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(71) Applicant *(for all designated States except US)*: **COLORADO STATE UNIVERSITY RESEARCH FOUNDATION** [US/US]; 601 S. Howes, 410 University Services Center, Fort Collins, CO 80521 (US).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **PRIETO, Amy L.** [US/US]; 4227 Lookout Lane, Fort Collins, CO 80526 (US). **JOHNSON, Derek C.** [US/US]; 1447 Mallard Drive, Johnstown, CO 80534 (US). **MOSBY, James M.** [US/US]; 3107 Silverthorne Drive, Fort Collins, CO 80526 (US).

(74) Agents: **FREUND, Samuel M.** et al.; Cochran Freund & Young LLC, 2026 Caribou Drive, Suite 201, Fort Collins, CO 80525 (US).

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— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

[Continued on next page]

(54) Title: SELF-ASSEMBLY OF COATINGS UTILIZING SURFACE CHARGE

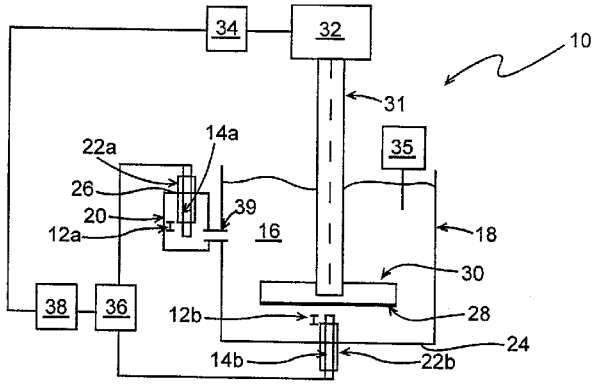

FIG. 1

(57) Abstract: An apparatus measuring the isoelectric pH for materials deposited onto and in contact with an electrode surface, and a method for utilizing the isoelectric pH to form self-assembled layers of nanometer thickness on the material. Forming such layers utilizing data information obtained about the isoelectric pH values of the substrate and the coating is advantageous since the growth of the coating is otherwise self-limiting. When the coating is self-limiting, once the surface charge has been neutralized there is no longer a driving force for the solid electrolyte coating thickness to increase. Thus, uniform coatings without pinhole defects will be produced because a local driving force for assembly will exist if any bare electrode material is exposed to the solution. The present self-assembly procedure, when combined with electrodeposition, may be used to increase the coating thickness of self-assembled layers for use in solid-state batteries.

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SELF-ASSEMBLY OF COATINGS UTILIZING SURFACE CHARGE

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present application claims the benefit of United States Provisional Patent Application Number 61/318,068 for "Isoelectric Determination Apparatus and Use In The Fabrication Of Batteries" by Amy L. Prieto et al., which was filed on March 26, 2010, the entire contents of which is hereby specifically incorporated by reference herein for all that it discloses and teaches.

BACKGROUND OF THE INVENTION

[0002] Secondary lithium-ion batteries have found multiple applications in portable electronics where high charge and discharge rates are not required to improve performance. However, high rates become important when considering the use of rechargeable lithium-ion batteries in the transportation industry. Electrode materials having irregular surfaces resulting in high interfacial surface areas and short characteristic diffusion lengths are expected to provide batteries with high power densities. Producing uniform, defect-free surface coatings for such electrodes for lithium-ion batteries having electrically insulating, but ionically conducting electrolytic separator materials on the nanoscale (for either the negative and/or positive electrodes), has proved to be difficult.

SUMMARY OF THE INVENTION

[0003] Self-assembly of surface coatings using electrostatic forces has not been widely pursued for high surface area structures in the past because of the difficulty in determining the isoelectric pH; that is, the pH at which there is no net surface charge.

[0004] Embodiments of the present invention overcome the disadvantages and limitations of the prior art by providing an apparatus and method for measuring the isoelectric pH of materials that can be deposited or otherwise affixed on and in electrical contact with an electrode surface.

[0005] It is further an object of embodiments of the present invention to provide a method utilizing the isoelectric pH of a material to form a self-assembled layer having nanometer thickness.

[0006] Another object of embodiments of the present invention is to provide a method for increasing the thickness of the self-assembled layer.

[0007] Additional objects, advantages and novel features of the invention will be set forth in part in the description which follows, and in part will become apparent to those skilled in the art upon examination of the following or may be learned by practice of the invention. The objects and advantages of the invention may be realized and attained by means of the instrumentalities and combinations particularly pointed out in the appended claims.

[0008] To achieve the foregoing and other objects, and in accordance with the purposes of the present invention, as embodied and broadly described herein, the apparatus for determining the isoelectric pH of a material, hereof, includes: a first chamber adapted for containing a solution having a chosen pH including: a circular disk having an axis, a first face, and an opposing second face onto which the material is disposed; a shaft attached to the first face of the disk; a first reference electrode disposed in the vicinity of the second face of the disk and in the vicinity of the axis; and a hollow tube affixed to a wall of the first chamber at an orifice therein; a second chamber in fluid communication with the first chamber through the tube, including a second reference electrode; means for rotating the shaft at a chosen rate; and means for measuring the potential difference between the first reference electrode and the second reference electrode.

