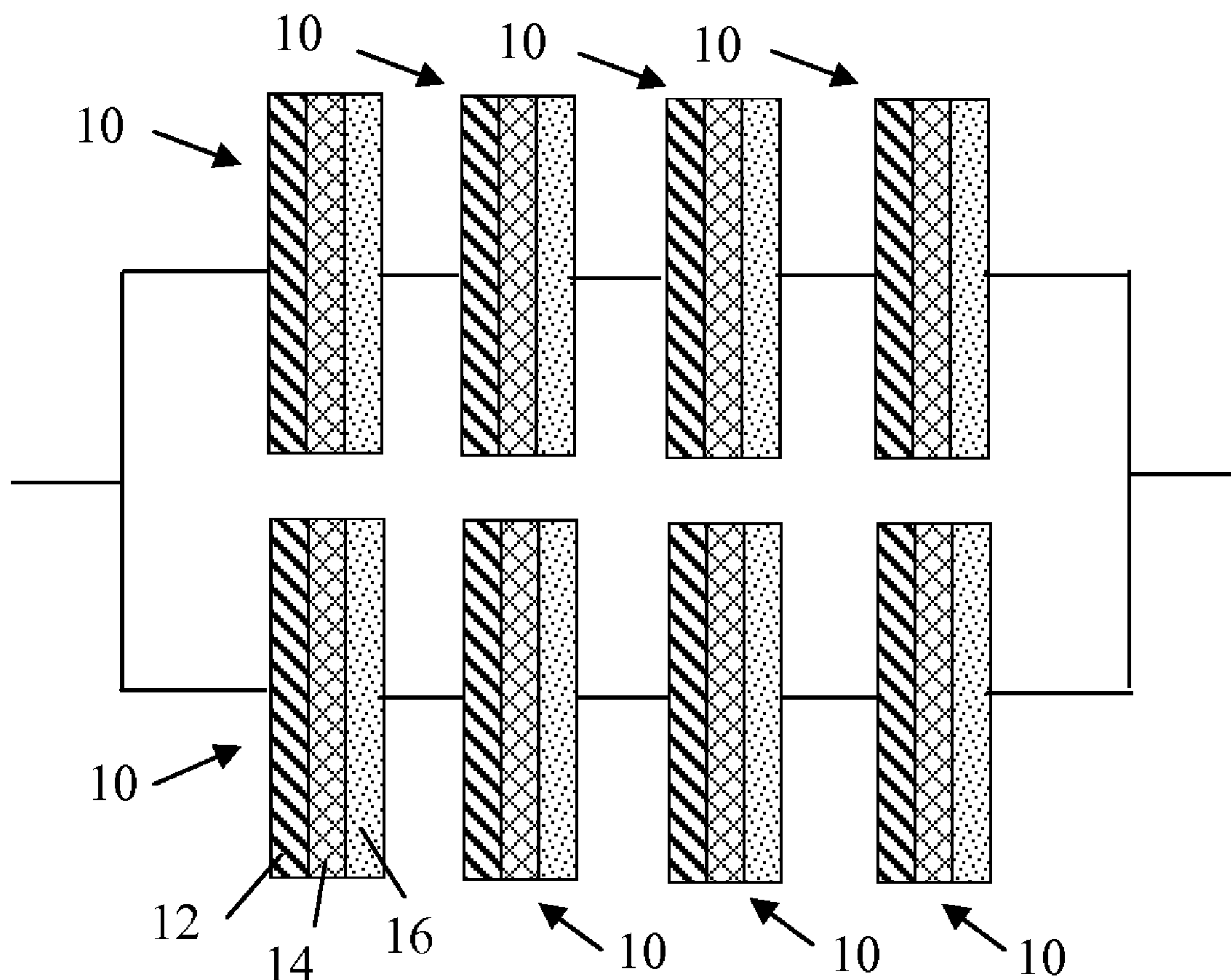


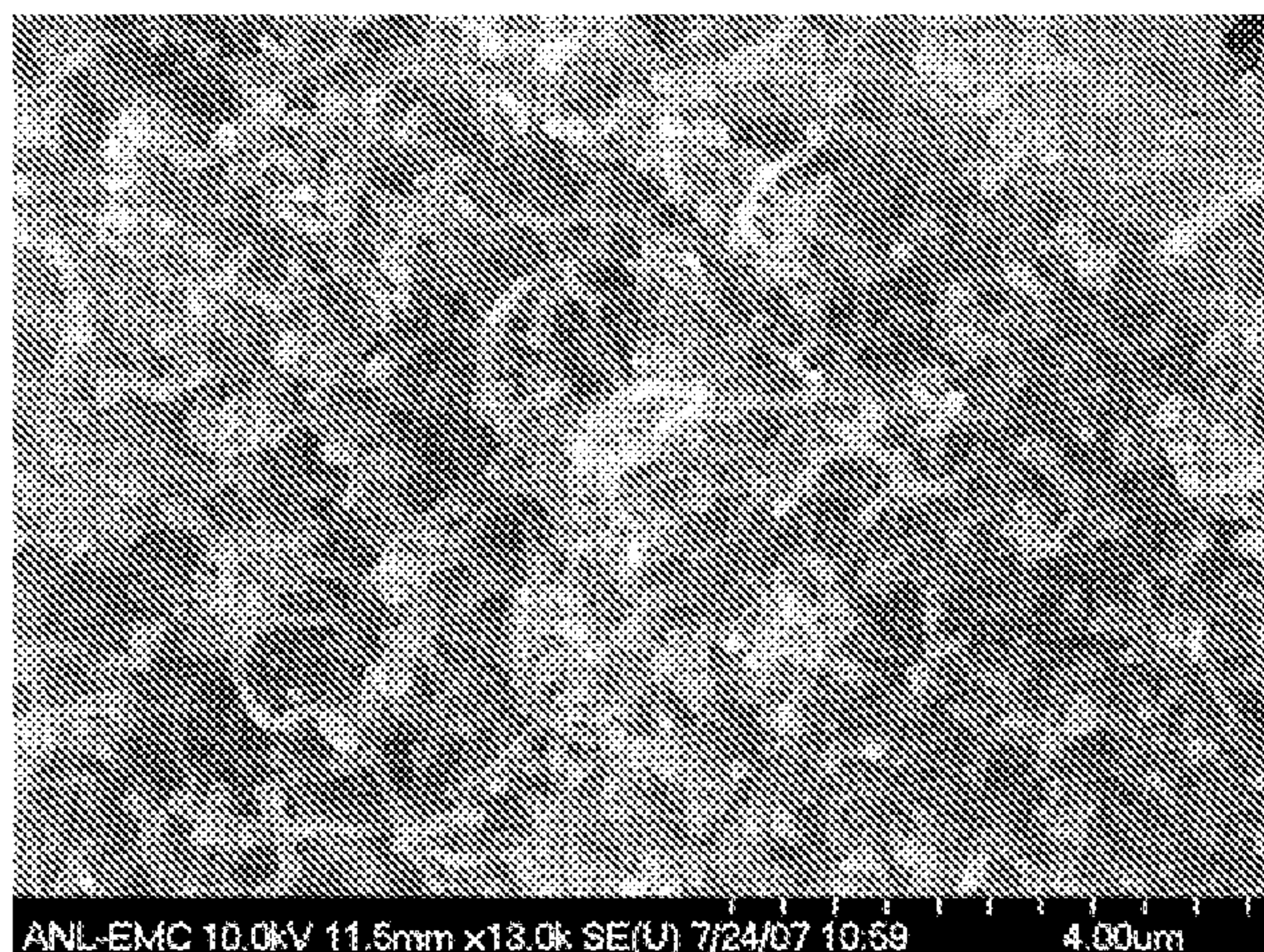
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(19) **United States**(12) **Patent Application Publication**
JOHNSON et al.(10) **Pub. No.: US 2011/0104576 A1**(43) **Pub. Date: May 5, 2011**(54) **LITHIUM-OXYGEN ELECTROCHEMICAL
CELLS AND BATTERIES****Publication Classification**(51) **Int. Cl.***H01M 12/06* (2006.01)*B82Y 30/00* (2011.01)(52) **U.S. Cl.** **429/405**; 977/742; 977/948(57) **ABSTRACT**

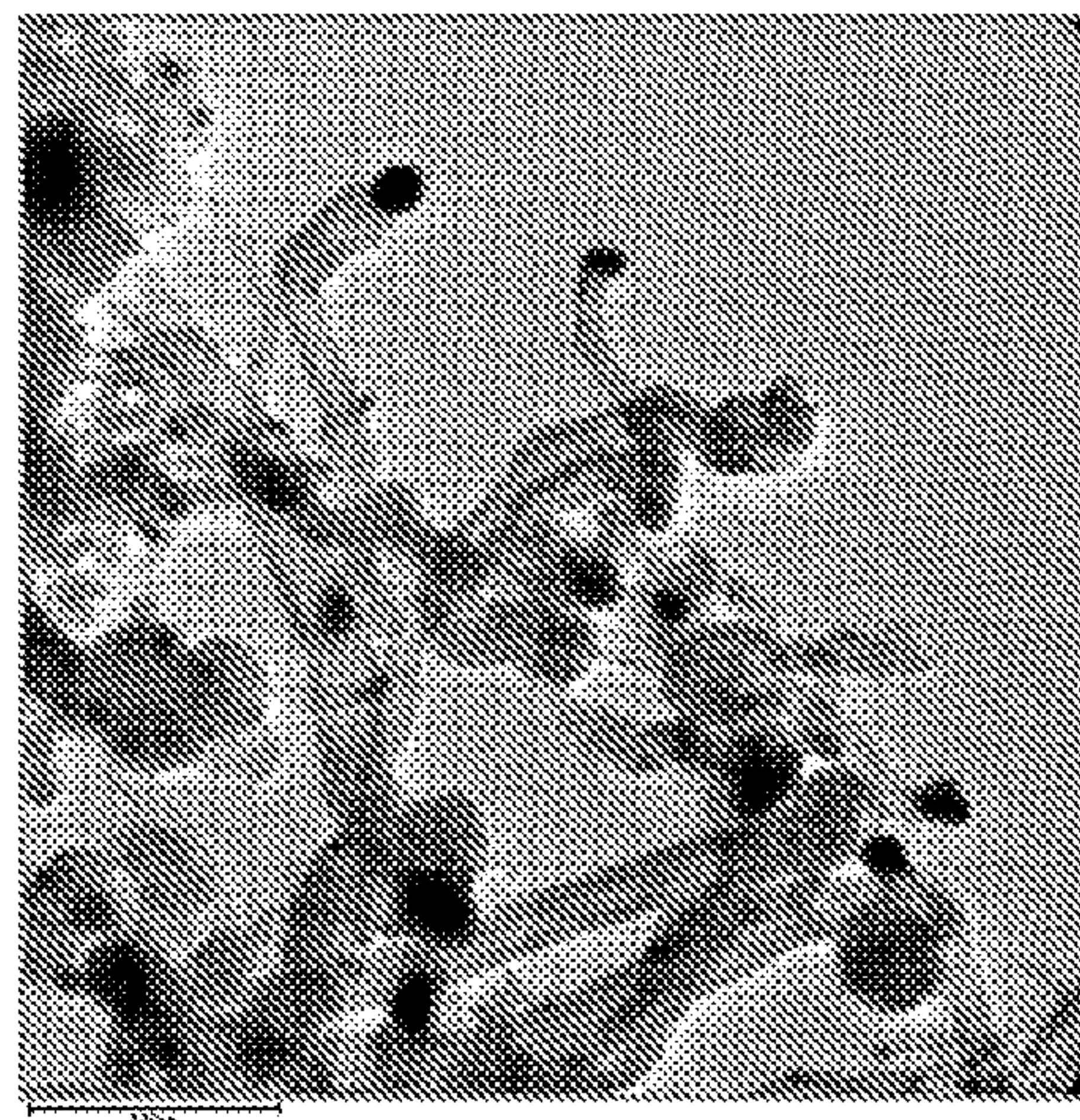
A lithium-oxygen electrochemical cell of the invention comprises a lithium-containing anode, an oxygen-permeable cathode, a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode, and a source of gaseous oxygen in fluid communication with the cathode; the cathode comprising an oxygen-permeable support bearing carbon nanotubes having at least one open end. In some embodiments, the cell is rechargeable and the cathode includes a nanoparticulate catalyst in contact with the carbon nanotubes; wherein the catalyst is adapted to facilitate the reversible interconversion between oxygen gas and an oxygen anion e.g., oxide ion, peroxide ion, or a combination thereof, during charge and discharge of the cell.

