural changes of intercalation materials as a function of voltage or electrode composition. Additionally, one may directly monitor the self-discharge mechanism within a battery cell, e.g., a LiMn_2O_4 /electrolyte/C Li-ion cell, caused
30 by the intercalation of lithium ions into the pure λ - MnO_2 phase. Such a technique may also be used to adjust the ratio of positive to negative electrode materials to ensure the optimum

composition and efficient operation of a Li-ion system, since continuously monitoring the lattice cell parameters of the positive and negative electrode permits one to know at any time and at any voltage the population of lithium ions in each
5 electrode. As a result, one can adjust the weight ratio of the electrodes in order for the positive electrode to be completely delithiated when the negative is fully lithiated.

An *in situ* x-ray diffraction apparatus and technique for
10 performing such studies have been described, for example, by Dahn et al., "In situ X-ray diffraction experiments on lithium intercalation compounds", *Can. J. Phys.*, 60 (1982), 307-313. A variation of *in situ* electrochemical x-ray study apparatus has also been described by Tarascon et al., "Electrochemical,
15 Structural, and Physical Properties of the Sodium Chevrel Phases $\text{Na}_x\text{Mo}_6\text{X}_{8-y}\text{I}_y$ ($X = \text{S}, \text{Se}$ and $y = 0$ to 2)", *J. Solid State Chem.*, 66 (1987), 204-224. In these prior procedures, where it is desired to study the effect of ion intercalation into an electrode material, the electrode layer is preferably disposed
20 as directly as possible in the path of incident x-radiation in order to obtain strong data responses and avoid diffraction data contamination by extraneous cell components. This end was readily accomplished in these earlier systems by placing the electrode layer upon or directly in contact with a beryllium
25 film serving the dual role of x-ray diffraction cell window and electrochemical cell current collector by means of which continuous cell cycling could be studied.

As the search for higher capacity and optimization of
30 electrode materials continues, intercalation compounds with high-voltage regions above about 4.3 volts are becoming more

important, since, for many layered intercalation materials, up to forty-five percent of the theoretical capacity lies in the region above this 4.3 volt threshold. Unfortunately, however, the study and analysis of these materials necessary for
5 improving capacity have not previously been available with an *in situ* x-ray electrochemical cell. A major problem, as described by Li et al., "In situ X-ray diffraction and electrochemical studies of $\text{Li}_{1-x}\text{NiO}_2$ ", *Solid State Ionics*, 67 (1993), 123-130, arises from the fact that, particularly when a
10 positive cell electrode layer under study is placed in contact with the diffraction cell window, the beryllium film suffers extreme corrosion at cycling potentials in excess of about 4.3 volts, thus severely limiting the utility of the apparatus.

15 Due to this limitation, the structural variations in these potentially useful intercalation materials could only be determined in isolation by delithiating a different sample at each voltage level in an operating cell cycle. Useful test results could only be obtained with great difficulty in this
20 manner and could seldom be correlated with any degree of reliability. The continuous, high-voltage method and apparatus of the present invention, however, have obviated these limitations and have enabled effective study and development of high capacity electrochemical cell electrode materials.

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SUMMARY OF THE INVENTION

30 The invention comprises an enclosed *in situ* x-ray electrochemical cell having an x-ray transmission window,



preferably of beryllium, and means for mounting an electrolytic cell within the enclosure in the path of incident x-radiation transmitted by the window while preventing contact between the window and a high-voltage electrode of the electrolytic cell.

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The invention also comprises an electrolytic cell structure in which a current collector element associated with an electrode, typically the higher voltage positive electrode, is situated away from the outer surface of the electrolytic cell, preferably being embedded at the electrode/separator interface in order to ensure that the electrode is disposed as an outermost element of the cell where it may receive unobstructed exposure to the incident x-radiation. The current collector element preferably extends beyond the perimeter of the overlying electrode to provide electrical continuity to an x-ray cell body terminal and permit the electrode to be separated from the beryllium window which could otherwise suffer destructive electrolytic corrosion.

20 A preferred *in situ* x-ray electrochemical cell of the present invention comprises a cell bottom member and a cell top member which has a beryllium window and is operatively attached to, yet electrically insulated from, the bottom member to form an enclosure within the cell. The invention further includes, 25 operatively situated in the enclosure between the cell bottom and top members, a polymeric rechargeable battery structure comprising an electrolyte/separator element disposed between positive and negative electrodes having electrical connection to terminals associated with the x-ray cell members. In order to 30 receive direct exposure to incident x-radiation, the battery is situated such that the electrode to be examined is facing the x-



ray cell window and, when that electrode constitutes the higher voltage positive element of the battery, is maintained at a distance therefrom by interposed spacing means.

5 The rechargeable battery structure normally also comprises at least one current collector element, typically disposed between the positive electrode and the separator element, through which electrical circuit is maintained between the electrode and the cell top member terminal. The current
10 collector is preferably formed of an electrically-conductive open-mesh grid in order to ensure ion mobility between the electrode and the electrolyte/separator element. The negative battery electrode is electrically connected to the cell bottom member terminal either directly, such as by contact with a
15 conductive bottom member, or through a second battery current collector element.

 In another embodiment, the x-ray cell also includes a beryllium window in the cell bottom member. The negative
20 electrode is situated to face this second window and, depending upon its electrical potential in the battery, either contacts or is spaced a distance from the window. In the latter arrangement, a second current collector formed of electrically-conductive open-mesh grid disposed between the negative
25 electrode and the separator element maintains electrical circuit with the cell bottom member terminal.

 A method in accordance with the present invention comprises the steps of providing an *in situ* x-ray electro-
30 chemical cell having at least one beryllium window in a cell enclosure member; mounting within the x-ray cell a rechargeable



battery comprising at least one outwardly-disposed electrode having a contiguous current collector element, the electrode facing toward and being separated from the beryllium window and the collector maintaining electrical circuit with an electrical terminal on the x-ray cell; directing x-radiation onto the electrode in reflective incidence through the window; and intercepting reflected x-radiation to obtain diffraction data. The method may alternatively include providing an *in situ* x-ray cell having two beryllium windows situated respectively in each of a cell top and bottom member; placing the outwardly-disposed positive battery electrode in spaced facing relationship with one window; placing the outwardly-disposed negative battery electrode in spaced facing relationship with the other window, the negative electrode maintaining electrical circuit with an electrical terminal on the x-ray cell by direct contact with the other window or through a contiguous current collector element; and selectively situating one or the other window in incident x-radiation to obtain diffraction data from one or the other of the electrodes.

A method in accordance with the present invention for preparing a battery structure to be used in the *in situ* x-ray cell comprises the steps of arranging, in sequence, a positive electrode element, an electrically-conductive open-mesh grid positive current collector element, a separator element, and a negative electrode element, and bonding the electrode and separator elements to adjacent such elements and to the contiguous collector by the application of heat and pressure to form a unitary flexible laminate structure. Alternatively, the positive electrode element and collector element may be so bonded prior to arranging and bonding the balance of the



structure elements. The method further comprises including an ion-conductive electrolyte in at least the separator element to form an active electrolytic battery. In a preferred embodiment, the method comprises forming each of the electrodes and
5 separator element as a flexible, self-supporting, film of polymeric composition comprising a compatible organic plasticizer, and, subsequent to bonding, replacing at least a portion of the plasticizer with a solution of ion-conductive electrolyte.

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An advantage of the present invention is its simplicity, which ensures that the beryllium window does not experience the corrosion problems of the related art. Another advantage is that the apparatus and method for monitoring structural changes
15 in a rechargeable battery may be used to analyze both the positive and negative electrodes.

BRIEF DESCRIPTION OF THE DRAWING

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The present invention will be described with reference to the accompanying drawing of which:

25 FIG. 1 is a perspective view, in partial section, of a typical laminated Li-ion battery cell structure;

FIG. 2 is an exploded perspective view of an apparatus in accordance with a preferred embodiment of the present invention
30 for monitoring structural changes in a battery;



FIG. 3 is a partial cross-sectional view taken along line 3-3 of FIG. 2 showing the cell top, spacer, and battery;

FIG. 4 is an exploded perspective view of a battery structure in accordance with one embodiment of the invention;

FIG. 5 is an exploded perspective view of another embodiment of a battery structure in accordance with one embodiment of the invention;

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FIG. 6 is an exploded perspective view of yet another embodiment of a battery structure;

FIG. 7 is an exploded perspective view of a further embodiment of a battery structure;

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FIG. 8 is an exploded perspective view of another embodiment of a battery structure;

FIG. 9 is an exploded perspective view of yet a further embodiment of a battery structure;

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FIG. 10 is an exploded perspective view of an apparatus in accordance with another preferred embodiment of the present invention for monitoring structural changes in a battery;

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FIG. 11 is a graph showing experimental results derived from using one embodiment of the present invention;

FIG. 12 is a graph showing additional experimental results derived from using one embodiment of the present

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invention;

FIG. 13 is a graph showing further experimental results derived from using one embodiment of the present invention;

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FIG. 14 is a graph showing a-axis parameter experimental results derived from using one embodiment of the present invention; and

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FIG. 15 is a graph showing c-axis parameter experimental results derived from using one embodiment of the present invention.