[0009] In another aspect of the present invention and in accordance with its objects and purposes, the method for determining the isoelectric pH of a material, hereof, includes: affixing the material onto one face of a circular disk having an axis of rotation and disposed in a solution having a selected pH value in a first chamber; rotating the disk at a chosen rate; measuring the potential difference between a first reference electrode disposed in the vicinity of both the axis of the disk and the material and a second reference electrode disposed in a second chamber in fluid communication through a tube with said first chamber; adjusting the pH of the solution such that the potential difference is approximately equal to the resting potential difference between the first reference electrode and the second reference electrode; and measuring the pH of the solution when the potential difference is approximately equal to the resting potential difference.

[0010] In yet another aspect of the present invention and in accordance with its objects and purposes, the method for depositing a coating material onto a substrate,

hereof, includes: determining the isoelectric pH of the substrate; determining the isoelectric pH of the coating material; preparing a solution of the coating material having a pH between the isoelectric pH of the substrate and the isoelectric pH of the coating material; and immersing the substrate into the solution for a time sufficient for self-assembly of the coating material onto the substrate.

[0011] Benefits and advantages of embodiments of the present invention include, but are not limited to, providing a method for measuring the isoelectric pH of materials whereby the pH may be determined for which the electrostatic formation of a solid electrolyte coating on a substrate is advantageous since the growth of the coating is self-limiting because once the surface charge has been neutralized there is no longer a driving force for the solid electrolyte coating thickness to increase, and since uniform coatings without pinhole defects will be produced because a local driving force for assembly will exist if any bare electrode material is exposed to the solution. The present self-assembly procedure, when combined with electrodeposition, may be used to increase the coating thickness. Self-assembly, with or without additional electrodeposition, allows intimate contact between the anode, electrolyte and cathode which is required for successful application to solid-state batteries, as an example.

BRIEF DESCRIPTION OF THE DRAWINGS

[0012] The accompanying drawings, which are incorporated in and form a part of the specification, illustrate the embodiments of the present invention and, together with the description, serve to explain the principles of the invention. In the drawings:

[0013] FIGURE 1 is a schematic representation of an embodiment of the present apparatus for determining the isoelectric pH.

[0014] FIGURE 2 is a graph of the measured potential difference as a function of pH for Cu_2Sb in a 1 mM KCl solution using the apparatus of FIG. 1.

[0015] FIGURE 3 is a graph of the capacity retention in percent as a function of the number of charging and discharging cycles for a Cu_2Sb anode and $LiCoO_2$ cathode in 1M $LiClO_4$ in a solution of ethyl carbonate, dimethyl carbonate and diethyl carbonate in a 1:1:1 ratio, for coated and uncoated Cu_2Sb.

[0016] FIGURE 4 is a schematic representation of an embodiment of an electrophoretic apparatus used to increase the deposited coating thickness.

[0017] FIGURE 5 is a graph of the current as a function of the applied potential, showing cyclic voltamograms for Cu_2Sb in an $AlPO_4$ deposition solution.

[0018] FIGURE 6 shows a survey X-Ray Photoelectron Spectrum (XPS) for electroplated Cu_2Sb, and high-resolution spectra for the copper 2p, phosphorous 2p, and aluminum 2p regions.

[0019] FIGURE 7 shows a survey XPS spectrum of a coating formed with a positive applied potential after the self-assembly process had been completed, and high-resolution spectra for the copper 2p, phosphorous 2p, and aluminum 2p regions for electroplated Cu_2Sb having a self-assembled $AlPO_4$ coating.

[0020] FIGURE 8 shows a survey XPS spectrum of a coating formed with a negative applied potential after the self-assembly process had been completed, and high-resolution spectra for the copper 2p, phosphorous 2p, and aluminum 2p regions for electroplated Cu_2Sb having a self-assembled $AlPO_4$ coating.

DETAILED DESCRIPTION OF THE INVENTION

[0021] Briefly, embodiments of the present invention include an apparatus and method for measuring the isoelectric pH for materials deposited on or otherwise affixed to and in contact with an electrode surface. Another embodiment of the invention is to provide a method for utilizing the isoelectric pH to form nanometer thickness, self-assembled layers on such materials. If the self-assembled thickness proves to be insufficient, an apparatus and method is provide for increasing the layer thickness by utilizing electrochemical methods in cooperation with self-assembly to obtain the desired properties.