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ZHANG**, Naperville, IL (US)(73) Assignee: **UCHICAGO ARGONNE, LLC**,
Chicago, IL (US)(21) Appl. No.: **12/915,580**(22) Filed: **Oct. 29, 2010****Related U.S. Application Data**(60) Provisional application No. 61/360,027, filed on Jun.
30, 2010, provisional application No. 61/280,025,
filed on Oct. 29, 2009.

(a)



(b)



(c)

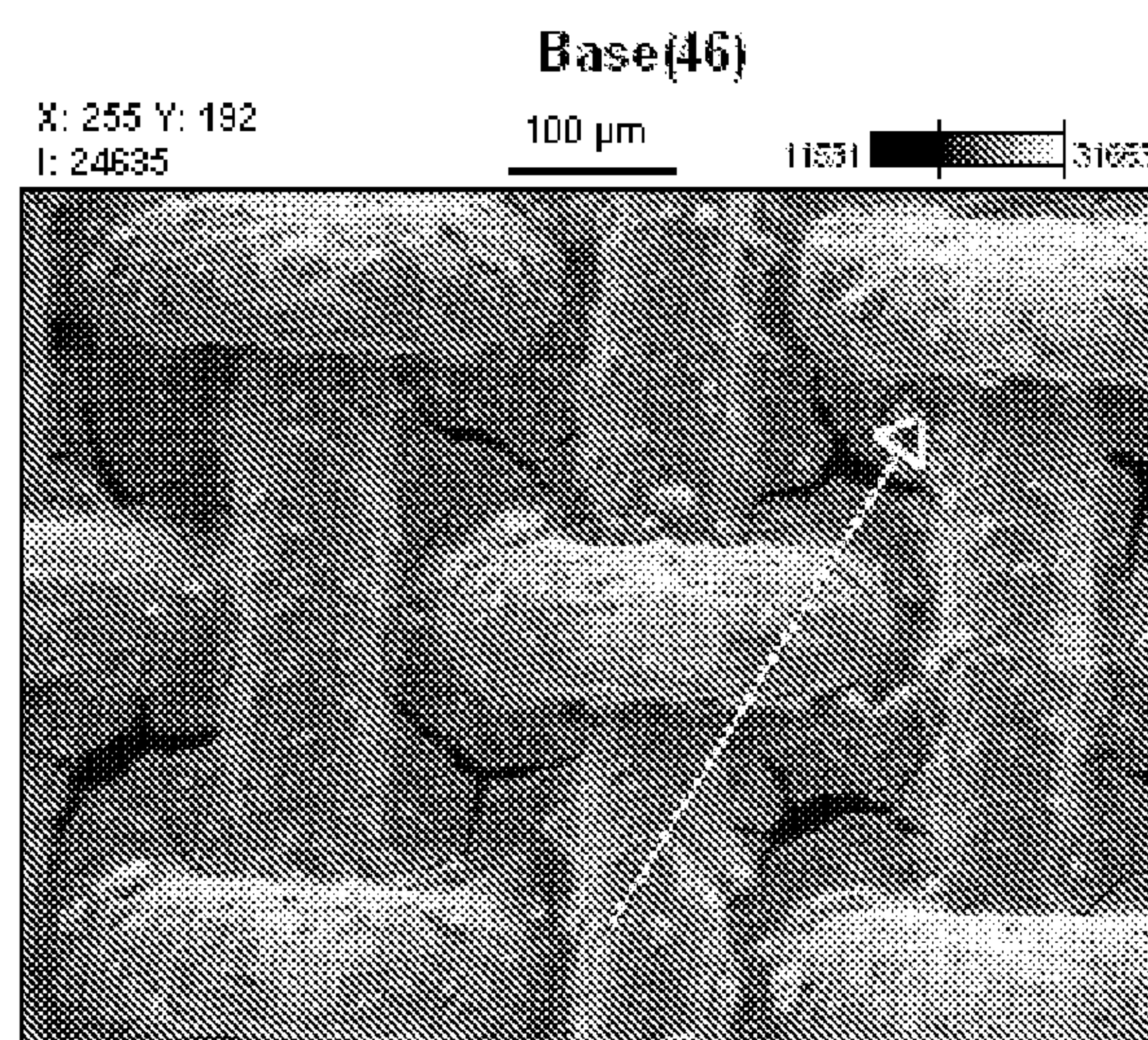


FIG. 1

(d)

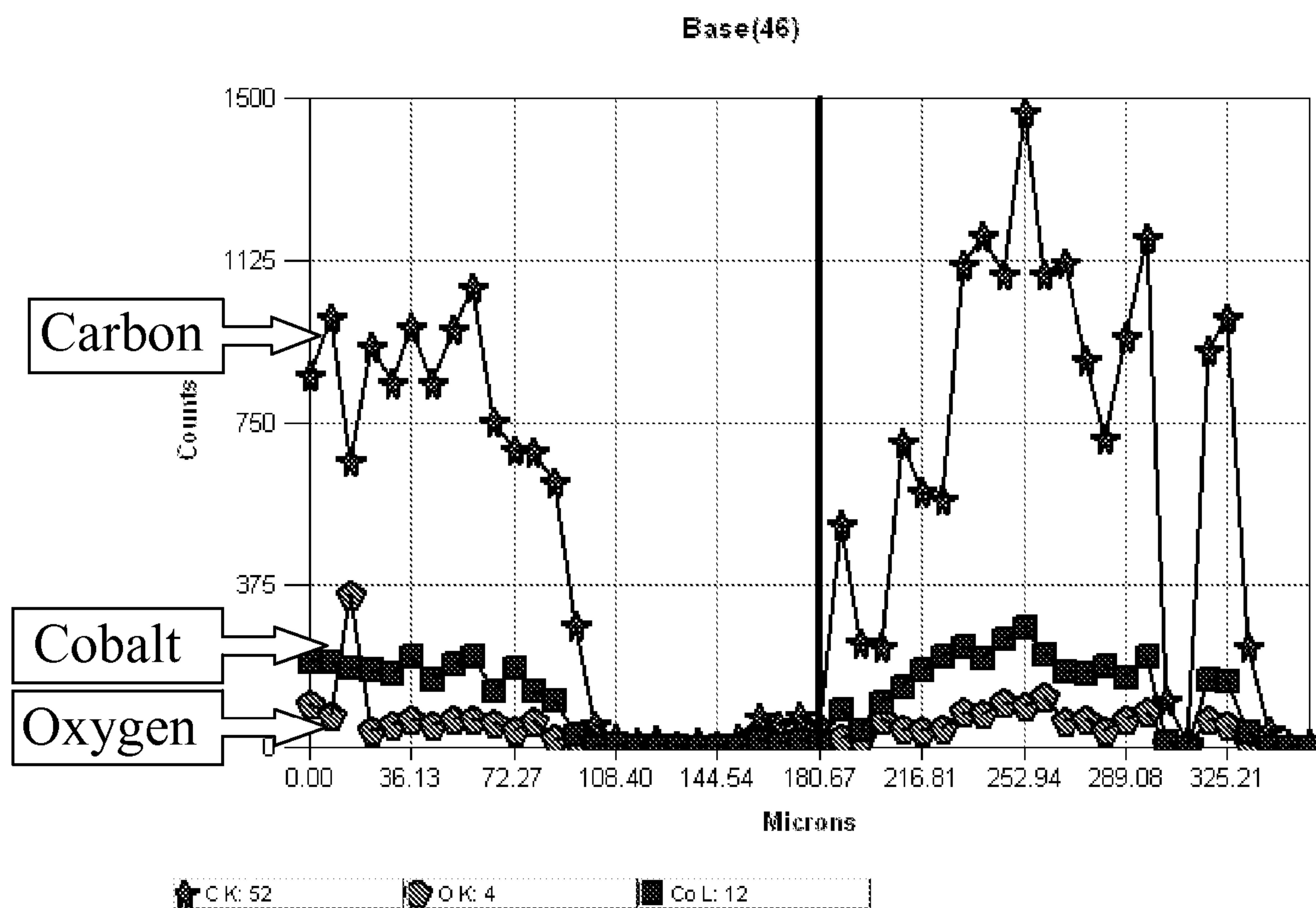
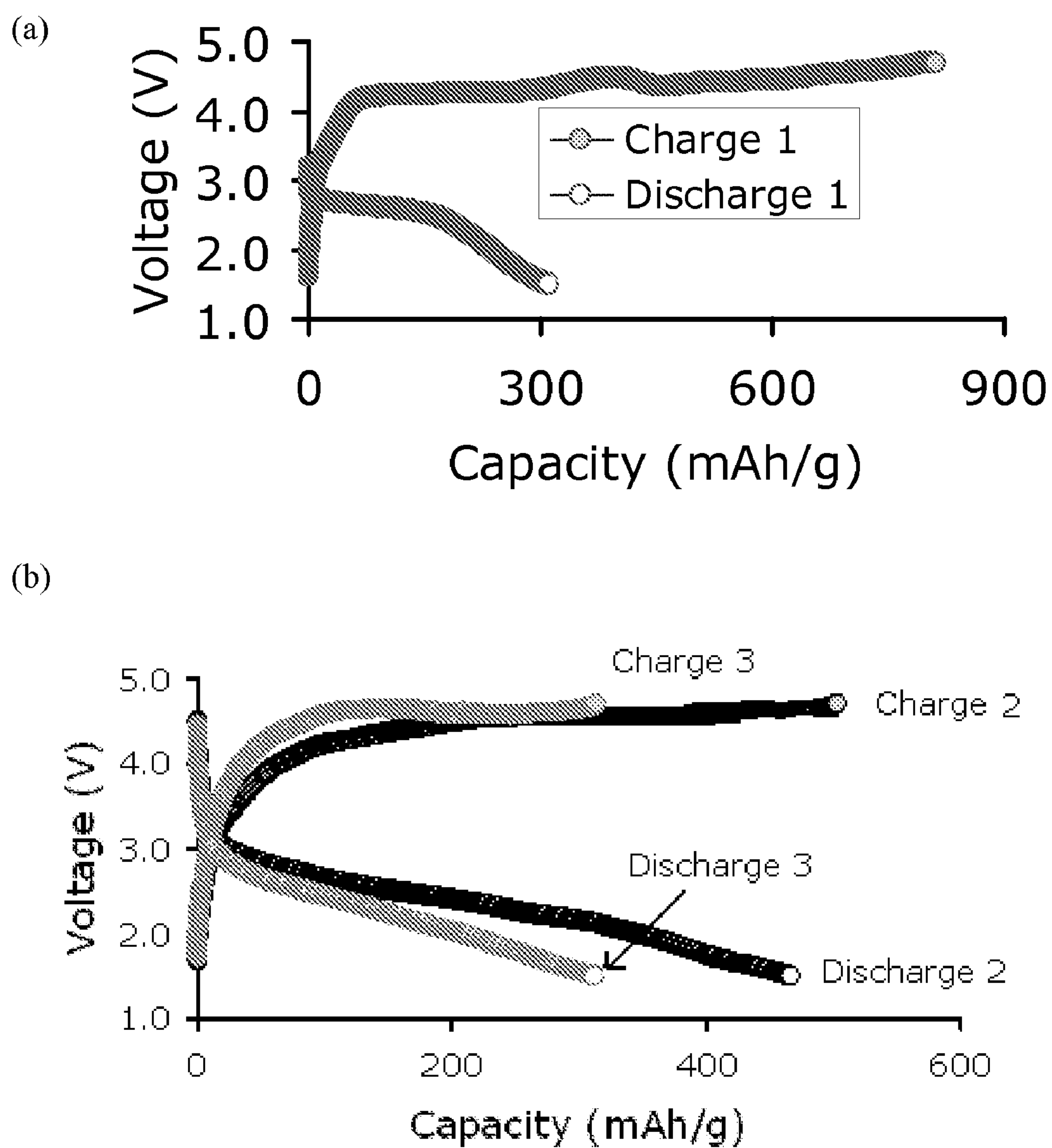