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DESCRIPTION OF THE INVENTION

FIG. 1 illustrates a laminated rechargeable battery cell structure of the type currently under development in the industry. This typical Li-ion cell structure comprises a negative current collector 11 of copper foil or grid upon which is laid a negative electrode membrane 13 comprising an intercalatable material, such as carbon or graphite, or a low-voltage lithium insertion compound, such as WO_2 , MoO_2 , or Al, dispersed in a plasticized polymeric binder matrix. An electrolyte/separator membrane 15, e.g., a plasticized VdF:HFP copolymer film, is positioned upon electrode element 15 and is covered with a positive electrode membrane 17 comprising a composition of a finely-divided lithium intercalation compound, such as LiMn_2O_4 , LiCoO_2 , or LiNiO_2 , in a similar polymeric binder matrix. An positive current collector 28 of aluminum foil or

grid completes the assembly, which is then pressed between platens (not shown) under heat and pressure to soften and bond the polymeric components and laminate the membrane layers and collector elements. Prior to use, the battery is activated by
5 extracting at least a portion of the plasticizer with a selective solvent that does not affect the polymer and replacing the plasticizer with a solution of lithium salt electrolyte, or simply by displacing the portion of plasticizer by contact with the electrolyte solution. Useful electrolyte
10 solution compositions include those described in the incorporated patent disclosures, particularly such compositions as LiPF_6 and mixtures with LiBF_4 dissolved in mixtures of ethylene carbonate and dimethyl carbonate.

15 Separator membrane element 15 is generally prepared from a composition comprising a flexible polymer, e.g., a copolymer of 75 to 92% vinylidene fluoride:8 to 25% hexafluoropropylene (available commercially from Atochem North America as Kynar FLEX), and a compatible organic plasticizer. Such a polymeric
20 composition is also preferred for the preparation of the electrode membrane elements, since subsequent laminate interface compatibility is ensured. The plasticizer may be one of the various organic compounds commonly used as solvents for electrolyte salts, e.g., propylene carbonate or ethylene
25 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.

30 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. Other organic polymers and copolymers may be used for the battery electrode and/or the separator. These
5 may be selected from polymers and copolymers such as vinyl chloride, acrylonitrile, vinyl chloride and vinylidene chloride, vinyl chloride and acrylonitrile, vinylidene fluoride, vinylidene fluoride with hexafluoropropylene, and vinylidene fluoride with hexafluoropropylene and an additional
10 component selected from vinyl fluoride, tetrafluoroethylene, and trifluoroethylene.

Any common procedure for casting or forming films or membranes of polymer compositions may be employed in the
15 preparation of these membrane materials. Where casting or coating of a fluid composition is used, e.g., with meter bar or doctor blade apparatus, the viscosity of the composition will normally be reduced by the addition of a readily evaporated casting solvent, such as tetrahydrofuran (THF), acetone, or the
20 like. Such coatings are normally air-dried at moderate temperature to yield self-supporting films of homogeneous, plasticized polymer compositions. A membrane material, particularly for use as a separator element, may also be formed by allowing the polymer in commercial form, i.e., bead or
25 powder, to swell in a proportionate amount of plasticizer and then pressing the swollen mass between heated (e.g., about 130°C) plates or rollers, or extruding the mixture.

The aluminum grid on the positive electrode, or cathode,
30 of the above-described battery cell structure could be used as the positive current collector of an in situ x-ray

electrochemical cell in place of the beryllium window typically used for this purpose. However, in doing so, the x-ray scattering due to aluminum prevents a useful arrangement, because too much of the cathode will be hidden by the aluminum grid. The aluminum causes Bragg peaks in the powder x-ray diffractogram which would greatly obscure the desired data of the electrode material under examination. Thus, such use of the usual rechargeable battery cell structure does not solve the problem of beryllium window corrosion within an *in situ* x-ray electrochemical cell. In order to ensure that a beryllium window of an x-ray cell does not experience corrosion causing potentials, the present invention provides an air gap between the window and the cathode layer of a battery cell structure and provides the necessary current collector within the battery itself.

An exemplary embodiment of an *in situ* x-ray cell useful in the present invention is similar to that described in the above-referenced paper by Tarascon et al. and is shown here in FIG. 2. The cell 30 comprises a cell bottom member 32 and a cell top member 34, generally of metal, operatively connected by means of screws 40 to form an enclosure to accommodate an electrolytic battery element 43, such as described later with respect to FIG. 4. Cell top member 34 has a beryllium window 36 to permit x-rays, indicated by arrows A, to enter and exit the x-ray cell 30. A polyethylene gasket 38 electrically separates top member 34 from bottom member 32, and plastic sleeves 42 maintain the electrical insulation when conductive screws 40 are used. The cell members 32, 34 have respective electrical terminals 52, 54 to provide electrical access to battery electrodes, as later described.

A battery 43 is placed in the enclosure of x-ray cell 30 between members 32, 34. To ensure a gap between the high voltage terminal of battery 43 and the beryllium window 36, a spacer 46 may be inserted between member 34 and battery 43. The spacer 46 is preferably made of 420 or 430 stainless steel. A copper block 48 may be used to electrically connect the cell bottom 32 to the battery 43. Where necessary, springs 50 may be included to apply pressure to the electrochemical x-ray cell elements. X-ray cell 30 further includes an off-axis adjustment screw 56 and cell aligner pins 58 associated with a nylon holder attachment 60 typically provided with the basic x-ray equipment, e.g, a Rigaku Miniflex diffractometer.

FIG. 3 shows a partial cross-section of FIG. 2 taken along line 3-3 and better illustrates a gap 62 between the beryllium window 36 and the battery 43 created by a spacer 46 and cell top member 34. It is this gap between the battery 43 and the beryllium window 36 which ensures that there is no contact between the positive battery electrode and beryllium window 36 at a potential which causes corrosion. The elimination of such contact with the beryllium window permits the continuous monitoring of the battery electrodes at various stages of charge and discharge.

FIGs. 4-7 show various embodiments of the rechargeable battery for use in an *in situ* x-ray electrochemical cell in accordance with the present invention. Each of the depicted battery structures include a positive electrode 64, a negative electrode 66, and an electrolyte/separator element 68 disposed between the positive and negative electrodes 64, 66. Electrolytic cell electrode and separator elements illustrated

in FIGs. 4-7 preferably utilize polymeric materials comprising a composition of poly (vinylidene fluoride) copolymer matrix and a compatible organic plasticizer which maintains a homogeneous composition in the form of a flexible, self-supporting film.

FIG. 4 depicts a positive current collector element 70 formed of an electrically-conductive open-mesh grid disposed between positive electrode 64 and separator element 68. Current collector element 70 is preferably made of aluminum and has a perimeter larger than that of positive electrode 64 so as to come into contact with the spacer 46. A second, negative current collector 72, preferably of an electrically conductive copper foil or grid, is placed beneath negative electrode 66 so as to ensure effective electrical contact with copper block 48 of the *in situ* x-ray electrochemical cell depicted in FIG. 2.

In the embodiment of FIG. 4, the rechargeable battery structure 43 is configured according to the invention by means of the lamination of electrode and electrolyte/separator cell elements which are individually prepared, by coating, extrusion, or otherwise, from compositions comprising the noted PVdF copolymer materials. For example, in the construction of a lithium-ion battery, a negative electrode membrane 66 formed as a layer of a powdered carbon dispersion in the polymeric matrix is overlaid upon a copper current collector foil 72. An electrolyte/separator membrane 68 formed as a layer of a composition comprising the described VdF:HFP copolymer and a compatible plasticizer is then overlaid upon negative electrode 66. A positive current collector 70 of open-mesh aluminum grid is overlaid upon separator 68 and the positive electrode

membrane 64 separately prepared as a layer of a dispersion of intercalation electrode composition, e.g., a LiMn_2O_4 powder in the copolymer matrix, is overlaid upon collector 70 to complete the cell assembly. This assembly is then heated under pressure to bond the plasticized copolymer matrix components and the collector grids to thereby effect the lamination of the cell elements into a unitary flexible battery cell structure. The grid structure of positive current collector 70 allows effective ion-conducting, bonded contact between positive electrode layer 64 and electrolyte/separator membrane 68, the collector grid 70 being thereby, in effect, embedded in the laminate structure at the interface of layers 64, 68. Battery 43 is thereafter activated with electrolyte solution prior to mounted in cell 30.

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As shown generally in FIG. 5, an alternative battery structure 53 for an x-ray cell is depicted without the negative current collector 72 of FIG. 4. In use, the negative electrode 66 electrically contacts the cell bottom 32 (FIG. 2) either directly or indirectly, such as through the copper block 48. A preferred use for the battery of FIG. 5 will be discussed below with reference to FIG. 10.

FIG. 6 illustrates a battery cell 63 adapted for examination of negative electrode materials. A negative open-mesh current collector grid 72, typically of copper, is disposed between negative electrode 66 and separator element 68 with electrode 66 facing and spaced from the window of the x-ray cell of FIG. 2. This configuration allows a researcher to study the negative electrode 66 and maintain a gap between the beryllium window 36 and the negative electrode 66 so as to

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prevent any corrosion of the window which might result from excessive electrical potential. The contact block 48 of the x-ray cell would preferably be fashioned of 420 or 430 stainless steel to avoid corrosion of a copper block by positive electrode 64.

FIG. 7 depicts a battery structure 73 having two open-mesh current collectors, the first of aluminum 70 disposed between the positive electrode 64 and separator 68, and the other of copper 72 disposed between the negative electrode 66 and separator 68. As shown, the perimeter of separator 68 extends sufficiently beyond those of collectors 70, 72 to provide effective electrical insulation of the two. This configuration is utilized in an *in situ* x-ray cell as shown in FIG. 10 which allows for the analysis of both the positive and negative electrodes through a beryllium window located in each of cell members 32, 34.

FIG. 8 depicts a battery structure 83 consisting essentially of positive electrode 64, negative electrode 66, and separator 68 disposed between the two electrodes. This is an extreme design for a rechargeable battery member of an x-ray cell, however, in which positive electrode 64 would be spaced from the beryllium window and contact the spacer 46 or cell top 34 to serve as both the electrode and current collector, although the electrical conductivity would be less than that achieved with an aluminum current collector grid.