[0022] Reference will now be made in detail to the present embodiments of the invention, examples of which are illustrated in the accompanying drawings. In the FIGURES, similar structure will be identified using identical reference characters. Turning now to FIG. 1, a schematic representation of an embodiment of the present apparatus, **10**, for determining the isoelectric pH is illustrated. Lengths of about 1 mm, **12a**, **12b**, of silver wire reference electrodes, **14a**, **14b**, are coated with AgCl and exposed to aqueous solution, **16**, contained in cylindrical chamber, **18**, having rectangular secondary chamber, **20**, in fluid communication therewith. Clearly, other chamber geometries may be employed. Leak-proof, insulating material, **22a**, **22b**, covers silver wires **14a**, **14b** as these wires passes through walls, **24**, and **26**, of chamber **18** and secondary chamber **20**. Material to be coated, **28**, is affixed to

circular disk, **30**, mounted on shaft, **31**, which is supported and turned by motor, **32**, controlled by motor controller, **34**. Means, **35**, for measuring the pH of solution **16** are provided. Voltmeter or potentiometer, **36**, measures the potential difference between AgCl-coated silver wires **14a** and **14b**, which is recorded on data processor, **38**, which also controls motor controller **34**.

[0023] Since the isoelectric pH is not a function of the material morphology or final geometric configuration, the use of a planar electrode surface in the apparatus is advantageous. Chamber **18** is filled with a solution containing a supporting electrolyte, for example, potassium chloride (KCl). Generally, the solvent will be water, as pH is most applicable to aqueous solutions. However, other solvents, or combinations of solvents, may be used, including aqueous solutions with other water-miscible solvents. Electrolyte solutions not containing water may also be employed where a supporting electrolyte has sufficient solubility to produce adequate conductivity for the electrolyte system; that is, the supporting electrolyte concentration must be sufficiently high that the solution resistance does not affect the potential readings of the two reference electrodes **14a** and **14b**. Electrolyte concentration must be sufficiently low such that when reference electrode **14b** is placed in the vicinity of material to be coated **28**, the aggregation of charged species in solution (often referred to as the diffuse or boundary layer), having opposite charge to that of the surface of material **28**, can be detected. Any electrolyte species that, when dissolved, meets these criteria may be used. The concentration of the electrolyte is generally between 0.001 and 100 mM. It should be noted, however, that the electrolyte concentration chosen, even within this range, will affect the ability to detect the aggregation of charged species near the surface of the material of interest.

[0024] Reference electrode **14b** is disposed in the center of chamber **18**. While other reference electrodes may be used, an Ag wire having an electrodeposited AgCl film was used for the present EXAMPLE. Insulating jacket **22b** surrounding Ag wire **14b** assures that only a small portion **12b** (approximately 1 mm) of reference electrode **14b** is exposed to the liquid containing the supporting electrolyte **16**. The area of the electroactive surface of material to be coated **28** exposed to solution **16** is chosen to be sufficiently large as to minimize edge effects. A minimum area is on the order of approximately 1 cm^2 for a circular disk. The maximum diameter of the electrode structure (disk plus material to be coated) was chosen to be smaller than

the diameter of the inner wall surface of the main chamber by approximately 20%, assuming a cylindrical chamber, to eliminate unwanted effects from solution interaction with the chamber walls. While the gap between rotating disk **30** and the main chamber inner wall surface can be made larger, a substantially smaller gap may adversely affect the measurements. The material to be coated **28** may have a diameter of about 5 cm.

[0025] Once the disk has been prepared, it is attached to shaft **31** which may be rotated by motor **32** at speeds between zero and tens of thousands of rpm. Faster spin rates facilitate the measurements as a larger potential drop is induced between the reference electrodes as the spin rate is increased. The disk/shaft assembly is placed in chamber **18** assuring that the center of disk **30** is directly over reference electrode **14b** at a distance $\leq$ 1 mm, the reference electrode being placed as close as possible to spinning disk **30** such that the aggregation of charged species on material surface **28**, which will be different than the equilibrium distribution in the bulk fluid, induces a potential difference between the two reference electrodes which can readily be detected. The reference electrode need not penetrate the diffuse layer, however.

[0026] Secondary chamber **20** in fluid communication with chamber **18** through tube, **39**, permits solution **16** from chamber **18** to enter and leave, contains second reference electrode **14a**. Openings in wall **26**, not shown in FIG. 1, permit pressure equalization between chamber **18** and secondary chamber **20**, thereby facilitating fluid movement between the two chambers. The secondary chamber isolates reference electrode **14a** from the convective mass transfer of ions dissolved in solution **16** that is induced by the spinning disk assembly. Reference electrode **14a** may have the same construction as the reference electrode **14b**, ensuring that there is approximately zero potential difference between the electrodes before disk **30** is placed in solution. However, reference electrode **14a** may be based on any redox chemistry for which the potential difference between that electrode and the reference electrode **14b** is known (hereinafter referred to as the "resting potential difference"), and *vice versa*, as long as both reference electrodes act identically with respect to voltage changes in the spatial location of charged species in solution. In practice, less than about 0.1 mV resting potential difference is advantageous.