FIG. 1 (CONT.)

**FIG. 2**

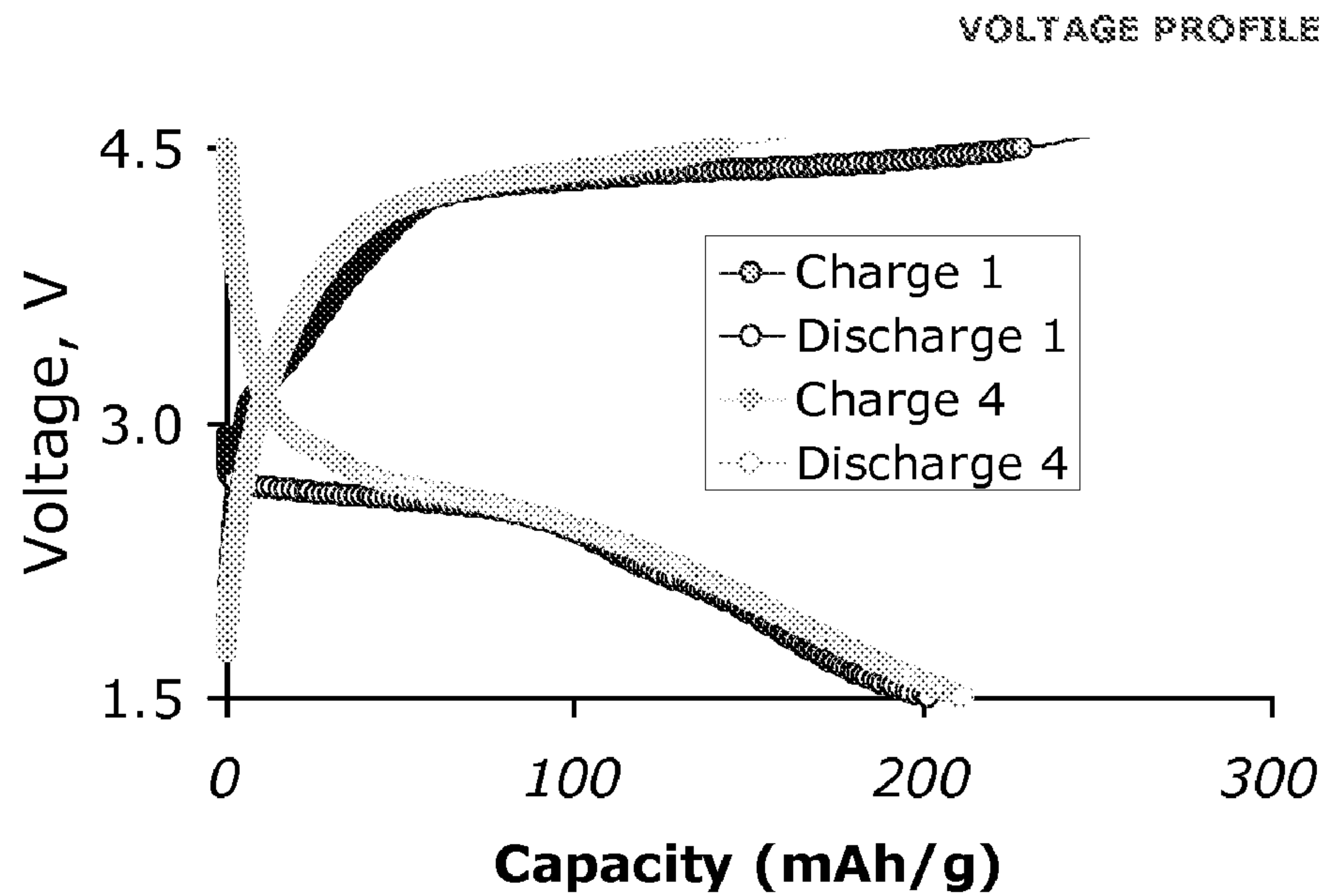


FIG. 3

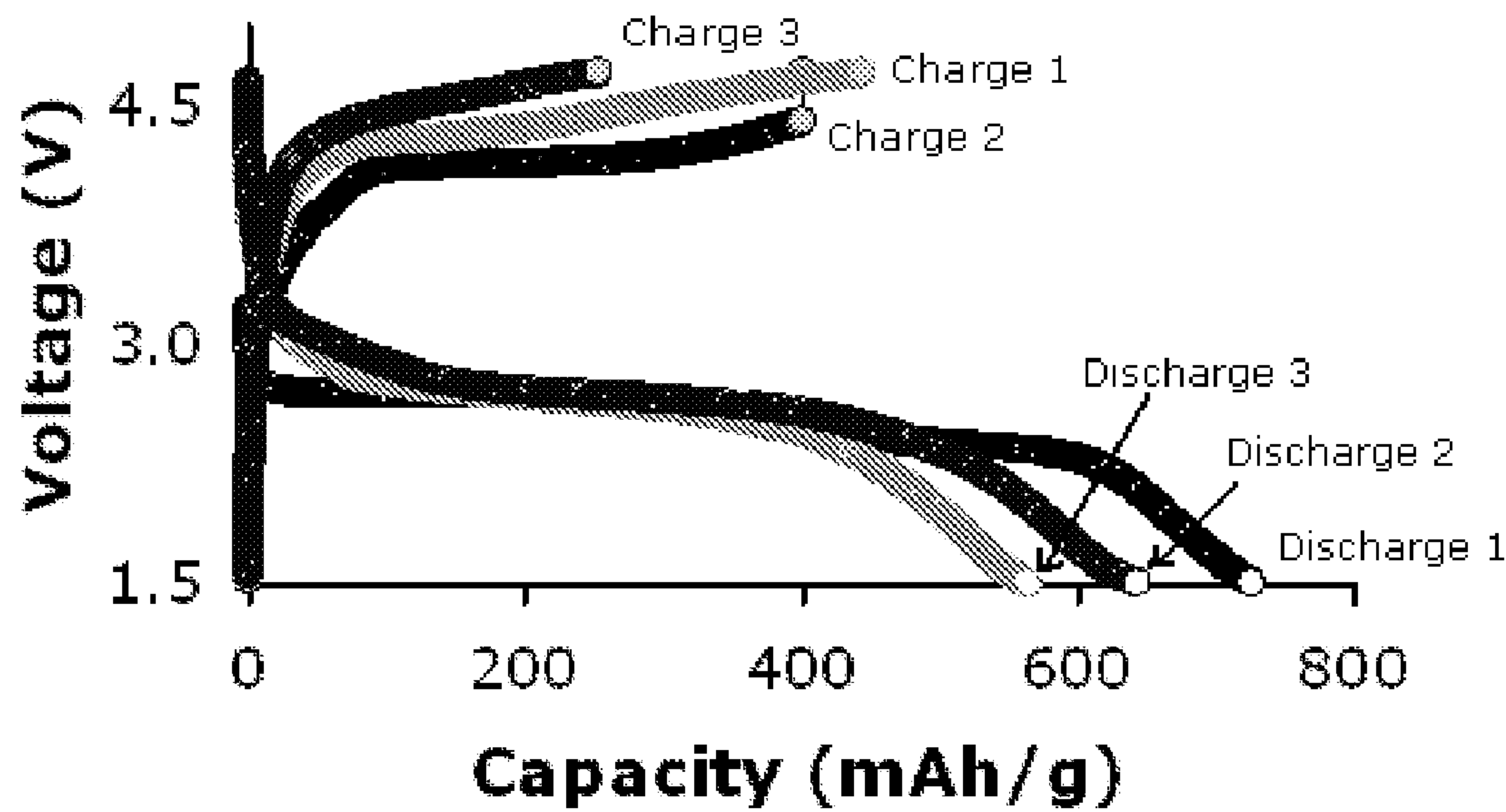
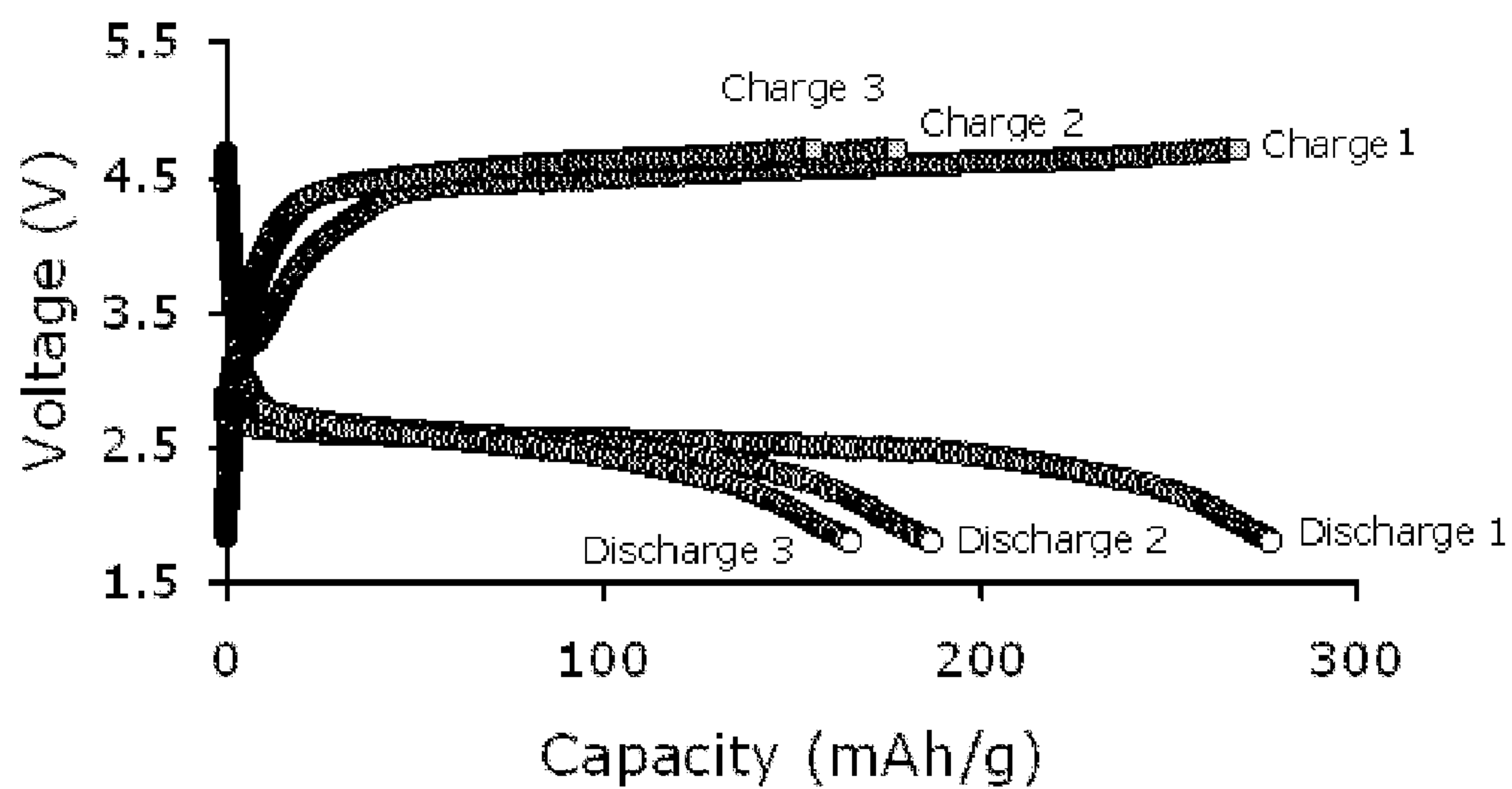
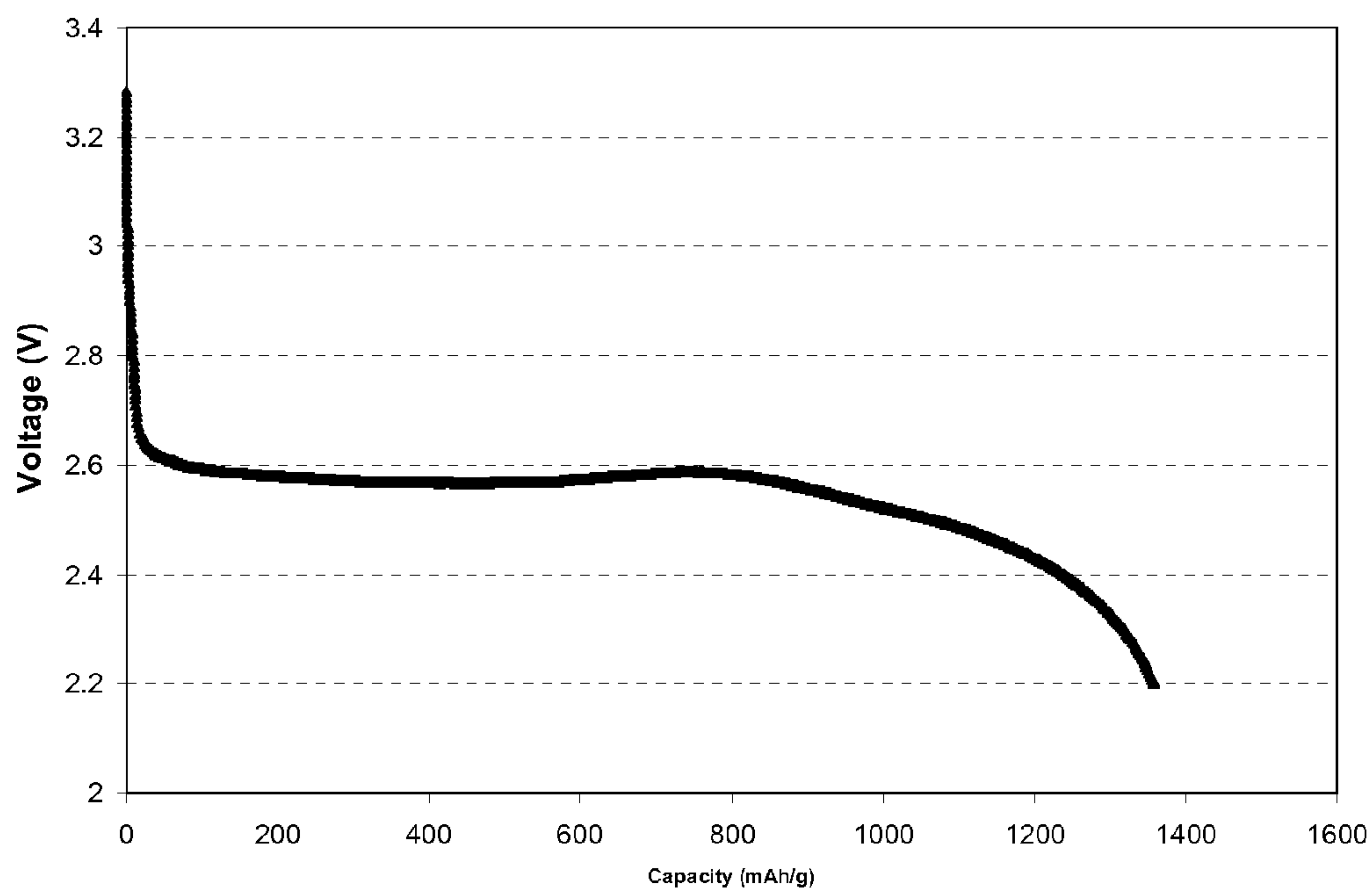
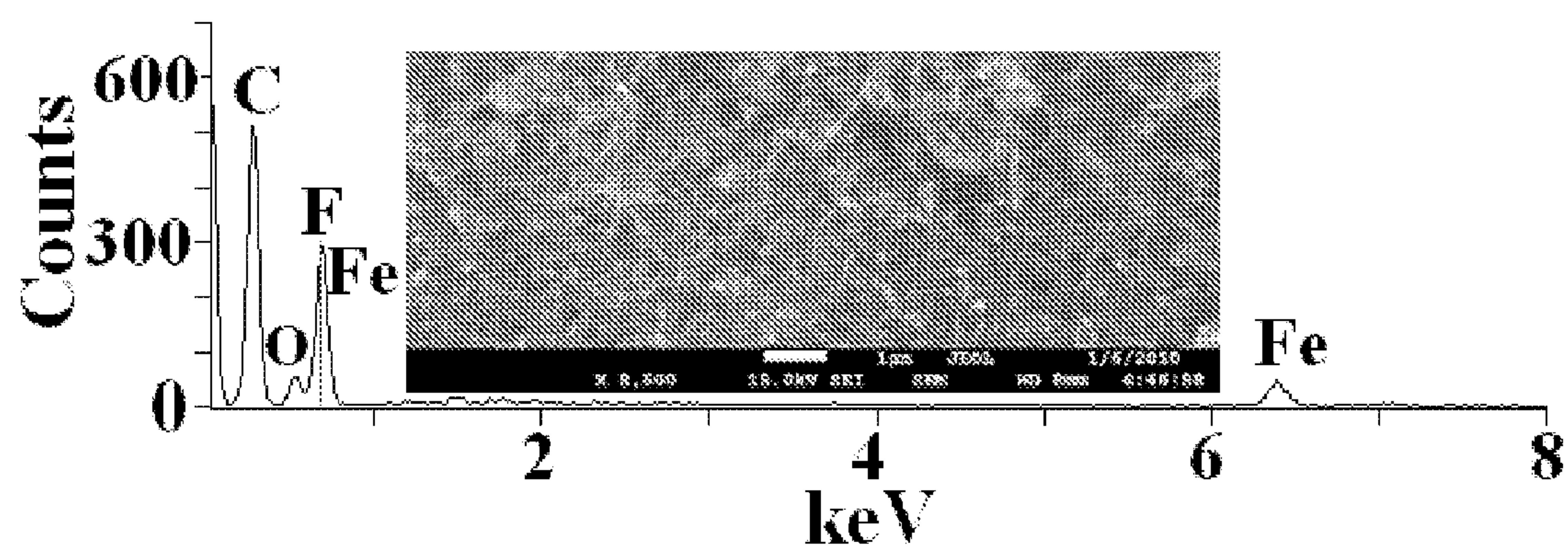


FIG. 4

**FIG. 5****FIG. 6**

(a)



(b)