FIG. 9 depicts a battery variant 93 in which separator 68 is disposed between positive electrode 64 and negative electrode 66 and a negative current collector 72 contacts

negative electrode 66 on the opposite side from that of separator 68.

FIG. 10 depicts an *in situ* x-ray electrochemical cell 33 which is similar to that shown in FIG. 2, except that the cell bottom member 32 provides a second beryllium window 37 to allow for the alternate monitoring of both the positive electrode 64 and the negative electrode 66 of a battery member. X-rays beams are thus permitted, upon rotation of the cell, to enter and exit the respective window exposing the positive or negative electrode. For use in x-ray cell 33, the preferred Li-ion battery may be as simply depicted in FIG. 5, since the negative electrode 66 which remains below about 3 volts in a Li-ion cell can be placed directly onto beryllium window 37 which can serve as current collector without risk of corrosion. Determining the voltage of a particular electrode allows one to determine when to use a battery member with an electrode, separator, and grid configuration that provides for maintaining a gap between the beryllium window and the electrode, and when one may simply place the electrode directly upon the beryllium window itself.

An x-ray cell 30 of FIG. 2, or 33 of FIG. 10, is preferably assembled with an activated rechargeable battery in a helium-filled dry box, then placed in an x-ray diffractometer to perform the analysis experiment. In the diffractometer, the x-ray cell is aligned by means of a screw 56 which moves back and forth along the cell aligner pins 58. In addition, the x-ray cell 33 of FIG. 10 can be rotated 180° using the diffractometer Phi to expose one and the other of the electrodes of the battery to incident x-radiation at any time during charge/discharge cycling.

To ensure that each respective electrode 64, 66 is aligned correctly upon rotation of x-ray cell 33, an adjustable out-of-center rotation is used. Since, in FIG. 5 for example, current collector 70 is embedded in battery 53 and a negative collector is not included, the battery will only be a few hundred micrometres thick, e.g., 300-400 μm . Thus, if the positive electrode 64 is in perfect x-plane alignment, the negative electrode 66 will only be a few hundred μm off in the alignment after x-ray cell 33 is rotated. This will have moderate effect on the peak data intensities, but the shift in these spacings can easily be corrected by an off-axis adjustment. For instance, if the battery is 300 μm thick and the positive electrode is in perfect alignment, rotation would result in a 300 μm off-axis for the negative electrode. Thus, the positive electrode is adjusted to be 150 μm off-axis in order that rotation results in the negative electrode being likewise only 150 μm off-axis.

The assembled x-ray cell may be mounted on any suitable diffractometer, e.g., a system commercially available from Rigaku or Scintag. The positive and negative terminals 52, 54 which are maintained in electrical continuity with battery electrodes 64, 66 are connected to a battery cycler that is driven by a computer for controlled charge and discharge of the battery. Measurement data of the x-ray diffraction patterns are collected within the range of $10 < 2\theta < 90$ while the cell is charged and discharged at a constant current. Usually a current of 140 μA is used and x-ray diffraction data are automatically collected when x in $\text{Li}_x\text{Mn}_2\text{O}_4$ changes by about 0.02. Therefore, more than 50 x-ray powder diffractograms may be collected for a single charge cycle. The same may be done during discharge. The

current rate is maintained low in order to maintain nearly equilibrium conditions and detect small structural changes.

The results of studies utilizing the present invention are illustrated in the graphs of FIGs. 11-15. It may be noted in the x-ray diffraction patterns of FIG.s 11-12 that the structure of a final delithiation product, λ - MnO_2 , is influenced significantly by the manner in which the starting LiMn_2O_4 material was synthesized, e.g., whether during an annealing operation it was low cooled or quenched, as indicated in FIGs. 11 and 12, respectively.

The effective performance of the *in situ* x-ray cell with other electrode materials can be seen in the diffraction patterns of various CoO_2 compounds, as depicted in FIG. 13. Utilizing the present x-ray cell, voltages were raised up to 5 volts to achieve, without difficulty, compound phases, e.g., of CoO_2 , which had previously been unattained. FIGs. 14-15 show graphically the results of accumulated test data from which are determined the variations of the crystallographic a- and c-axis parameters as a function of the amount of intercalated lithium in a hexagonal LiCoO_2 positive electrode material. While the preferred embodiments of the battery structure have centered on rechargeable Li-ion batteries, it is also well within the scope of the present invention to implement this design with other rechargeable batteries, as well, including aqueous systems.

With the increasing importance of the rechargeable Li-ion technology, it is anticipated that any battery manufacturers or research labs searching for new intercalation electrodes will find this type of research tool to be invaluable. The use of an

in situ x-ray electrochemical cell with a specially designed rechargeable battery structure which does not corrode the beryllium window is, among other things, an excellent research tool for obtaining the best cathode, anode, or polymeric component materials. Additionally, research generated from such tests provides ways to characterize final materials used in commercial rechargeable batteries.

While there has been illustrated and described what is at present considered to be a preferred embodiment of the present invention, it will understood by those skilled in the art that various changes and modifications may be made, and equivalents may be substituted without departing from the true scope of the invention. Therefore, it is intended that this invention not be limited to the particular embodiment disclosed herein, but that the invention include all embodiments falling within the scope of the appended claims.

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This Sheet Has Been Replaced



What is claimed is:



1. Apparatus for *in situ* x-ray study of an electrochemical
5 cell which comprises an electrochemical cell comprising a
positive electrode, a negative electrode, and an interposed
separator element in contact with said electrodes; means
enclosing said electrochemical cell comprising first and second
opposed electrically-conductive members electrically isolated
10 from one another and respectively providing positive and
negative electrical terminals, which means includes at least
one window element for transmission of x-radiation to incidence
upon said cell; and means mounting said electrochemical cell in
the path of incident x-radiation and comprising means for
15 electrically connecting said positive electrode to said first
conductive member and said negative electrode to said second
conductive member

c h a r a c t e r i z e d i n t h a t

- 20 a) said electrochemical cell comprises a current collector
element in contact with the first of said electrodes and
situated away from the outer surface of said electrode;
b) said electrochemical cell is disposed in said mounting
means to present said outer electrode surface to x-radiation
transmitted by said window element; and
25 c) said mounting means comprises means for maintaining said
cell surface spaced from and out of contact with said window
element.



2. Apparatus according to claim 1 wherein said collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, said first electrode and said separator element.

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3. Apparatus according to claim 2 wherein said collector element comprises an electrically-conductive open-mesh grid.

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4. Apparatus according to claim 2 wherein said collector element is in electrical circuit with one of said opposed conductive member terminals.

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5. Apparatus according to claim 2 wherein said first electrode is the positive electrode of said electrochemical cell.

20 6. Apparatus according to claim 1

characterized in that said enclosing means includes a second window element situated to transmit x-radiation to incidence upon the outer surface of the other electrode.

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7. Apparatus according to claim 6 wherein said electrochemical cell further comprises a second current collector element in contact with said other electrode and in electrical circuit with the respective one of said opposed conductive member terminals.

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8. Apparatus according to claim 7 wherein said second collector element is an electrically-conductive open-mesh grid disposed substantially at the interface between said other electrode and said separator element.

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9. A method for monitoring structural changes in electrode materials of a rechargeable battery during operation which comprises providing an in situ x-ray electrochemical cell
10 having at least one beryllium window element in a cell enclosure member, mounting within the x-ray cell a rechargeable battery comprising at least one outwardly-disposed subject electrode facing toward the window, directing x-radiation onto the subject electrode in reflective incidence through the window,
15 and intercepting reflected x-radiation to obtain diffraction data

c h a r a c t e r i z e d i n t h a t
said battery is mounted so as to situate said subject electrode out of contact with said window element, thereby preventing
20 electrolytic corrosion of said window element otherwise occurring at the electrical potential of said electrode.

10. A method according to claim 9 which comprises interposing a
25 spacer element between said subject electrode and said window element to so situate said electrode.

11. A method according to claim 9 wherein said battery
30 comprises a positive electrode, a negative electrode, and an interposed separator element in contact with said electrodes,



and wherein said cell enclosure comprises first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals

5 c h a r a c t e r i z e d i n t h a t

a) a current collector element is positioned in contact with said subject electrode and is situated away from the outer surface of said electrode; and

b) said collector element is connected in electrical
10 circuit with one of said electrical terminals.

12. A method according to claim 11 wherein said positive battery electrode is selected as said subject electrode and
15 said collector element is connected in circuit with said positive terminal.