[0027] To determine the isoelectric pH of material **18**, using apparatus **10** of FIG. 1 hereof, electrolyte solutions are prepared at different pH values. The disk assembly was spun at a chosen angular velocity in a solution with a selected pH and the potential difference between reference electrodes **14a** and **14b** was measured using a digital multimeter, as an example of an effective potential difference measurement apparatus. In general, higher spin rates provide better results, but rates > 0 rpm to about 10,000 rpm are effective. Since the measured potential difference is dependent on the spin rate, measurements may be taken as a function of spin rate at a given pH to improve the accuracy of the data. Such measurements are repeated for solutions having different pH values until the measured potential difference between the reference electrodes is equal to zero or equal to the resting potential difference for reference electrodes having dissimilar redox potentials. This is the isoelectric pH of the material. A single solution where the pH is adjusted by small additions of acid, base, buffer, etc. between measurements, may also be used.

[0028] Returning to apparatus **10** of FIG. 1, as stated hereinabove, reference electrode **14a** disposed in secondary chamber **20** is separated from solution **16** in chamber **18** by tube **39** such that the ions in solution from both chambers can communicate without the influence of convective mass transfer. This has resulted in measured potential differences an order of magnitude higher than what is typically reported by Paul J. Sides and James D. Hoggard in "Measurement of the Zeta Potential of Planar Solid Surfaces by Means of a Rotating Disk," Langmuir 2004, **20**, 11493-11498. As an example, Sides and Hoggard reports differences on the order of 0.1 mV; whereas, differences on the order of a millivolt (FIG. 5 of Sides and Hoggard) are observed by Sides and Hoggard in only the most advantageous conditions, and for materials with high zeta potentials. Potential differences measured using apparatus **10** of FIG. 1 hereof are typically on the order of mV, as may be observed in FIG. 2, hereof, which is a graph of the measured potential difference as a function of the pH of the solution for Cu_2Sb as material **28**. The typical measured potential differences between the two reference electrodes reported by Side and Hoggard are difficult to distinguish from noise; thus, the embodiment described herein alleviates the most severe constraint of Sides and Hoggard, that the measurements are recorded at solution concentrations of less than about 1 mM. These solutions generate less than a 0.1 mV difference between the

reference electrodes, which is difficult to quantitatively distinguish from noise for such measurements.

[0029] Another embodiment of the present invention is to use the measured isoelectric pH for the deposition of an electrolyte separation layer. Once the isoelectric pH for a material has been determined by the above-described procedure, or obtained from other sources thereof, solid-state ceramics which have shown to be electrically insulating but ionically conducting at nanoscale thicknesses may be self-assembled onto both anode and cathode materials. Example materials are $AlPO_4$, Al_2O_3, ZnO, and Bi_2O_3. $AlPO_4$ has been shown by other investigators to function as a solid-state electrolyte for lithium-ion batteries. Self-assembly methodology includes: (1) dissolving the appropriate precursors for the solid-state electrolyte in an aqueous solution; (2) adjusting the solution pH so that it is between the isoelectric pH of the electrode material, and that for the desired solid-state electrolyte, for which the isoelectric pH values are available in the literature; and (3) contacting the electrode material which can now be of any morphology and in any geometric configuration with the solution. The driving force for the self-assembly is electrostatics, where the overall net charge on the surface of the electrode material is opposite to the charge on the surface of the solid-state electrolyte. The above-mentioned ceramic and oxide materials can exist in solution as a colloidal suspension, and the surface charge of the material is controlled by the solution pH. Selection of the solution pH approximately midway between the isoelectric pH electrode material and that of the desired solid-state electrolyte material (coating material) generates coatings having the strongest binding to the substrate (the electrode material). For some applications, it may be useful to select a pH other than midway between the isoelectric pH of the two materials in order to vary the thickness of the film, despite the loss of some adhesion strength of the coating to the electrode. Generally however, the solution pH should be somewhere between the respective isoelectric pH values. Coatings typically form in approximately 30 min., although shorter times are possible if electrostatic equilibrium has been reached.

[0030] Electrostatic formation of a solid electrolyte coating is advantageous. First, the growth of the coating is self-limiting because once the surface charge has been neutralized there is no longer a driving force for the solid electrolyte coating thickness to increase. Anticipated thicknesses for the resulting coatings using this methodology are between about 1 and 20 nm (typically, on the order of 5 nm), and

can be somewhat adjusted by choosing the pH and/or applied potential (as will be discussed hereinbelow). Second, uniform coatings without pinhole defects will be formed because a local driving force for assembly will exist if any bare electrode material is exposed to the solution. The results of self-assembled $AlPO_4$ deposited using the apparatus and method disclosed hereinabove demonstrate that uniform coatings having mechanical stability can be formed at ambient pressure and temperature from aqueous solutions. This apparatus and procedure can be used to coat a broad range of materials with varying morphologies and surface areas with coatings that can be tailored to provide the mechanical, electrical, and/or ionic conductivity properties of interest.