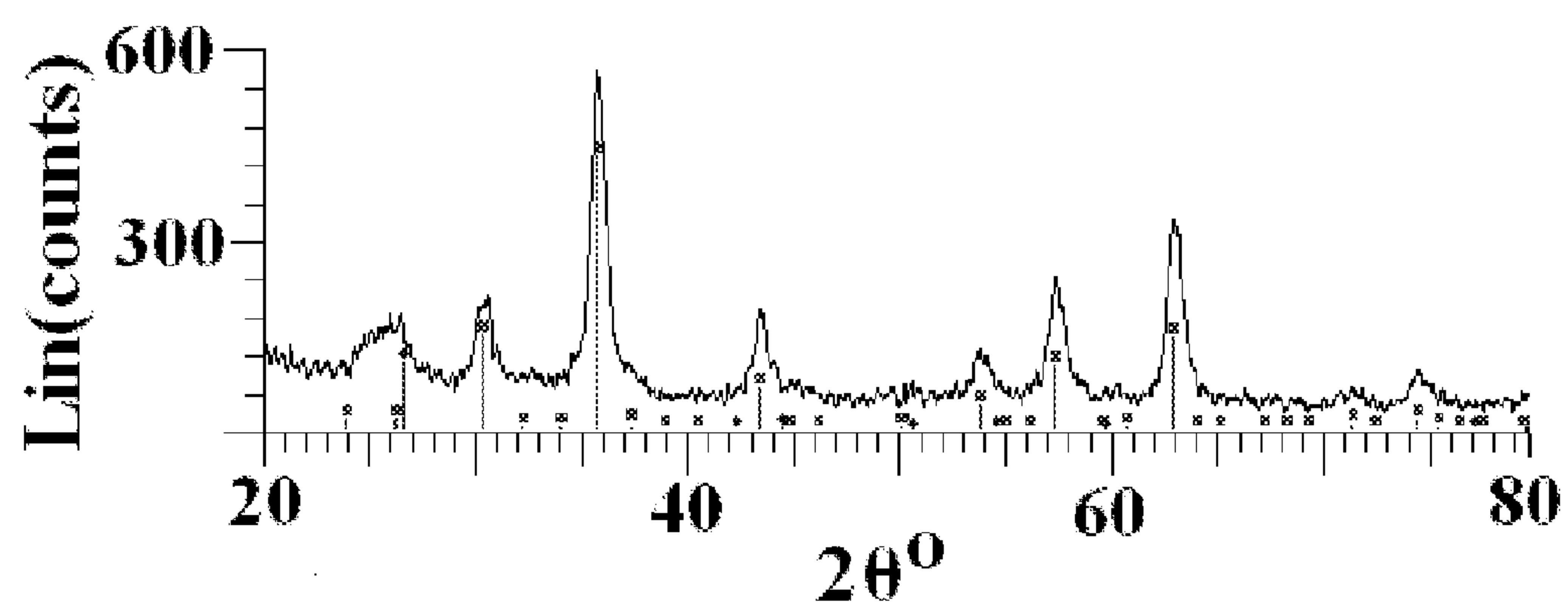
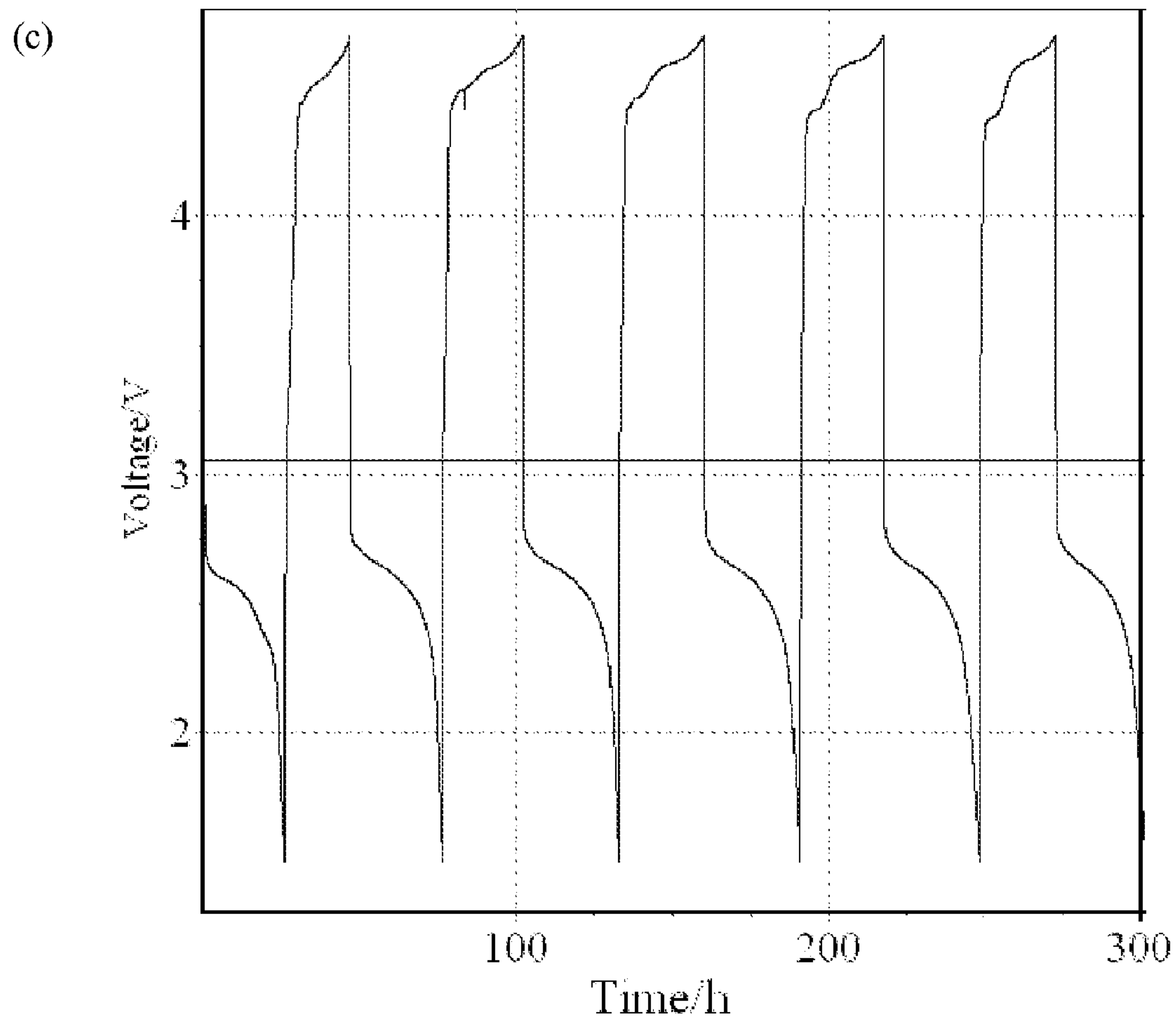