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This Sheet Has Been Replaced



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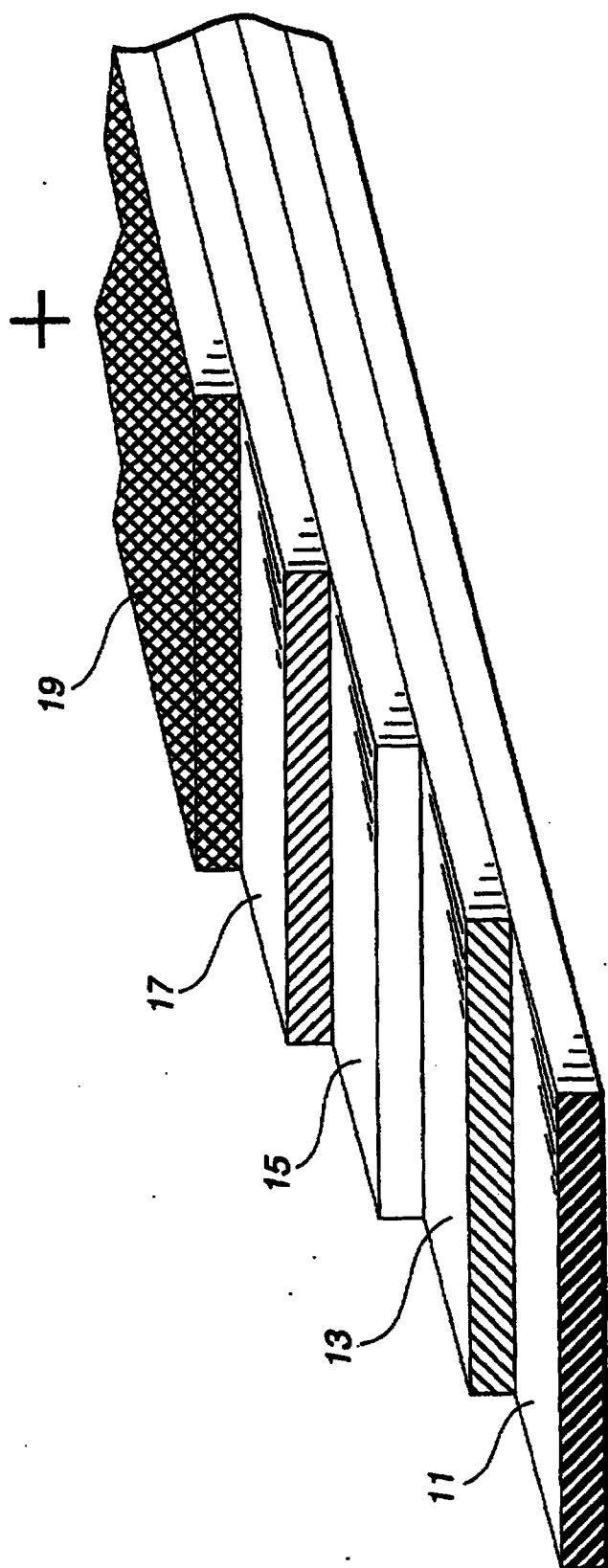


FIG. 1

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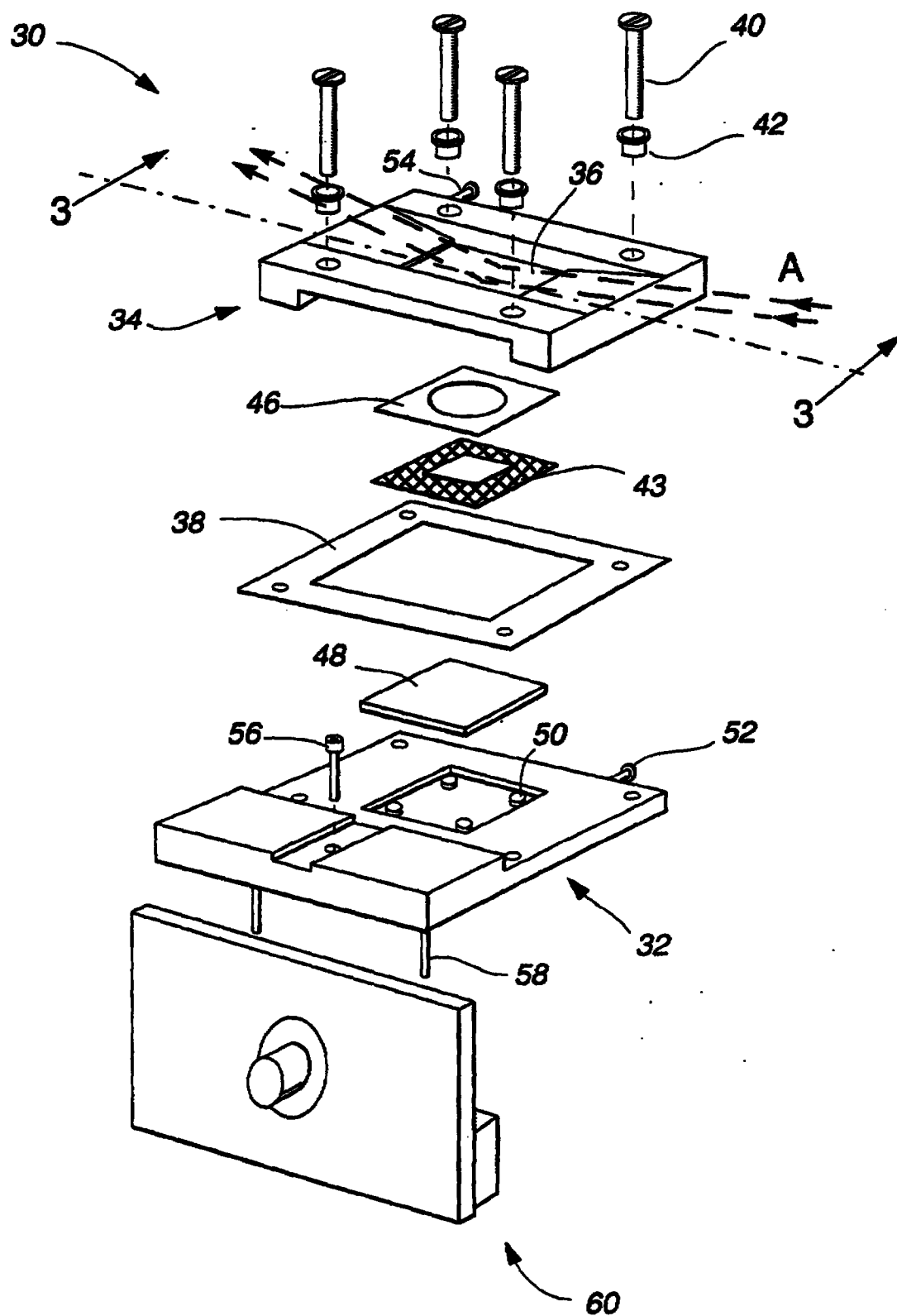


FIG. 2

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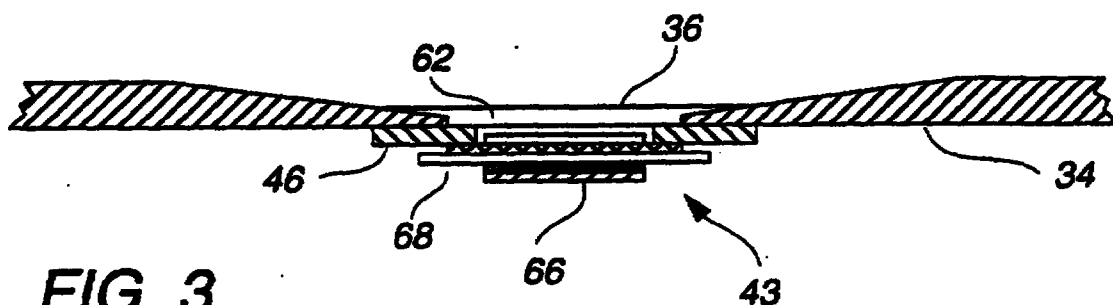