[0031] As will be set forth in detail in the EXAMPLES hereinbelow, if the thickness obtained from self-assembly is insufficient to stop electron tunneling or is otherwise insufficiently insulating, a slight overpotential (generally in the range between about one millivolt and about one volt, but typically between 10 and 100 mV) can be applied to increase the thickness of the coating through an electrodeposition procedure. Chronoamperometry or a pulsed chronoamperometry is expected to initiate an electrophoretic mechanism for the above-mentioned ceramics. Other electrodeposition techniques may also prove to be effective.

[0032] Having generally described embodiments of the present invention, the following example provides additional details.

EXAMPLE 1

[0033] Using electrodeposition, Cu_2Sb (an anode material for lithium-ion batteries) was deposited on a copper circular disk with a diameter of approximately 5 cm in accordance with J.M. Mosby and A.L. Prieto, Direct Deposition of Cu_2Sb for Lithium-Ion Battery Anodes," J. Am. Chem. Soc. 2008, **130**, 10656-10661. A stainless steel shaft was connected to the disk and installed in apparatus **10** of FIG. 1, hereof. The isoelectric pH of the Cu_2Sb was determined using 1 mM KCl as the supporting electrolyte, Ag/AgCl as the reference electrodes, and a spin rate of approximately 750 rpm. The pH of the solution was controlled by adding either dilute hydrochloric acid to lower the pH or dilute ammonium hydroxide to increase the pH. Other reagents may be employed to adjust the solution pH. The isoelectric pH of Cu_2Sb was determined to be approximately 7.5 (FIG. 2, hereof).

[0034] The reported isoelectric pH reported for $AlPO_4$ is 4.7 (See, e.g., J. Liu and A. Manthiram, Understanding the Improvement in the Electrochemical Properties of

Surface Modified 5 V $LiMn_{1.42}Ni_{0.42}Co_{0.16}O_4$ Spinel Cathodes in Lithium-Ion Cells," Chem. Mater. 2009 **21**, 1695-1707). Therefore, the pH of the electrodeposition solution is about 6.1, the midpoint between the isoelectric pH of $AlPO_4$ and Cu_2Sb. This solution pH assures the maximum magnitude of opposite surface charges on the $AlPO_4$ and Cu_2Sb to promote self-assembly since, as the solution pH becomes increasingly positive, that is, more basic, when compared to the isoelectric pH, the magnitude of the net surface charge becomes increasingly negative. Conversely, when the solution pH becomes increasingly negative, that is, more acidic, the magnitude of the net surface charge becomes increasingly positive.

[0035] $AlPO_4$ was coated onto Cu_2Sb thin films that had been electroplated onto copper substrates by self-assembly in a solution described in EXAMPLE 2, hereof including approximately 2 mM of $NH_4H_2PO_4$ (ammonium phosphate monobasic), 1.8 mM of $Al(NO_3)_3 \cdot 9\ H_2O$ (aluminum nitrate nonahydrate), and the pH was adjusted to 6.1 using NH_4OH (ammonium hydroxide). The concentrations of the two precursors were in an approximately 1:1 molar ratio of $NH_4H_2PO_4$ to $Al(NO_3)_3 \cdot 9\ H_2O$, and in millimolar concentrations, in order to avoid agglomeration of the colloids once the pH is adjusted.

[0036] X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) techniques were used to confirm that $AlPO_4$ self assembly onto the Cu_2Sb had occurred. Although XPS peaks from Al and P confirm that $AlPO_4$ had self-assembled, Sb and Cu XPS peaks were observed to also be present, indicating a thin $AlPO_4$ layer. Negative electrodes having bare Cu_2Sb, and Cu_2Sb coated with self-assembled AlP_{O4} were tested in full cells with a $LiCoO_2$ cathode based positive electrode in a liquid electrolyte consisting of 1M $LiClO_4$ in ethylene carbonate (EC), dimethyl carbonate (DMC) and diethyl carbonate (DEC) in a (1:1:1) ratio by volume. The negative electrode modified with $AlPO_4$ showed much better capacity retention than the bare negative electrode during cycling as shown in FIG. 3, indicating that self-assembled $AlPO_4$ provides mechanical stability during cycling, thereby reducing the capacity loss that is found from material pulverization and material loss from volume expansion and other electrochemical processes associated with cycles of charging and discharging. The solid squares and circles of FIG. 3 show the charge and discharge capacity retention of the cell with the negative electrode comprising Cu_2Sb covered with self-assembled $AlPO_4$, respectively, while the open boxes and circles

show the charge and discharge capacity retention for cells having bare Cu_2Sb anodes, respectively. Cells were charged and discharged between 2.75 and 3.35 V.