FIG. 7

**FIG. 7 (CONT.)**

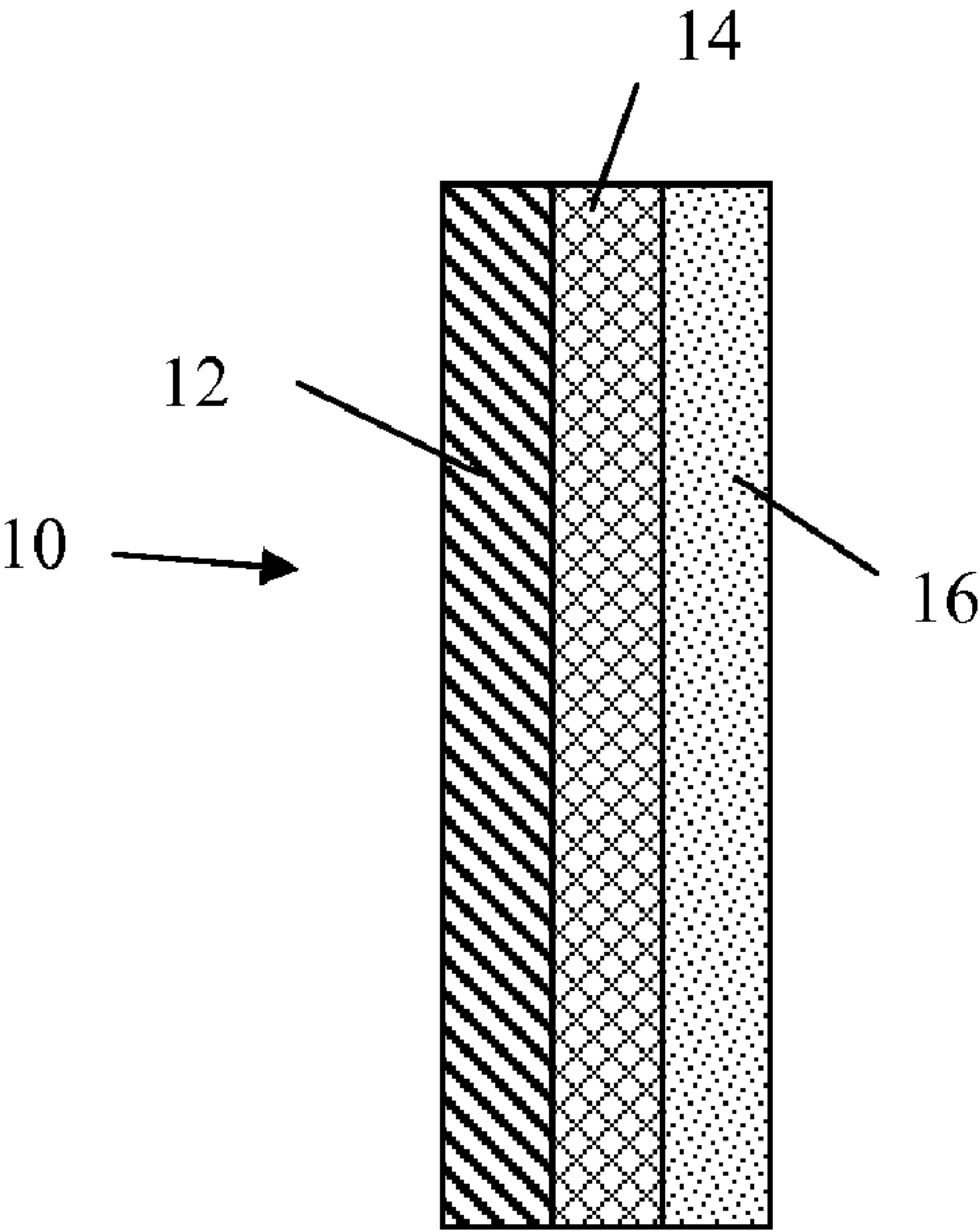


FIG. 8

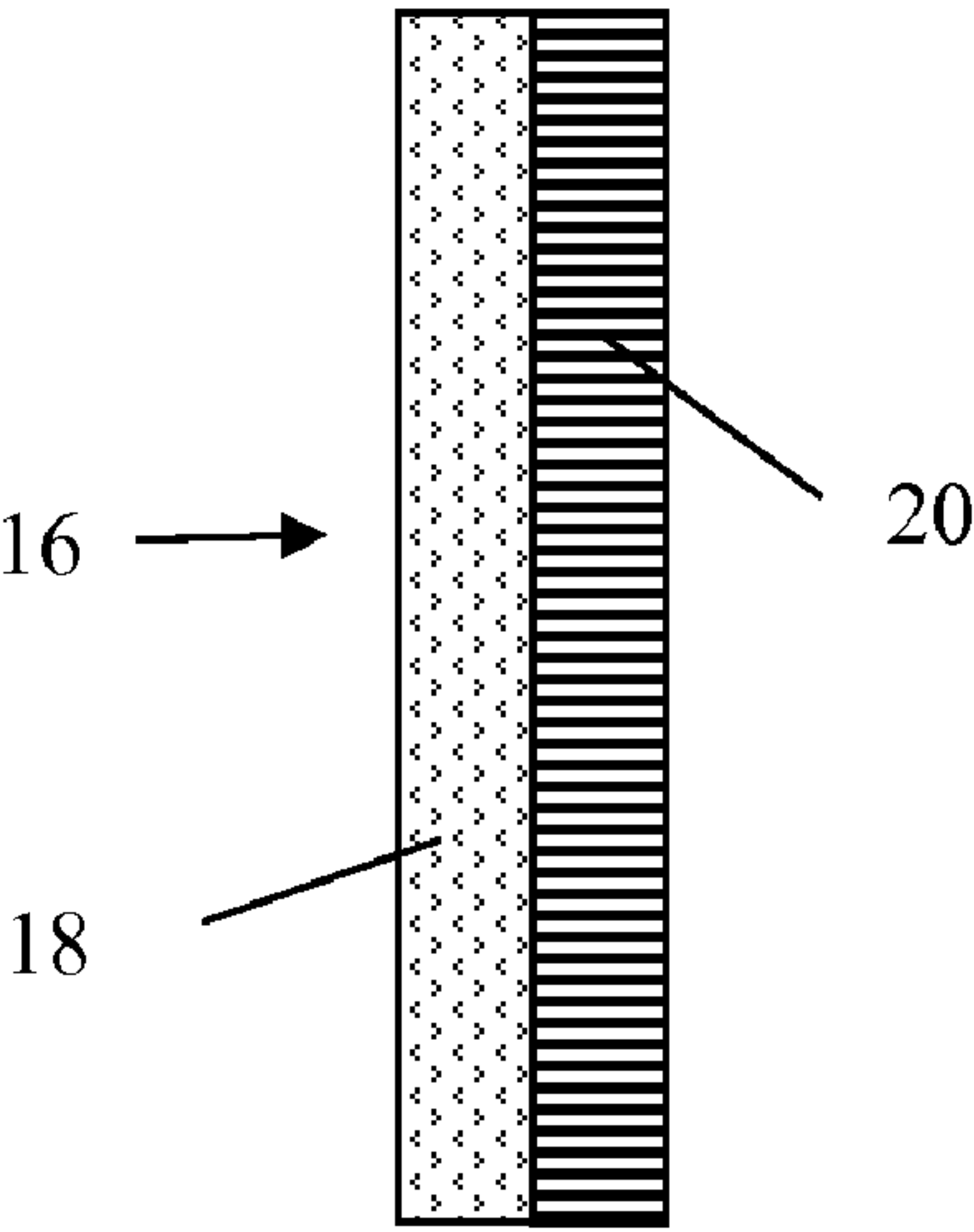


FIG. 9

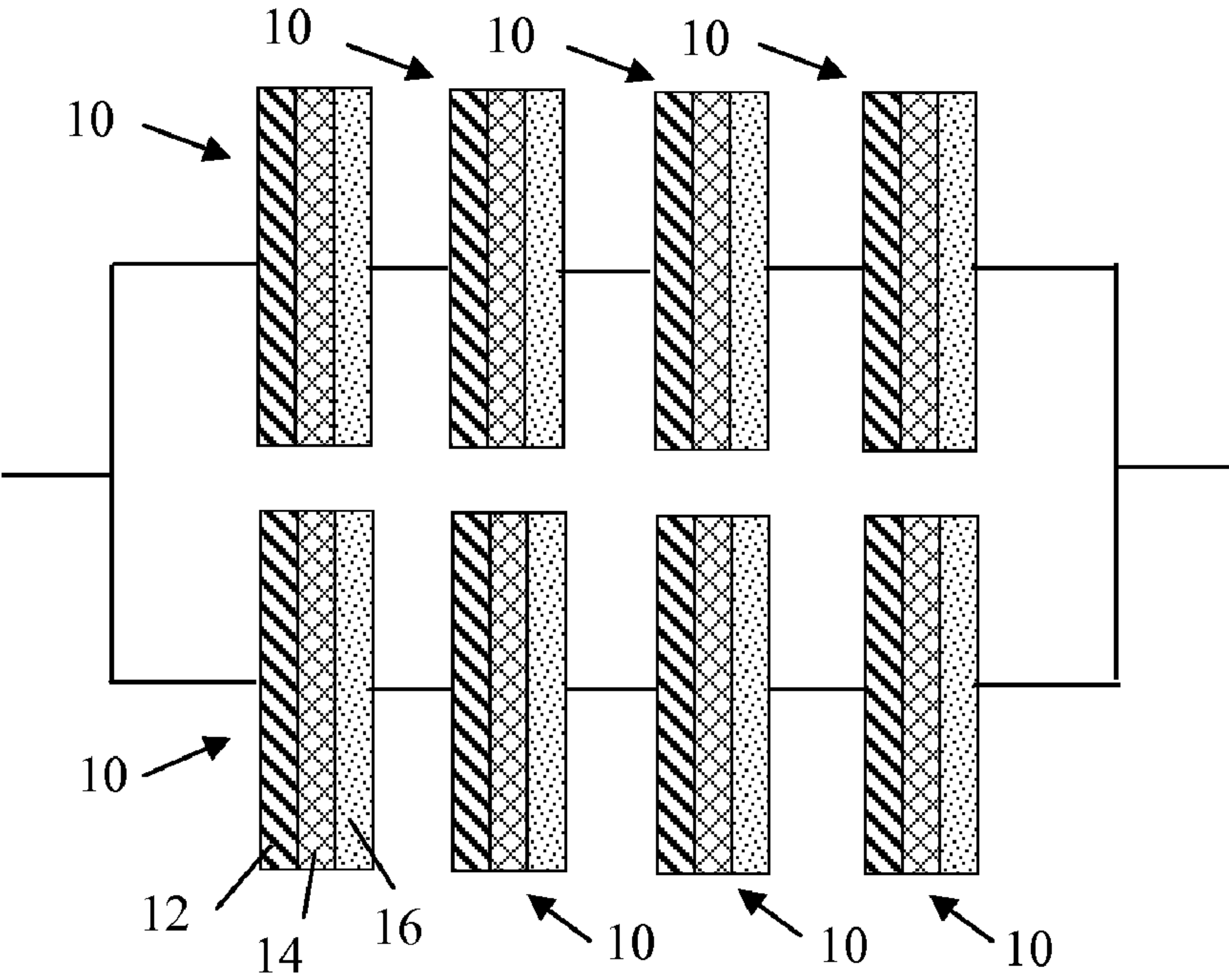


FIG. 10

LITHIUM-OXYGEN ELECTROCHEMICAL CELLS AND BATTERIES

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application Ser. No. 61/360,027, filed on Jun. 30, 2010, and of U.S. Provisional Application Serial No. 61/280,025, filed on Oct. 29, 2009, each of which is incorporated herein by reference in its entirety.

CONTRACTUAL ORIGIN OF THE INVENTION

[0002] The United States Government has rights in this invention pursuant to Contract No. DE-ACO2-06CH11357 between the United States Government and UChicago Argonne, LLC representing Argonne National Laboratory.

FIELD OF THE INVENTION

[0003] This invention relates to energy storage devices, notably electrochemical cells and batteries and, more particularly, lithium-oxygen electrochemical cells. The present invention provides electrochemical cells and batteries that include a carbon nanotube-based cathode.

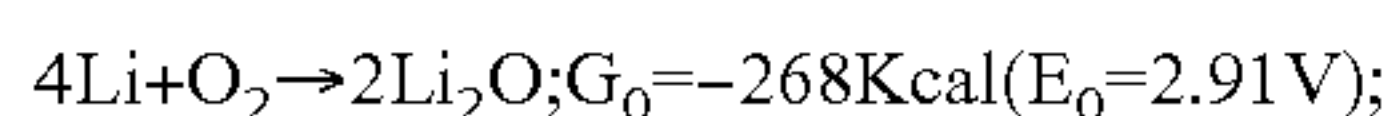
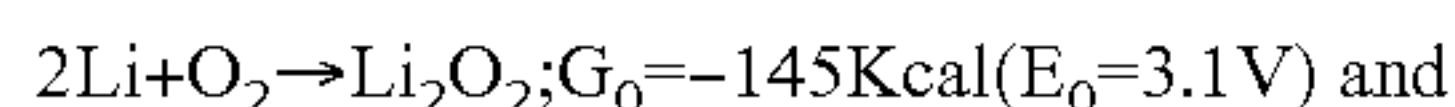
BACKGROUND

[0004] Metal-oxygen (e.g., metal-air) batteries combine a metal anode, similar to that used in conventional primary batteries, and an oxygen (air) gas-diffusion cathode similar to that used in fuel cells. During operation, the metal anode typically based on Zn, Al, Mg, Ca, or Li is electrochemically oxidized for the expense of the oxygen from air, which is reduced on the gas-diffusion cathode. Some properties of metal-oxygen electrochemical cells are presented in Table 1. A classic example of a household zinc-air system is a so-called “hearing aid” cell. Besides that, these power sources occupy several other niches in the energy market.

TABLE 1

Properties of metal-air batteries			
Metal/ O ₂ battery	Calculated OCV, V	Theoretical specific energy, Wh/kg (including oxygen)	Theoretical specific energy, Wh/kg (excluding oxygen)
Li/O ₂	2.91	5200	11140
Na/O ₂	1.94	1677	2260
Ca/O ₂	3.12	2990	4180
Mg/O ₂	2.93	2789	6462
Zn/O ₂	1.65	1090	1350

[0005] In the case of lithium-oxygen cells, the possible discharge cell reactions and the associated cell voltages are:



based on experimental discharge data from a Li/O₂ test cell. It has been reported that the main discharge reaction is the reduction of oxygen to form Li₂O₂ based on Raman spectroscopic analysis of the products in a non-aqueous cell.

[0006] A lithium-oxygen (Li—O₂) battery can be rechargeable when the carbon cathode contains catalysts derived from complexes or oxides of metals such as cobalt. The catalyst can be viewed as lowering the over-voltage for the oxidation of

Li₂O₂ or Li₂O to form metallic Li and oxygen. The first example of a Li—O₂ rechargeable cell utilized non-aqueous conducting gel polymer electrolytes that were used to construct polymer-Li-air cells based on poly(acrylonitrile)(PAN) and poly(vinylidene difluoride) (PVdF). Non-aqueous lithium-air batteries represent a class of potentially ultrahigh energy density power sources useful for a variety of civilian applications. However, such systems generally exhibit a limited number of recharge cycles.