FIG. 3

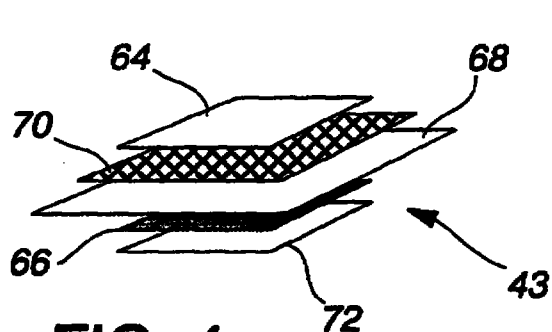


FIG. 4

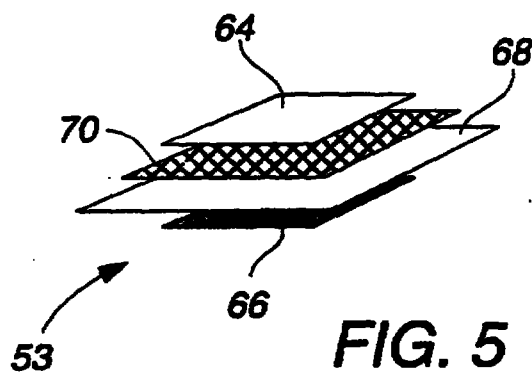


FIG. 5

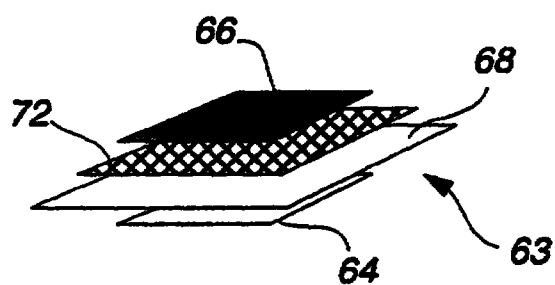


FIG. 6

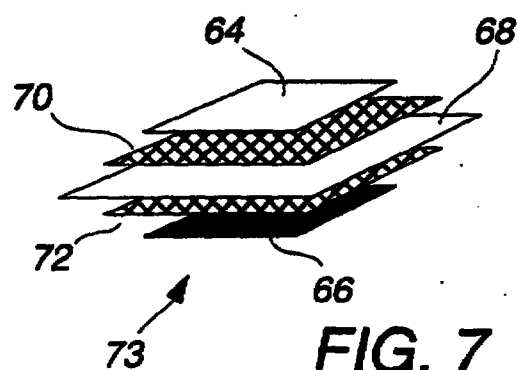


FIG. 7

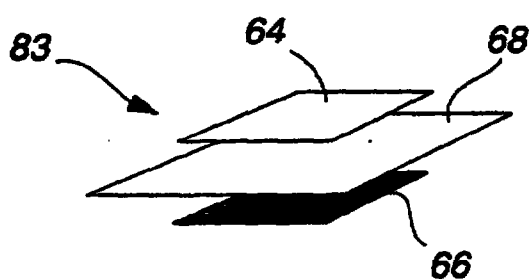


FIG. 8

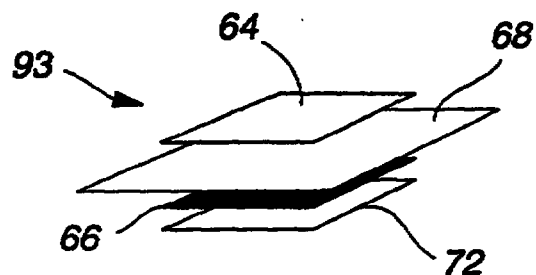


FIG. 9

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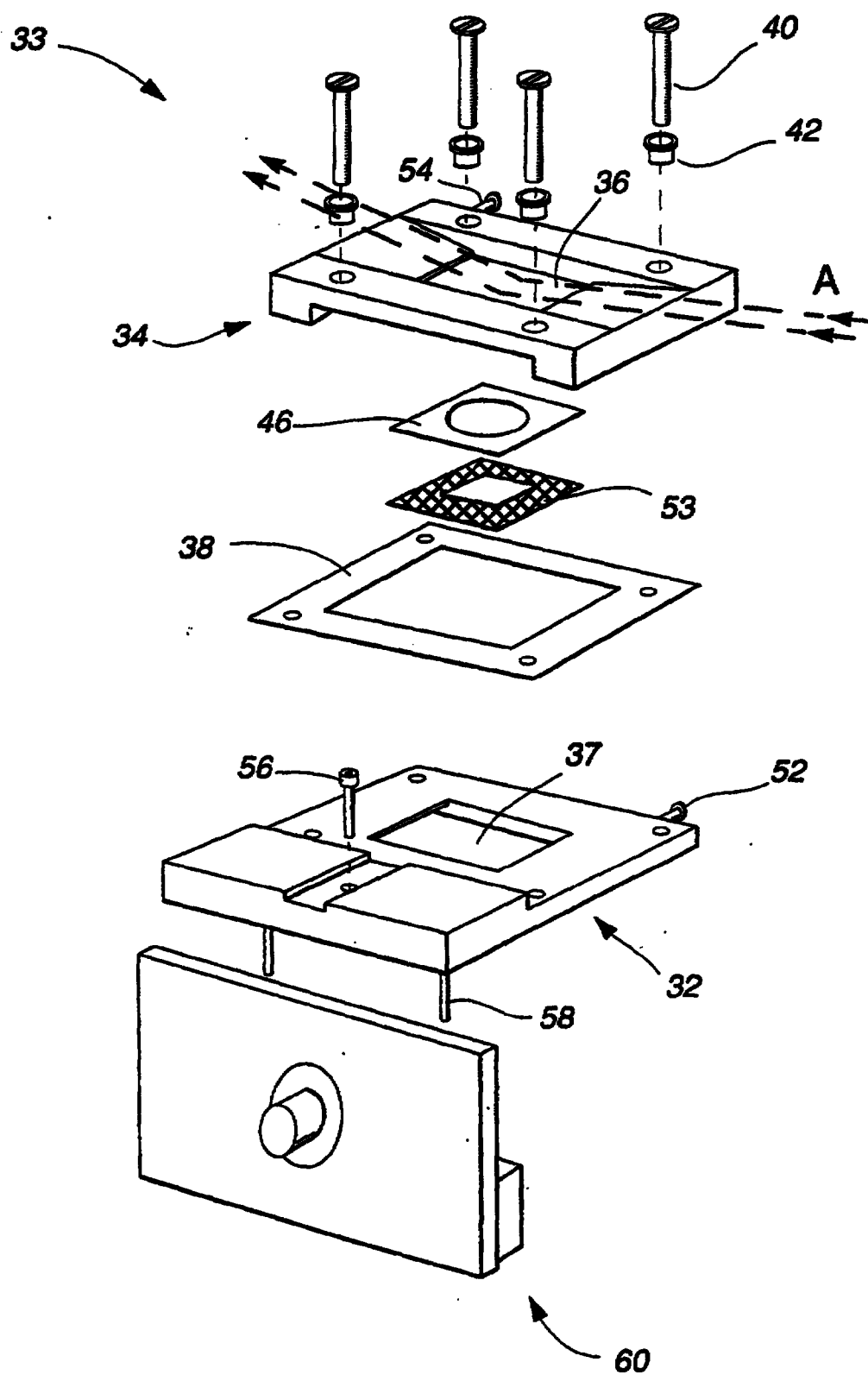


FIG. 10

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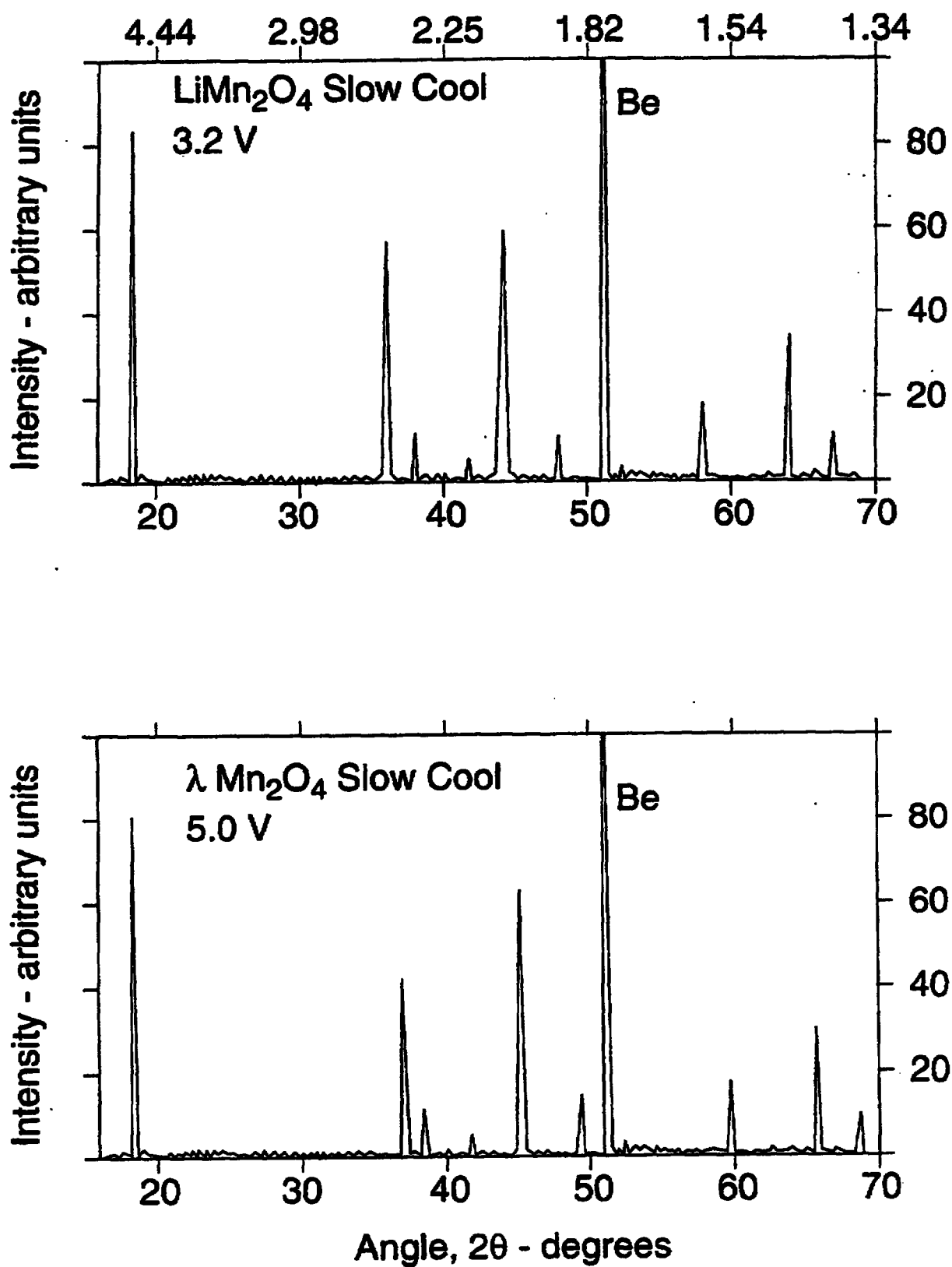