[0037] To ensure that the $AlPO_4$ coating was robust, SEM images and EDS spectra were collected after electrochemical cycling. SEM images of uncoated Cu_2Sb films electrodeposited onto a copper substrate before electrochemical cycling showed the cubic morphology of the Cu_2Sb, while SEM images of a Cu_2Sb electrodeposited film coated with $AlPO_4$ by self-assembly clearly showed the $AlPO_4$ coating. To establish the presence of the aluminum and phosphorous in the coated Cu_2Sb, and the absence of these elements in the uncoated Cu_2Sb, EDS spectra of the respective films were collected. EDS spectra of the uncoated Cu_2Sb confirmed the presence only of copper and antimony with trace amounts of oxygen and carbon due to a thin oxide layer, and graphitic carbon on the Cu_2Sb surface, respectively. The EDS spectra for the $AlPO_4$ coated Cu_2Sb verified the presence of aluminum and phosphorous in addition to the elements identified for the uncoated film. The observed presence of chlorine is due to residual lithium perchlorate, $LiOCl_4$, from the electrochemical cycling experiments.

EXAMPLE 2

[0038] The combination of the self-assembly procedure described hereinabove with electrodeposition to increase the coating thickness, is now described with a Cu_2Sb substrate coated with $AlPO_4$ as an example.

[0039] In order to increase the solid electrolyte coating thickness using an electrodeposition procedure, the bare electrode material is physically attached to a current collector, such as copper foil. The self-assembled coating is then added using the above-described procedure. Once self-assembly is complete, a counter and reference electrode may be placed in the solution and the electrode material attached to the current collector is made the working electrode. A potential is then applied to the working of the correct polarity with respect to the open circuit potential. The potential polarity will be specific to the electrode and solid electrolyte material, and is applied until the current decays to a desired value, most often approximately zero. The magnitude and polarity of the applied potential compared to the open circuit potential; the time for which the potential is applied; and the pH of the solution are three independent variables that will determine the rate at which the solid electrolyte coating will be deposited, and the final thickness of the coating. While

one may conduct electrodeposition at the pH for which the self-assembly occurs, other pH values may be employed.

[0040] FIGURE 4 is a schematic representation of an embodiment of the electrophoretic deposition apparatus, **40**, used to increase the $AlPO_4$ coating thickness. Electrophoretic deposition implies that charged particles (such as for a suspension of colloidal particles having a net surface charge) are moving in response to an applied external electric field, while electrodeposition implies that current is being passed to initiate a chemical reaction from an electrode resulting in a deposition of material onto the electrode. An $AlPO_4$ deposition solution, **42**, is placed in deposition chamber, **44**, containing working electrode, **46** (Cu_2Sb that has been electrodeposited onto a copper substrate, in this example), counter electrode, **48** (platinum in this case, but other materials such as stainless steel may also be used), and reference electrode, **50** (sodium saturated calomel electrode (SSCE), as an example). Potentiostat/galvanostat, **52**, applies voltage between working electrode **46** and counter electrode **48**, and measures the current flowing therebetween. Potentiostat/galvanostat, **52** also measures the voltage between working electrode **46** and reference electrode **50**.

[0041] The placement of the electrodes and their spatial relationship to each other may affect the deposition process. To determine the potential range, with respect to the open circuit potential (OCP), cyclic voltamograms of Cu_2Sb in $AlPO_4$ deposition solution were plotted in Figure 5. The Cu_2Sb was electroplated onto a copper current collector having a surface area of 0.32 cm^2. The OCP is defined as the potential at which no current passes through the cell. For this system, a potential window of approximately 75 mV exists as illustrated by the vertical dashed lines. The electrodeposition solution was the same as that for the self-assembly solution, but supporting electrolytes may be added facilitate transfer of charged species. However, supporting electrolytes are chosen such that they do not undergo redox reactions or other detrimental processes under the electrodeposition conditions used to increase the coating thickness, thereby adversely affecting the deposition.

[0042] $AlPO_4$ was coated onto Cu_2Sb thin films that had been electroplated onto copper substrates by self-assembly in the solution set forth in EXAMPLE 1, hereof. Once the self-assembly process is completed, electrodeposition may be used to increase the $AlPO_4$ coating thickness. In this example, electrophoretic deposition is appropriate, although other electrodeposition techniques may be utilized. Two

conditions were chosen: (a) 30 mV more positive than the OCP; (b) 30 mV more negative than the OCP. These potentials were chosen because they both are within the range determined from the cyclic voltamograms contained in FIGURE 5. Additionally, the more positive potential is expected to induce a positive surface charge on the Cu_2Sb whereas the negative potential a negative surface charge. To compare the effect of applying a positive and negative potential when compared to the OCP, X-Ray Photoelectron Spectroscopy (XPS) was used since it is a quantitative surface sensitive characterization technique.