[0007] There are a number of factors that can limit the rechargeability of Li—O₂ cells. These include the structural and chemical design of the air-diffusion cathode, the kinetics of the redox reactions, the solubility and rates of dissolution of the reaction products during charging, and the need for high oxygen solubility in the non-aqueous electrolyte.

[0008] The cathode in all known types of metal-oxygen cells and batteries is an gas-diffusion electrode, in which oxygen (either pure or diluted in another gas, e.g., air) diffuses through the cathode, generally on a continuous basis. Such gas-diffusion electrodes typically comprise a porous, thin plate or sheet, which serves as a wall for the metal-oxygen cell and separates the electrolyte in the cell from the surrounding oxygen-containing gas (e.g., air). The dual purpose of the porous plate poses some conflicting requirements for cathode design. For example, the cathode must be highly porous and permeable to gaseous oxygen while simultaneously preventing leakage of the electrolyte through the porous cathode. The cathode must be electrically conductive and must possess enough mechanical strength to withstand the hydrostatic pressure of the electrolyte and any hydrodynamic shocks that may eventually occur. If the Li-oxygen cell is to be rechargeable, the porous cathode must contain an active catalyst for electrochemical oxidation of oxide and peroxide ions to form oxygen in contact with the electrolyte. Stable operation of the oxygen (air) cathode with time is also needed. Cathodes for metal-oxygen cells can contain various forms of carbon, for example, in the electrochemically active material, as conductive additive, and as part of the current collector.

[0009] Lithium-oxygen (e.g., Li-air) electrochemical cells and batteries have been targeted as the next generation energy storage system, possessing a very high theoretical specific energy that renders such batteries attractive for a number of power source applications including electric vehicles (EVs). Based on the high electropositive voltage of lithium and its low atomic weight, and the ready source of atmospheric oxygen, the theoretical specific energy for a lithium-air cell is 5200 Wh/kg, including oxygen. This is much higher than is achievable with a typical Li-ion battery, which has a specific energy value near 600 Wh/kg. In practice, oxygen is not stored in the battery, but is rather supplied by ambient air. The theoretical specific energy of a lithium-air cell, excluding oxygen, is 11140 Wh/kg. Oxygen from the ambient atmosphere enters the pores of the carbon cathode to serve as the cathode active material. In the discharge of a Li-air battery utilizing a porous carbon electrode, this oxygen is reduced, and the products are stored in the pores of the carbon electrode. As a result, the cell capacity is expressed as ampere-hour per kilogram of the carbon in the cathode. The specific characteristics, such as Ah/kg and AWL of metal-air batteries are significantly higher than that of the classical electrochemical systems with the same metal anode. Theoretical data show that Li and Ca possess very high energy densities of 13172 and 4560 Ah/kg, respectively, but these metals are not

suitable to be used as anodes when aqueous electrolytes are utilized. Consequently, non-aqueous electrolytes must be used in such systems. When fully developed, lithium-oxygen batteries could exhibit practical specific energies of 1000-3000 Wh/kg.