FIG. 11

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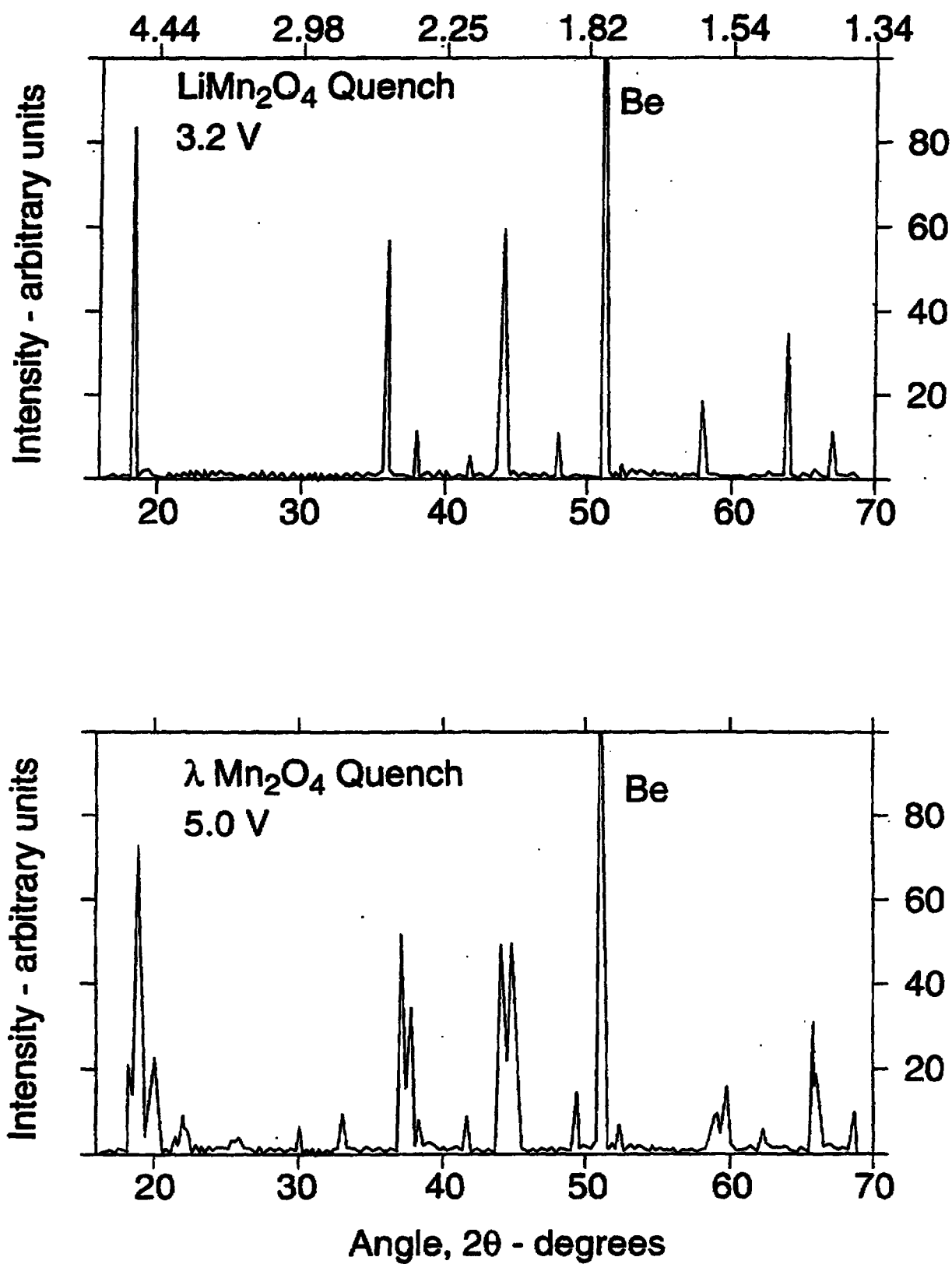


FIG. 12

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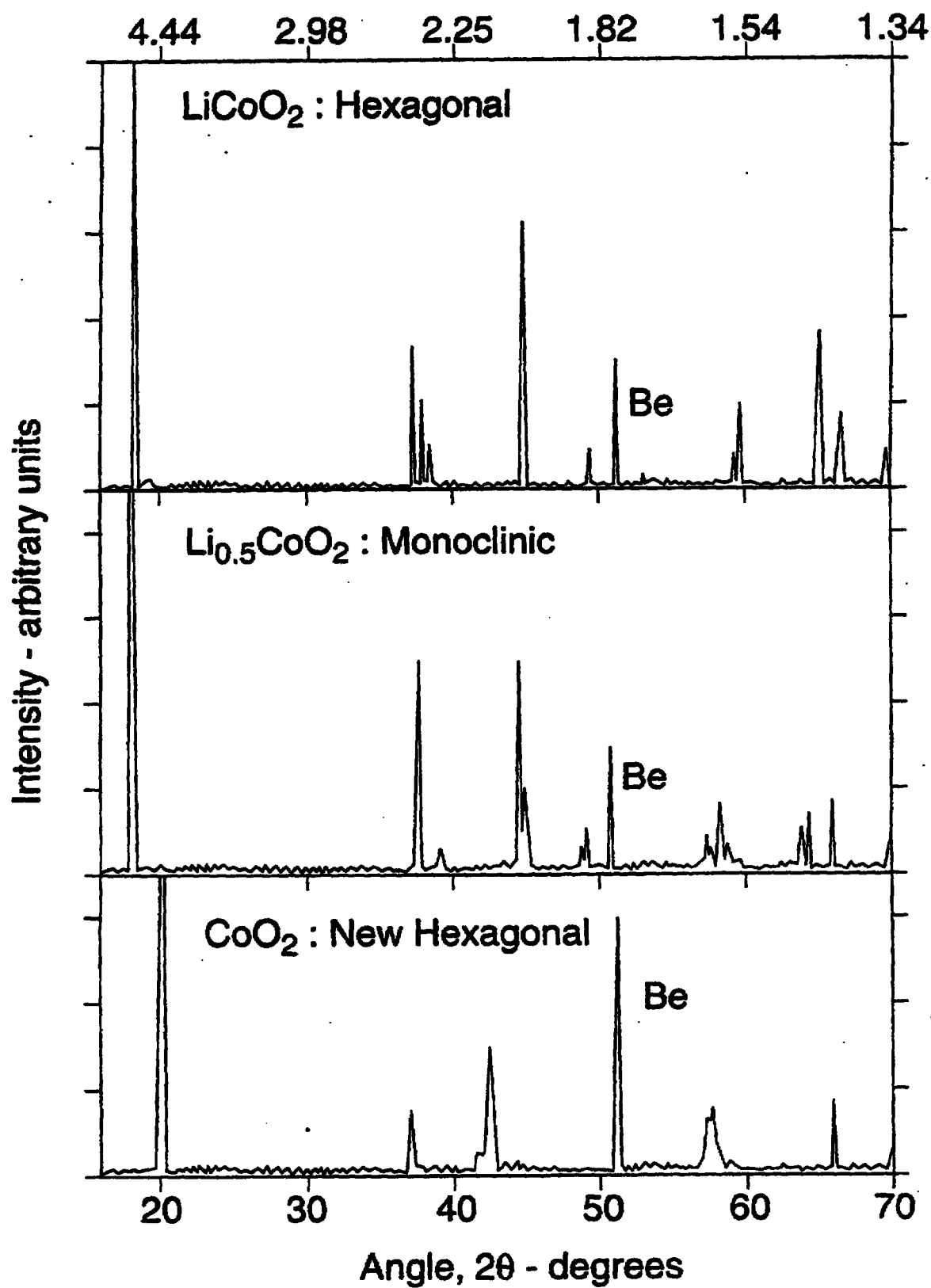


FIG. 13

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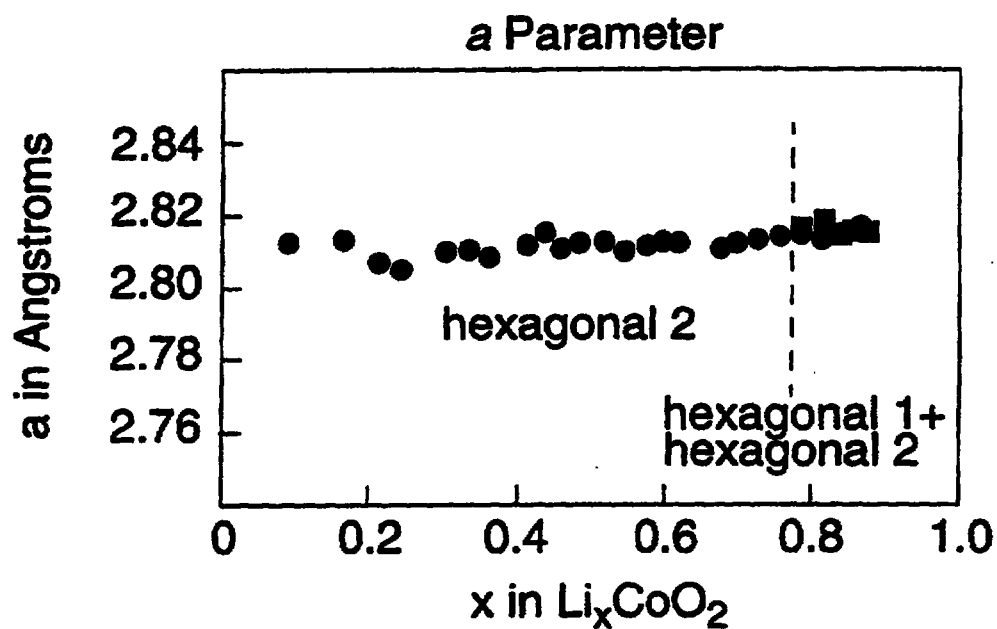