[0043] FIGURE 6 shows XPS spectra of electroplated Cu_2Sb. The survey spectrum and high resolution spectra do not show the presence of aluminum or phosphorous, which confirms that an $AlPO_4$ coating is not present. Note that the region of the phosphorous 2p and aluminum 2p peaks are in close proximity to copper 3s and copper 3p peaks, respectively. FIGURE 7 shows XPS spectra of a coating formed with a positive applied potential after the self-assembly process had been completed. A clear difference between the spectra in FIGURES 6 and 7 may be observed. In the phosphorous 2p region of FIG. 7, a peak is present, while for FIG. 6 a peak in the same region is not observed. Additionally, this peak may be located in the survey spectrum in close proximately to the copper 3s peak; the phosphorous 2p peak is equivalent in magnitude to the copper 3s peak. When analyzing the aluminum 2p region in FIG. 7, the peak shape has changed due to the presence of the aluminum 2p peak when compared to the same region plotted in FIG. 6.

[0044] FIGURE 8 shows XPS spectra of a coating formed with a negative applied potential after the self-assembly process had been completed. By observing the phosphorous 2p region, these XPS spectra are more indicative of an $AlPO_4$ coating that has been self-assembled onto the surface of Cu_2Sb without the addition of an applied potential. While a peak is observed in both the high-resolution and survey spectra, the peak is approximately half the magnitude of the copper 3s peak. Applying a negative potential when compared to the OCP, therefore, does not increase the coating thickness when compared to a coating that has been self-assembled using the procedures described hereinabove. This is likely the result of the application of a negative potential inducing a negative surface charge. Since the net surface charge of the $AlPO_4$ in solution is also negative, there is insufficient driving force to promote the assembly of additional $AlPO_4$ onto the Cu_2Sb surface to

increase the coating thickness. By contrast, applying a positive potential when compared to the OCP results in a positive surface charge which produces in an increase in the $AlPO_4$ coating thickness. This is confirmed by the phosphorous 2p peak in Figure 7 which is approximately twice the magnitude of the peak contained in Figure 8 when using the copper 3s peak as a reference. Since XPS is a quantitative surface sensitive technique, the increase in the phosphorous 2p peak magnitude when compared to the copper 3s peak is indicative of an increase in the surface $AlPO_4$ coating thickness.

[0045] The foregoing description of the invention has been presented for purposes of illustration and description and is not intended to be exhaustive or to limit the invention to the precise form disclosed, and obviously many modifications and variations are possible in light of the above teaching. The embodiments were chosen and described in order to best explain the principles of the invention and its practical application to thereby enable others skilled in the art to best utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

[0046] WHAT IS CLAIMED IS:

1. An apparatus for determining the isoelectric pH of a material, comprising in combination:

a first chamber adapted for containing a solution having a chosen pH comprising:

a circular disk having an axis, a first face, and an opposing second face onto which said material is disposed;

a shaft attached to the first face of said disk;

a first reference electrode disposed in the vicinity of the second face of said disk and in the vicinity of the axis; and

a hollow tube affixed to a wall of said first chamber at an orifice therein;

a second chamber in fluid communication with said first chamber through said tube, comprising a second reference electrode;

means for rotating said shaft at a chosen rate; and

means for measuring the potential difference between said first reference electrode and said second reference electrode.

2. The apparatus of claim 1, further comprising means for measuring the pH of the solution.

3. The apparatus of claim 1, wherein said material is deposited onto the second face of said disk.

4. A method for determining the isoelectric pH of a material, comprising the steps of:

affixing the material on one face of a circular disk having an axis of rotation and disposed in a solution having a selected pH value in a first chamber;

rotating the disk at a chosen rate;

measuring the potential difference between a first reference electrode disposed in the vicinity of both the axis of the disk and the material and a second reference electrode disposed in a second chamber in fluid communication through a tube with said first chamber;

adjusting the pH of the solution such that the potential difference is approximately equal to the resting potential difference between the first reference electrode and the second reference electrode; and

measuring the pH of the solution when the potential difference is approximately equal to the resting potential difference.

5. The method of claim 4, wherein the material comprises Cu_2Sb.

6. The method of claim 5, wherein said step of affixing the Cu_2Sb on one face of a circular disk is achieved by deposition.

7. The method of claim 6, wherein the deposition comprises electrodeposition.

8. The method of claim 5, wherein the disk is rotated at approximately 750 rpm.

9. The method of claim 4, wherein the solution comprises aqueous KCl.

10. The method of claim 4, wherein said step of adjusting the pH of the solution is achieved using hydrochloric acid to lower the pH and ammonium hydroxide to raise the pH of the solution.