[0010] In a primary Li—O₂ cell, Li metal is electrochemically oxidized at expense of oxygen from air, which is reduced at the cathode, producing either Li₂O₂ (3.1 V vs. Li⁺/VLi⁰) or Li₂O (2.91 V vs. Li⁺/Li⁰) or a combination of both. In the discharge of the Li-air battery, this oxygen is reduced and the products are stored in the cathode (typically high surface area carbon black). The Li—O₂ battery may also be charged in the presence of a high-surface area carbon black and a manganese oxide catalyst such as α-MnO₂ (hollandite structure) that is used to assist in the oxidation of the discharge product, Li₂O₂ and/or Li₂O to oxygen. While high values of energy density have been realized for the Li—O₂ cell as a primary power source, the utilization of the device as a rechargeable cell have been hindered by many obstacles.

[0011] Electrodes that utilize nanostructures for energy storage are increasingly prevalent. An example is synthesized nanostructured carbon-free LiFePO₄ olivine, which reportedly has a high-rate for Li-ion battery applications. Nanostructured materials that feature high-surface areas, fast ion diffusion and high electronic conductivity due to their very small particle size have led to higher rates of electrochemical reactions in various applications. The evolution and improvement of Li-air batteries ultimately will involve tailored nanostructured materials that can support the rigors of the air-cathode during operation.

SUMMARY OF THE INVENTION

[0012] A lithium-oxygen electrochemical cell of the present invention comprises a lithium-containing anode, an oxygen-permeable cathode, a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode, and a source of gaseous oxygen in fluid communication with the cathode. The cathode comprises an oxygen-permeable support bearing carbon nanotubes having at least one open end.

[0013] A rechargeable lithium-oxygen electrochemical cell of the present invention comprises a lithium-containing anode, an oxygen-permeable cathode in fluid communication with an oxygen source (e.g., ambient air), and a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode. The cathode comprises an oxygen-permeable support bearing carbon nanotubes having at least one open end and a nanoparticulate catalyst in contact with the carbon nanotubes. The catalyst is adapted to facilitate the reversible interconversion between oxygen gas and an oxygen anion (e.g., oxide ion, peroxide ion, or both), during charge and discharge of the cell.

[0014] Batteries of the invention comprise two or more electrochemical cells connected in series, in parallel, or both.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The invention includes certain novel features and a combination of parts hereinafter fully described, illustrated in the accompanying drawings, and particularly pointed out in various aspects of the invention, it being understood that various changes in the details may be made without departing from the spirit, or sacrificing any of the advantages of the described invention.

[0016] FIG. 1 depicts (a) a scanning electron micrograph (SEM) and (b) a transmission electron micrograph (TEM) of carbon nanotubes (CNTs) containing a nanoparticulate cobalt metal catalyst within the tubes and/or at the open ends of the tubes (referred to herein as “Co-CNT” for convenience); Panel (c) provides a SEM of a cathode formed from a Ni mesh coated with the Co-CNTs shown in panels (a) and (b); Panel (d) shows energy dispersive X-ray spectroscopy (EDS) mapping of the cathode shown in Panel (c), which confirms the Co-CNT composition, namely the amounts of carbon, cobalt and oxygen.

[0017] FIG. 2 depicts electrochemical discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising the CNTs and a cobalt catalyst; Panel (a) shows the first cycle, and Panel (b) shows the second and third cycles.

[0018] FIG. 3 depicts the electrochemical first and fourth discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising the CNTs and a cobalt catalyst.

[0019] FIG. 4 depicts the electrochemical first, second and third discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising CNTs combined with nanoparticulate MnO₂ and cobalt catalysts.

[0020] FIG. 5 depicts the electrochemical discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising the CNTs combined with a Li₄Ti₅O₁₂ catalyst.

[0021] FIG. 6 depicts the electrochemical discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising about 50 wt % of CNTs and about 50 wt % of a Vinyl fluoride resin (2801) binder.

[0022] FIG. 7 depicts in Panel (a) the SEM and EDS of a nanoparticulate Fe₃O₄ catalyst; Panel (b) depicts the X-ray powder diffraction pattern confirming the Fe₃O₄ phase; and Panel (c) depicts the electrochemical discharge-charge voltage profiles of a Li—O₂ cell having a cathode comprising CNTs and a Fe₃O₄ nanoparticle catalyst.

[0023] FIG. 8 schematically illustrates an embodiment of an electrochemical cell of the invention.

[0024] FIG. 9 schematically illustrates an embodiment of cathode for use in an electrochemical cell of the invention.

[0025] FIG. 10 schematically illustrates an embodiment of a battery of the invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0026] The present invention provides lithium-oxygen (e.g., lithium-air) electrochemical cells and batteries formed from such cells. A lithium-oxygen electrochemical cell of the present invention comprises a lithium-containing anode, an oxygen-permeable cathode, a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode, and a source of gaseous oxygen in fluid communication with the cathode. The cathode comprises an oxygen-permeable support bearing carbon nanotubes having at least one open end.

[0027] A rechargeable lithium-oxygen electrochemical cell of the present invention comprises a cathode that also contains a nanoparticulate catalyst in contact with the CNTs, which is adapted to facilitate the reversible interconversion between oxygen gas and an oxygen anion e.g., oxide ion, peroxide ion, or a combination thereof, during charge and discharge of the cell. One preferred catalyst comprises cobalt metal. Another preferred catalyst comprises a cobalt oxide. Yet other preferred catalysts include nanoparticulate manganese dioxide (MnO₂), ferric oxide (Fe₂O₃), WO₃, CeO₂,

MoO₂, MoO₃, ferric/ferrous oxide (Fe₃O₄), Li₄Ti₅O₁₂ (2Li₂O·5TiO₂), TiO₂ or their mixtures with noble metals such as Pt, Au, Ru and the like. The catalyst can be located at the tip of the carbon nanotubes, within the nanotubes, or intermixed with the carbon nanotubes, nanofibers and grapheme sheets.

[0028] Suitable carbon nanotubes can be obtained by any method known to produce open-ended carbon nanotubes. One such method is described in U.S. Patent Application Publication No. 2010/0178232, which is incorporated herein by reference in its entirety, and which involves thermal decomposition of low density polyethylene in an autogenic pressure reactor in the presence of a metal salt such as a cobalt salt. This method provides CNTs containing nanoparticulate cobalt. Another method of producing CNTs, e.g., from recycled polymeric materials (e.g., LDPE and HDPE) and a catalyst such as Ni, Co, Fe, and oxides thereof, is described in U.S. 2010/0178232. The carbon nanotubes of the electrochemical cells of the invention typically have a average tube diameter in the range of about 50 to about 100 nm, preferably in the range of about 80 to about 90 nm. Typically, the carbon nanotubes have an average length in the range of about 200 nm to about 7 μm, preferably about 1000 nm to about 10 μm. The carbon nanotubes preferably have an average aspect ratio (length-to-diameter) in the range of about 20 to about 100.

[0029] The carbon nanotubes can be intermixed with an inert material, or with another active cathode material, if desired. In some preferred embodiments, the carbon nanotubes are intermixed another porous carbon material, such as carbon black.

[0030] The carbon nanotube-based cathode can include a binder to help maintain the cathode in a particular shape or configuration and to adhere the carbon nanotubes and catalyst, when present, to the support. Any binder that is stable to the electrochemical conditions of a lithium-oxygen battery can be utilized in the present invention. Many such materials are known in the art. One preferred binder is polyvinylidene difluoride (PVdF).

[0031] The support for the cathode can be any gas-permeable material suitable for use in metal-oxygen cells (e.g., materials that are not chemically reactive with oxygen and with typical electrolyte materials under the electrochemical conditions of cell charge and discharge), many of which are well known in the art. In some preferred embodiments, the support comprises a metal mesh (e.g., a nickel mesh). In other embodiments, the support comprises a non-woven fibrous material, such as a glass fiber mat or paper. The carbon nanotubes and optional catalyst can be applied to the support in any way that will provide a thin, even coating on the support (e.g., by spraying, dipping, painting, etc.). For example, the carbon nanotubes, catalyst, and a binder can be suspended in a volatile liquid (e.g., water, an organic solvent, and the like) and then painted onto the surface of the support. The liquid is then evaporated to leave a coating of carbon nanotubes and catalyst on the support surface.

[0032] The anode of the electrochemical cell can be any lithium-containing material suitable for use in lithium-oxygen cells and batteries. Some exemplary materials include metallic lithium, and lithium oxide containing materials that are known to be useful as anodes in lithium-oxygen or lithium ion electrochemical cells.

[0033] The electrochemical cells can include any non-aqueous electrolyte suitable for use in lithium-oxygen (e.g., lithium-air) cells and batteries, many of which are well known in the art. Typically, these non-aqueous electrolytes comprise an inert polar organic liquid, such as an organic carbonate (e.g., dimethyl carbonate, ethylmethyl carbonate, ethylene carbonate, propylene carbonate, and the like), or a polymer-

based gel. The liquid or gel contains a lithium salt (e.g., LiPF₆, LiB(C₂O₄)₂, LiBF₂C₂O₄, LiBF₄, LiPF₂(C₂O₄)₂, LiPF₄C₂O₄, and the like) that is soluble in the liquid or gel. The following examples describe the principles of the invention as contemplated by the inventors, but they are not to be construed as limiting examples.

Example 1

[0034] Carbon nanotubes containing a nanoparticulate cobalt catalyst (Co-CNTs) were prepared via thermal decomposition of low density polyethylene (LDPE) containing about 20 percent by weight (wt %) cobalt acetate (CoAc; Co(C₂H₄O₂)₂) catalyst in a sealed autoclave (made up of Haynes 230 alloy) under a nitrogen atmosphere. The autoclave was heated at about 700° C. to about 750° C. for about 2 to 3 hours followed by gradual cooling. The mixture of LDPE and catalyst in the autoclave generated about 50 pounds-per-square inch (psi) of pressure upon heating up to about 680° C., which increased to about 1000 psi at about 700° C. A chemical reaction took place under the autogenic pressure generated in the autoclave during the thermolysis of LDPE in the presence of CoAc, leading to the growth of Co-CNTs in about 40% yield.

[0035] Panel (a) of FIG. 1 shows a SEM of these carbon nanotubes (CNTs). The dark dots at the tip of the carbon nanotubes in the SEM are the Co catalyst that was converted to nano-sized cobalt metal particles. The SEM demonstrates that the diameters of the multiwalled carbon nanotubes are about 80 nm. A nanotube length of more than a micron was obtained within about 2 hours of initiating the heating of the autoclave, demonstrating that the growth of the Co-CNTs is a function of reaction time. In comparison with the known methods for the fabrication of CNTs, this particular method appears to be one of the easiest, least expensive and most environmentally friendly ways to produce CNTs. The Co-CNTs are grown randomly and the cobalt nanoparticles are trapped at the tip or inside of the nanotubes. The as-prepared CNTs possessed about 11 wt % of encapsulated cobalt, confirmed by EDS analysis.

[0036] Although the SEMs taken using secondary electrons demonstrate the one-dimensional fiber-like nanotubes, a transmission electron micrograph (TEM) further confirmed the hollow tubular structures of the CNTs, as shown in FIG. 1, Panel (b), which also confirmed that the one ends of the carbon nanotubes are open. Panel (c) of FIG. 1 provides a TEM of a cathode formed by painting a slurry of another sample of Co-CNTs prepared in the same manner) and PVdF binder on a Ni mesh. N-Methyl-2-pyrrolidone was the solvent used to make the slurry of Co-CNT and PVdF. The cathode coating comprised about 75 wt % carbon nanotubes and about 14 wt % Co catalyst, and about 12 wt % PVdF binder. Panel (d) of FIG. 1 shows the EDS signal obtained along the arrow shown in Panel (c), confirming the carbon and cobalt composition of the nanotubes.