FIG. 14

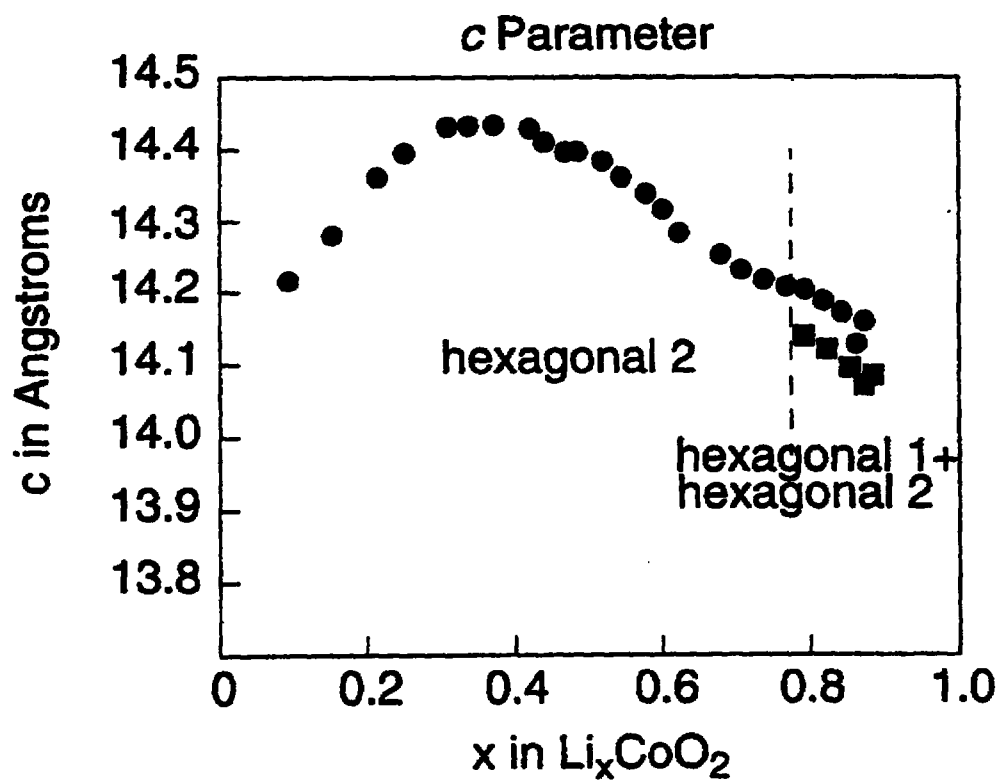


FIG. 15

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important, since, for many layered intercalation materials, up to forty-five percent of the theoretical capacity lies in the region above this 4.3 volt threshold. Unfortunately, however, the study and analysis of these materials necessary for improving capacity have not previously been available with an *in situ* x-ray electrochemical cell. A major problem, as described by Li et al., "In situ X-ray diffraction and electrochemical studies of $\text{Li}_{1-x}\text{NiO}_2$ ", *Solid State Ionics*, 67 (1993), 123-130, arises from the fact that, particularly when a positive cell electrode layer under study is placed in contact with the diffraction cell window, the beryllium film suffers extreme corrosion at cycling potentials in excess of about 4.3 volts, thus severely limiting the utility of the apparatus.

Due to this limitation, the structural variations in these potentially useful intercalation materials could only be determined in isolation by delithiating a different sample at each voltage level in an operating cell cycle. Useful test results could only be obtained with great difficulty in this manner and could seldom be correlated with any degree of reliability. The continuous, high-voltage method and apparatus of the present invention, however, have obviated these limitations and have enabled effective study and development of high capacity electrochemical cell electrode materials.

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SUMMARY OF THE INVENTION

According to the invention there is provided an apparatus for *in situ* x-ray study of an electrochemical cell which comprises an electrochemical cell comprising a positive electrode, a negative electrode, and an interposed separator element in contact with the electrodes; means enclosing the electrochemical cell comprising first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals, which means includes at least one window element for transmission of x-radiation to incidence upon the cell; and means mounting the electrochemical cell in the path of incident x-radiation and comprising means for electrically connecting the positive electrode to the first conductive member and the negative electrode to the second conductive member characterized in that

- a) the electrochemical cell comprises a current collector element in contact with the first of the electrodes and situated away from the outer surface of the electrode;
- b) the electrochemical cell is disposed in the mounting means to present the outer electrode surface to x-radiation transmitted by the window element; and
- c) the mounting means comprises means for maintaining the cell surface spaced from and out of contact with the window element.

Preferably, the collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, the first electrode and the separator element.

Preferably, the collector element comprises an electrically-conductive open-mesh grid.

Preferably, the collector element is in electrical circuit with one of the opposed conductive member terminals.

Preferably, the first electrode is the positive electrode of the electrochemical cell.

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Preferably, the enclosing means includes a second window element situated to transmit x-radiation to incidence upon the outer surface of the other electrode.

Preferably, the electrochemical cell further comprises a second current collector element in contact with the other electrode and in electrical circuit with the respective one of the opposed conductive member terminals.

Preferably, the second collector element is an electrically-conductive open-mesh grid disposed substantially at the interface between the other electrode and the separator element.

According to a second aspect of the invention there is provided a method for monitoring structural changes in electrode materials of a rechargeable battery during operation which comprises providing an *in situ* x-ray electrochemical cell having at least one beryllium window element in a cell enclosure member, mounting within the x-ray cell a rechargeable battery comprising at least one outwardly-disposed subject electrode facing toward the window, directing x-radiation onto the subject electrode in reflective incidence through the window, and intercepting reflected x-radiation to obtain diffraction data characterized in that

the battery is mounted so as to situate the subject electrode out of contact with the window element, thereby preventing electrolytic corrosion of the window element otherwise occurring at the electrical potential of the electrode.

Preferably, the method comprises interposing a spacer element between the subject electrode and the window element to so situate the electrode.

Preferably, the method wherein the battery comprises a positive electrode, a negative electrode, and an interposed separator element in contact with the electrodes, and wherein the cell enclosure comprises first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals

is characterized in that

- a) a current collector element is positioned in contact with the subject electrode and is situated away from the outer surface of the electrode; and
- b) the collector element is connected in electrical circuit with one of the electrical terminals.

Preferably, the positive battery electrode is selected as the subject electrode and the collector element is connected in circuit with the positive terminal.

According to a third aspect of the invention there is provided an apparatus for *in situ* x-ray study of electrochemical cells which comprises an electrochemical cell comprising a positive electrode, a negative electrode, and an interposed electrolyte/separator element in contact with the electrodes, means for mounting the electrochemical cell in the path of incident x-radiation, the mounting means comprising means enclosing the electrochemical cell which includes at least one window element for transmission of the x-radiation to incidence upon the cell, the enclosing means comprising first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals characterized in that the mounting means further comprises

- a) means for electrically connecting the positive electrode to the first conductive member and the negative electrode to the second conductive member; and
- b) means for maintaining the cell spaced from and out of contact with the window element.

Preferably, the electrochemical cell is disposed in the mounting means to present the outer surface of at least one of the electrodes to x-radiation transmitted by the window element.

Preferably, the electrochemical cell further comprises a current collector element in contact with and situated away from the outer surface of the at least one electrode.

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Preferably, the collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, the at least one electrode and the separator element.

Preferably, the collector element comprises an electrically-conductive open-mesh grid.

Preferably, the collector element is in electrical communication circuit with one of the opposed conductive member terminals.

Preferably, the at least one electrode is the positive electrode of the electrochemical cell.

Preferably, the enclosing means includes a second window element situated to transmit x-radiation to incidence upon the outer surface of the other of the electrodes.

Preferably, the electrochemical cell further comprises a second current collector element in contact with the other electrode and in electrical communication with the respective one of the opposed conductive member terminals.

Preferably, the second collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, the other electrode and the electrolyte/separator element.

Preferably, the second collector element comprises an electrically-conductive open-mesh grid.

Preferably, the electrochemical cell comprises a rechargeable battery structure wherein:

a) each of the electrodes and electrolyte/separator element comprises a flexible, self-supporting, polymeric matrix composition film; and

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b) each film is bonded to contiguous films at its respective interface to form a unitary flexible laminate structure.

Preferably, at least the electrolyte/separator comprises an electrolyte providing ion mobility.

Preferably, a current collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, the positive electrode and the electrolyte/separator element.

Preferably, the collector element comprises an electrically-conductive open-mesh grid.

Preferably, the positive electrode comprises a lithium intercalation compound homogeneously distributed in a matrix having the polymeric composition of the separator.

Preferably, the intercalation compound has a nominal formula selected from LiMn_2O_4 , LiCoO_2 , and LiNiO_2 .

Preferably, the negative electrode comprises a carbon intercalation compound homogeneously distributed in a matrix having the polymeric composition of the separator.

According to a fourth aspect of the invention there is provided an apparatus comprising:

- a) an *in situ* x-rays study electrochemical cell holder comprising:
 - 1) a cell holder bottom; and
 - 2) a cell holder top operatively attached to the bottom, the top having a beryllium window; and
- b) a rechargeable battery cell structure comprising:
 - 1) a positive electrode element;
 - 2) a negative electrode element;

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3) an electrolyte/separator element disposed between the positive and negative electrode elements; and

4) a current collector element disposed between the positive electrode element and the electrolyte/separator element, the current collector element being formed of an electrically-conductive open-mesh grid, the positive electrode element facing toward and spaced from the beryllium window the negative electrode element electrically contacting the bottom, and the current collector element electrically contacting the top.

Preferably, the apparatus further comprises a conductive spacer contacting the cell holder top and the current collector element and providing a gap between the beryllium window and the positive electrode element.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will be described with reference to the accompanying drawing of which:

FIG. 1 is a perspective view, in partial section, of a typical laminated Li-ion battery cell structure;

FIG. 2 is an exploded perspective view of an apparatus in accordance with a preferred embodiment of the present invention for monitoring structural changes in a battery;

in situ x-ray electrochemical cell with a specially designed rechargeable battery structure which does not corrode the beryllium window is, among other things, an excellent research tool for obtaining the best cathode, anode, or polymeric component materials. Additionally, research generated from such tests provides ways to characterize final materials used in commercial rechargeable batteries.

While there has been illustrated and described what is at present considered to be a preferred embodiment of the present invention, it will be understood by those skilled in the art that various changes and modifications may be made, and equivalents may be substituted without departing from the true scope of the invention. Therefore, it is intended that this invention not be limited to the particular embodiment disclosed herein, but that the invention include all embodiments falling within the scope of the appended claims.

The invention comprises an enclosed *in situ* x-ray electrochemical cell having an x-ray transmission window, preferably of beryllium, and means for mounting an electrolytic cell within the enclosure in the path of incident x-radiation transmitted by the window while preventing contact between the window and a high-voltage electrode of the electrolytic cell.