Example 2

[0037] The coated cathode described in Example 1 was evaluated in a lithium-oxygen electrochemical cell with a lithium metal foil as the anode, and an electrolyte consisting of 1.2M LiPF₆ in a 3:7 (w/w) mixture of ethylene carbonate (EC) and ethylmethyl carbonate (EMC), between the anode and the cathode. The cells were assembled in helium-filled glove box. After bringing the lithium-air cell out of the glove box, it was purged with oxygen, and then filled with O₂ at about 20 psi pressures. FIG. 2 depicts the electrochemical voltage profiles that were obtained by galvanostatically

cycling the cells between about 1.5 V (discharge) and 4.7 V (charge). The observed current density was about 35 mA/g, at a C/20 rate. Panel (a) shows the first cycle, while Panel (b) shows the second and third cycles. The observed discharge capacity was about 300 mAh/g, and the observed charge capacity was about 800 mAh/g. The average discharge voltage was about 2.5 V, and the average charge voltage was about 4.4 V. The electrochemical charge/discharge voltage profiles of the cell exhibited reversibility, and demonstrated the utility of the cobalt-containing CNT cathode. With further cycling, the discharge and charge capacities show better coulombic efficiency. The second discharge capacity was about 470 mAh/g, and the second charge capacity was about 500 mAh/g.

Example 3

[0038] A charge-discharge cycling evaluation was also carried out on cells of the same construction described in Example 2. The cell was galvanostatically discharged and charged between 1.5 V and 4.7 V, respectively. The observed current density was about 75 mA/g at a C/4 rate, as shown in FIG. 3. The data in FIG. 3 were obtained using a cathode analogous to the one described in Example 2 with C/4 fast cycling rate; the figure depicts discharge and charge cycle numbers two and three.

Example 4

[0039] Another cathode was prepared on a nickel mesh, with a coating containing about 15 wt % electrolytic MnO_2 catalyst, about 35.5 wt % Co-CNTs comprising 4.5 wt % Co nanoparticles, about 30 wt % carbon black, and about 15 wt % PVdF binder. The CNTs preparation and dimensions are discussed in Example 1. The cathode was evaluated in a cell of the same design as described in Example 1, as well. FIG. 4 depicts the observed electrochemical voltage profiles, galvanostatically discharged and charged between 1.5 and 4.7 V, respectively. The observed current density was about 10 mA/g, at a C/90 rate. The first cycle discharge capacity was about 730 mAh/g at an average voltage of about 2.8 V, and the first charge capacity was about 400 mAh/g at an average voltage of about 4.3 V.

Example 5

[0040] Another cathode was prepared comprising a nickel mesh coated with about 24 wt % of CNTs (purchased from Stream Chemicals), about 33 wt % KYNAR® 2801 vinyl fluoride resin binder, and about 42 wt % of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ catalyst (40 nm), with a propylene carbonate (PC) plasticizer. The CNTs had a diameter of about 50 nm and a length of several micrometers. FIG. 5 depicts the electrochemical voltage profiles that were carried out in a cell of similar design to that described in Example 2, but with an electrolyte consisting of 1M LiPF_6 in PC. The cell was cycled between 1.5 V and 4.7 V. The observed current density was about 35 mA/g, at a C/20 rate.

Example 6

[0041] A cathode comprising a coating of 50 wt % CNTs (purchased from Stream Chemicals) and 50 wt % KYNAR® 2801 vinyl fluoride resin binder coated on glass fiber filter paper was evaluated in a cell of similar design to that described in Example 2, with a lithium foil anode and an electrolyte comprising 1M LiPF_6 in a PC (pressurized with 20

psi of oxygen). The CNTs had a diameter of about 50 nm and a length of several micrometers. FIG. 6 depicts the electrochemical voltage profiles that were obtained with this cell. An average voltage of about 2.6 V vs. Li^+/Li was observed. This value is at a higher potential than the previously reported value of 2.33 V for an electrode utilizing carbon black, thus demonstrating a higher specific energy or less overpotential for the cathodes comprising CNTs versus conventional high-surface area carbon black. The discharge process was stopped at about 2.2 V. The specific capacity per gram carbon in this example was about 1352 mAh/g at a C/25 rate or 53 mA/g at C/1.

Example 7

[0042] A cathode was composed of about 33 wt % CNTs, about 33 wt % Fe_3O_4 nanoparticles, and about 33 wt % KYNAR® 2801 vinyl fluoride resin binder, coated on a glass fiber filter paper was prepared as described above. Panel (a) of FIG. 7 depicts the SEM of nanoparticulate Fe_3O_4 catalyst, well dispersed among carbon nanotubes. The EDS in Panel (a) confirms the presence of Fe and carbon in the material. The XRD measurement at Panel (b) confirms the purity of Fe_3O_4 nanoparticles. Panel (c) depicts the electrochemical voltage profiles that were obtained in lithium air cells using a lithium metal foil as anode. The cell contained an electrolyte composed of 1M LiPF_6 in a PC, and was pressurized with about 20 psi of oxygen prior to discharge and charge cycling between 1.5 to 4.7 V. The observed current density was about 25 mA/g at a C/25 rate.

[0043] FIG. 8 provides schematic representation of a typical electrochemical cell of the present invention. The cell comprises an anode 12 and an oxygen-permeable cathode 16 with a non-aqueous electrolyte 14 there between. Cathode 16 comprises carbon nanotubes that optionally include a catalyst material. Electrolyte 14 comprises a non-aqueous liquid, such as an organic carbonate (e.g., dimethyl carbonate, ethylene carbonate, propylene carbonate, and the like) containing a lithium salt (e.g., LiPF_6).

[0044] FIG. 9 illustrates one form of oxygen-permeable cathode 16, which comprises a porous support 18 (e.g., a nickel metal mesh or a glass fiber mat or paper) having a coating 20 comprising the carbon nanotubes and any catalyst that may be included in the cathode.

[0045] FIG. 10 illustrates a battery 30 comprising a plurality of electrochemical cells 10 arranged in series and in parallel.

[0046] The use of the terms “a” and “an” and “the” and similar referents in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. The terms “comprising,” “having,” “including,” and “containing” are to be construed as open-ended terms (i.e., meaning “including, but not limited to,”) unless otherwise noted. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein. All methods described herein can be performed in any suitable order unless otherwise indicated herein or otherwise clearly contradicted by context. The use of any and all examples, or exemplary language (e.g., “such as”) provided herein, is intended merely to better illuminate the invention and does

not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

[0047] Preferred embodiments of this invention are described herein, including the best mode known to the inventors for carrying out the invention. Variations of those preferred embodiments may become apparent to those of ordinary skill in the art upon reading the foregoing description. The inventors expect skilled artisans to employ such variations as appropriate, and the inventors intend for the invention to be practiced otherwise than as specifically described herein. Accordingly, this invention includes all modifications and equivalents of the subject matter recited in the claims appended hereto as permitted by applicable law. Moreover, any combination of the above-described elements in all possible variations thereof is encompassed by the invention unless otherwise indicated herein or otherwise clearly contradicted by context.

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

1. A lithium-oxygen electrochemical cell comprising a lithium-containing anode, an oxygen-permeable cathode, a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode, and a source of gaseous oxygen in fluid communication with the cathode; the cathode comprising an oxygen-permeable support bearing carbon nanotubes having at least one open end.

2. The electrochemical cell of claim 1 wherein the source of oxygen is ambient air.

3. The electrochemical cell of claim 1 wherein the gas-permeable support comprises a nickel mesh.

4. The electrochemical cell of claim 1 wherein the gas-permeable support comprises a glass fiber mat.

5. The electrochemical cell of claim 1 wherein the cathode comprises a binder to adhere the carbon nanotubes to the support.

6. The electrochemical cell of claim 1 wherein the cathode comprises a nanoparticulate catalyst in contact with the carbon nanotubes; the catalyst being adapted to facilitate the reversible interconversion between oxygen gas and an oxygen anion selected from oxide ion, peroxide ion, and a combination thereof, during charge and discharge of the cell.

7. The electrochemical cell of claim 6 wherein the catalyst comprises nanoparticles of a metal, a metal oxide, or a combination thereof.

8. The electrochemical cell of claim 7 wherein the catalyst comprises nanoparticles of at least one material selected from the group consisting of cobalt, manganese, iron, and an oxide of any of the foregoing.

9. The electrochemical cell of claim 7 wherein the catalyst comprises $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

10. The electrochemical cell of claim 7 wherein at least some of the nanoparticles are located at the open end of a carbon nanotube, within the carbon nanotubes, or both.

11. The electrochemical cell of claim 1 wherein the carbon nanotubes have an average tube diameter in the range of about 80 to about 90 nm.

12. The electrochemical cell of claim 1 wherein the carbon nanotubes have an average length in the range of about 200 nm to about 7 μm .

13. The electrochemical cell of claim 1 wherein the carbon nanotubes have an average length-to-diameter aspect ratio in the range of about 20 to about 100.

14. The electrochemical cell of claim 1 wherein the non-aqueous liquid comprises an organic carbonate.

15. The electrochemical cell of claim 1 wherein the lithium salt comprises LiPF_6 .

16. The electrochemical cell of claim 1 wherein the lithium-containing anode comprises metallic lithium.

17. The electrochemical cell of claim 1 wherein the lithium-containing anode comprises lithium metal.

18. A rechargeable lithium-oxygen electrochemical cell comprising a lithium-containing anode, an oxygen-permeable cathode in fluid communication with ambient air, and a non-aqueous electrolyte comprising a lithium salt in a non-aqueous liquid between the anode and the cathode; the cathode comprising an oxygen-permeable support bearing carbon nanotubes having at least one open end, and a nanoparticulate catalyst in contact with the carbon nanotubes; wherein the catalyst is adapted to facilitate the reversible interconversion between oxygen gas and an oxygen anion selected from oxide ion, peroxide ion, and a combination thereof, during charge and discharge of the cell.

19. The electrochemical cell of claim 18 wherein the catalyst comprises nanoparticles of a metal, a metal oxide, or a combination thereof.

20. The electrochemical cell of claim 18 wherein the catalyst comprises nanoparticles of at least one material selected from the group consisting of cobalt, manganese, iron, and an oxide of any of the foregoing.

21. The electrochemical cell of claim 18 wherein the catalyst comprises $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

22. The electrochemical cell of claim 18 wherein the carbon nanotubes have an average tube diameter in the range of about 50 to about 100 nm.

23. The electrochemical cell of claim 18 wherein the carbon nanotubes have an average length in the range of about 200 nm to about 7 μm .

24. The electrochemical cell of claim 18 wherein the carbon nanotubes have an average length-to-diameter aspect ratio in the range of about 20 to about 100.

25. The electrochemical cell of claim 18 wherein the non-aqueous liquid comprises an organic carbonate.

26. The electrochemical cell of claim 18 wherein the lithium salt comprises LiPF_6 .

27. The electrochemical cell of claim 18 wherein the lithium-containing anode comprises metallic lithium.

28. The electrochemical cell of claim 18 wherein the lithium-containing anode comprises lithium metal.

29. A battery comprising a plurality of electrochemical cells of claim 1 arranged in parallel, in series, or both.

30. A battery comprising a plurality of electrochemical cells of claim 18 arranged in parallel, in series, or both.

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