The invention also comprises an electrolytic cell structure in which a current collector element associated with an electrode, typically the higher voltage positive electrode, is situated away from the outer surface of the electrolytic cell, preferably being embedded at the electrode/separator interface in order to ensure that the electrode is disposed as an outermost element of the cell where it may receive unobstructed exposure to the incident x-radiation. The current collector element preferably extends beyond the perimeter of the overlying electrode to provide electrical continuity to an x-ray cell body terminal and permit the electrode to be separated from the beryllium window which could otherwise suffer destructive electrolytic corrosion.

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A preferred *in situ* x-ray electrochemical cell of the present invention comprises a cell bottom member and a cell top member which has a beryllium window and is operatively attached to, yet electrically insulated from, the bottom member to form an enclosure within the cell. The invention further includes, operatively situated in the enclosure between the cell bottom and top members, a polymeric rechargeable battery structure comprising an electrolyte/separator element disposed between positive and negative electrodes having electrical connection to terminals associated with the x-ray cell members. In order to receive direct exposure to incident x-radiation, the battery is situated such that the electrode to be examined is facing the x-ray cell window and, when that electrode constitutes the higher voltage positive element of the battery, is maintained at a distance therefrom by interposed spacing means.

The rechargeable battery structure normally also comprises at least one current collector element, typically disposed between the positive electrode and the separator element, through which electrical circuit is maintained between the electrode and the cell top member terminal. The current collector is preferably formed of an electrically-conductive open-mesh grid in order to ensure ion mobility between the electrode and the electrolyte/separator element. The negative battery electrode is electrically connected to the cell bottom member terminal either directly, such as by contact with a conductive bottom member, or through a second battery current collector element.

In another embodiment, the x-ray cell also includes a beryllium window in the cell bottom member. The negative electrode is situated to face this second window and, depending upon its electrical potential in the battery, either contacts or is spaced a distance from the window. In the latter arrangement, a second current collector formed of electrically-conductive open-mesh grid disposed between the negative electrode and the separator element maintains electrical circuit with the cell bottom member terminal.

A method in accordance with the present invention comprises the steps of providing an *in situ* x-ray electro-chemical cell having at least one beryllium window in a cell enclosure member; mounting within the x-ray cell a rechargeable battery comprising

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at least one outwardly-disposed electrode having a contiguous current collector element, the electrode facing toward and being separated from the beryllium window and the collector maintaining electrical circuit with an electrical terminal on the x-ray cell; directing x-radiation onto the electrode in reflective incidence through the window; and intercepting reflected x-radiation to obtain diffraction data. The method may alternatively include providing an *in situ* x-ray cell having two beryllium windows situated respectively in each of a cell top and bottom member; placing the outwardly-disposed positive battery electrode in spaced facing relationship with one window; placing the outwardly-disposed negative battery electrode in spaced facing relationship with the other window, the negative electrode maintaining electrical circuit with an electrical terminal on the x-ray cell by direct contact with the other window or through a contiguous current collector element; and selectively situating one or the other window in incident x-radiation to obtain diffraction data from one or the other of the electrodes.

A method in accordance with the present invention for preparing a battery structure to be used in the *in situ* x-ray cell comprises the steps of arranging, in sequence, a positive electrode element, an electrically-conductive open-mesh grid positive current collector element, a separator element, and a negative electrode element, and bonding the electrode and separator elements to adjacent such elements and to the contiguous collector by the application of heat and pressure to form a unitary flexible laminate structure. Alternatively, the positive electrode element and collector element may be so bonded prior to arranging and bonding the balance of the structure elements. The method further comprises including an ion-conductive electrolyte in at least the separator element to form an active electrolytic battery. In a preferred embodiment, the method comprises forming each of the electrodes and separator element as a flexible, self-supporting, film of polymeric composition comprising a compatible organic plasticizer, and, subsequent to bonding, replacing at least a portion of the plasticizer with a solution of ion-conductive electrolyte.

An advantage of the present invention is its simplicity, which ensures that the beryllium window does not experience the corrosion problems of the related art. Another

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advantage is that the apparatus and method for monitoring structural changes in a rechargeable battery may be used to analyze both the positive and negative electrodes.

and wherein said cell enclosure comprises first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals characterized in that

- a) a current collector element is positioned in contact with said subject electrode and is situated away from the outer surface of said electrode; and
- b) said collector element is connected in electrical circuit with one of said electrical terminals.

12. A method according to claim 11 wherein said positive battery electrode is selected as said subject electrode and said collector element is connected in circuit with said positive terminal.

13. Apparatus for *in situ* x-ray study of electrochemical cells which comprises an electrochemical cell comprising a positive electrode, a negative electrode, and an interposed electrolyte/separator element in contact with said electrodes, means for mounting said electrochemical cell in the path of incident x-radiation, said mounting means comprising means enclosing said electrochemical cell which includes at least one window element for transmission of said x-radiation to incidence upon said cell, said enclosing means comprising first and second opposed electrically-conductive members electrically isolated from one another and respectively providing positive and negative electrical terminals characterized in that said mounting means further comprises

- a) means for electrically connecting said positive electrode to said first conductive member and said negative electrode to said second conductive member; and
- b) means for maintaining said cell spaced from and out of contact with said window element.

14. Apparatus according to claim 13 characterized in that said electrochemical cell is disposed in said mounting means to present the outer surface of at least one of said electrodes to x-radiation transmitted by said window element.

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15. Apparatus according to claim 14 characterized in that said electrochemical cell further comprises a current collector element in contact with and situated away from said outer surface of said at least one electrode.
16. Apparatus according to claim 15 wherein said collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, said at least one electrode and said separator element.
17. Apparatus according to claim 16 wherein said collector element comprises an electrically-conductive open-mesh grid.
18. Apparatus according to claim 15 wherein said collector element is in electrical communication circuit with one of said opposed conductive member terminals.
19. Apparatus according to claim 15 wherein said at least one electrode is the positive electrode of said electrochemical cell.
20. Apparatus according to claim 14 characterized in that said enclosing means includes a second window element situated to transmit x-radiation to incidence upon the outer surface of the other of said electrodes.
21. Apparatus according to claim 20 wherein said electrochemical cell further comprises a second current collector element in contact with said other electrode and in electrical communication with the respective one of said opposed conductive member terminals.
22. Apparatus according to claim 21 wherein said second collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, said other electrode and said electrolyte/separator element.

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23. Apparatus according to claim 22 wherein said second collector element comprises an electrically-conductive open-mesh grid.
24. Apparatus according to claim 13 characterized in that said electrochemical cell comprises a rechargeable battery structure wherein:
- a) each of said electrodes and electrolyte/separator element comprises a flexible, self-supporting, polymeric matrix composition film; and
 - b) each said film is bonded to contiguous films at its respective interface to form a unitary flexible laminate structure.
25. Apparatus according to claim 24 wherein at least said electrolyte/separator comprises an electrolyte providing ion mobility.
26. Apparatus according to claim 24 wherein a current collector element is disposed substantially at the interface between, and includes means providing ion-conductive contact between, said positive electrode and said electrolyte/separator element.
27. Apparatus according to claim 26 wherein said collector element comprises an electrically-conductive open-mesh grid.
28. Apparatus according to claim 24 wherein said positive electrode comprises a lithium intercalation compound homogeneously distributed in a matrix having the polymeric composition of said separator.
29. Apparatus according to claim 28 wherein said intercalation compound has a nominal formula selected from LiMn_2O_4 , LiCoO_2 , and LiNiO_2 .
30. Apparatus according to claim 24 wherein said negative electrode comprises a carbon intercalation compound homogeneously distributed in a matrix having the polymeric composition of said separator.

31. An apparatus comprising:

- a) an *in situ* x-rays study electrochemical cell holder comprising:
 - 1) a cell holder bottom; and
 - 2) a cell holder top operatively attached to said bottom, said top having a beryllium window; and
- b) a rechargeable battery cell structure comprising:
 - 1) a positive electrode element;
 - 2) a negative electrode element;
 - 3) an electrolyte/separator element disposed between said positive and negative electrode elements; and
 - 4) a current collector element disposed between said positive electrode element and said electrolyte/separator element, said current collector element being formed of an electrically-conductive open-mesh grid, said positive electrode element facing toward and spaced from said beryllium window said negative electrode element electrically contacting said bottom, and said current collector element electrically contacting said top.

32. The apparatus of claim 31 which further comprises a conductive spacer contacting said cell holder top and said current collector element and providing a gap between said beryllium window and said positive electrode element.

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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 23/20, 33/20		A1	(11) International Publication Number: WO 96/2523
			(43) International Publication Date: 25 July 1996 (25.07.96)
(21) International Application Number: PCT/US96/00054		(81) Designated States: BR, CA, JP, MX, SG, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).	
(22) International Filing Date: 16 January 1996 (16.01.96)			
(30) Priority Data: 08/373,830 ✓ 17 January 1995 (17.01.95) US		Published With international search report	
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(54) Title: APPARATUS AND METHOD FOR IN SITU X-RAY STUDY OF ELECTROCHEMICAL CELLS

(57) Abstract

An apparatus and method for monitoring structural changes of an electrode in a rechargeable battery include an *in situ* x-ray electrochemical cell (30) comprising top and bottom cell members (32, 34) including at least one beryllium window element (36) for transmission of diffractometer x-radiation. A rechargeable battery (43) mounted within the x-ray cell enclosure comprises an electrolyte/separator element (68) interposed between positive and negative electrodes (64, 66). A current collector element (70) formed of an electrically-conductive open-mesh grid is disposed between the positive electrode and the separator to enable ion-conducting contact of the electrode and separator while maintaining electrical continuity between the electrode and an external x-ray cell terminal (54). As a result of this arrangement, the positive electrode need not contact the window element to establish an electrical battery circuit, but may be sufficiently spaced from the window to avoid electrolytic corrosion of the beryllium element. The *in situ* x-ray electrochemical cell and battery structure allow for continuous monitoring of the structural changes in electrode materials during charge/discharge cycling.

No covering letter