11. A method for depositing a coating material onto a substrate, comprising the steps of:

determining the isoelectric pH of the substrate;

determining the isoelectric pH of the coating material;

preparing a solution of the coating material having a pH between the isoelectric pH of the substrate and the isoelectric pH of the coating material; and

immersing the substrate into the solution for a time sufficient for self-assembly of the coating material onto the substrate.

12. The method of claim 11, wherein the pH of the solution is approximately the average of the isoelectric pH of the substrate and the isoelectric pH of the coating material.

13. The method of claim 11, wherein said substrate comprises Cu_2Sb.

14. The method of claim 11, wherein said coating material is chosen from $AlPO_4$, Al_2O_3, ZnO, and Bi_2O_3.

15. The method of claim 11, further comprising the step of increasing the thickness of the coating material on the substrate.

16. The method of claim 15, wherein said step of increasing the thickness of the coating material comprises electrodeposition of additional coating material onto the self-assembled coating material.

17. The method of claim 16, wherein said electrodeposition comprises electrophoretic deposition.

18. The method of claim 17, wherein said substrate comprises Cu_2Sb.

19. The method of claim 18, wherein said Cu_2Sb is electroplated onto a copper current collector.

20. The method of claim 15, wherein said coating material is chosen from $AlPO_4$, Al_2O_3, ZnO, and Bi_2O_3.

21. The method of claim 17, wherein said substrate comprises Cu_2Sb, said self-assembled coating comprises $AlPO_4$, and the electrophoretic deposition of the $AlPO_4$ onto the self-assembled coating of $AlPO_4$ on said Cu_2Sb substrate is performed with the self-assembled coating at a positive voltage relative to open circuit potential.

22. The method of claim 21, wherein the solution of the coating material for said electrophoretic deposition is the same solution used for said self-assembly of said coating material.

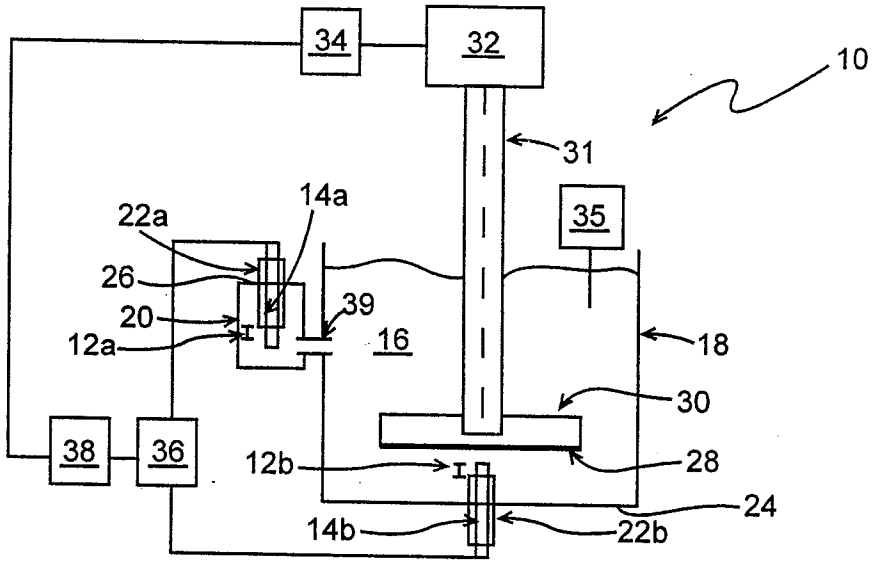
34
32
10
31
35
14a
22a
26
20
12a
39
16
18
30
38
36
12b
28
24
14b
22b

FIG. 1

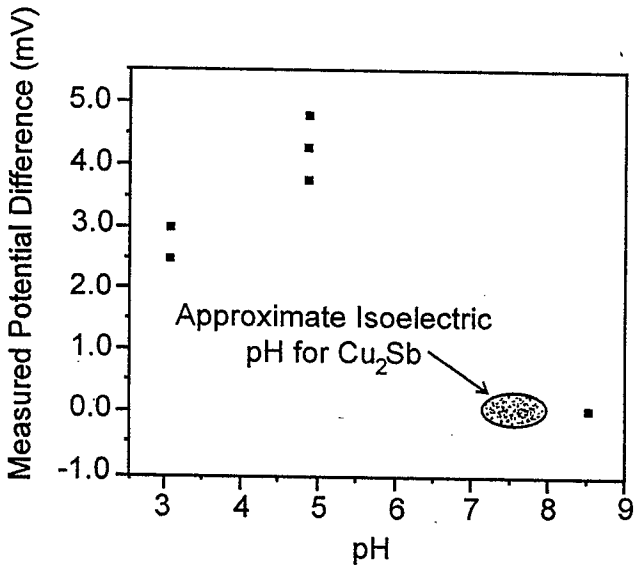
Measured Potential Difference (mV)
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
3
4
5
6
7
8
9
pH
Approximate Isoelectric
pH for Cu2Sb

FIG. 2

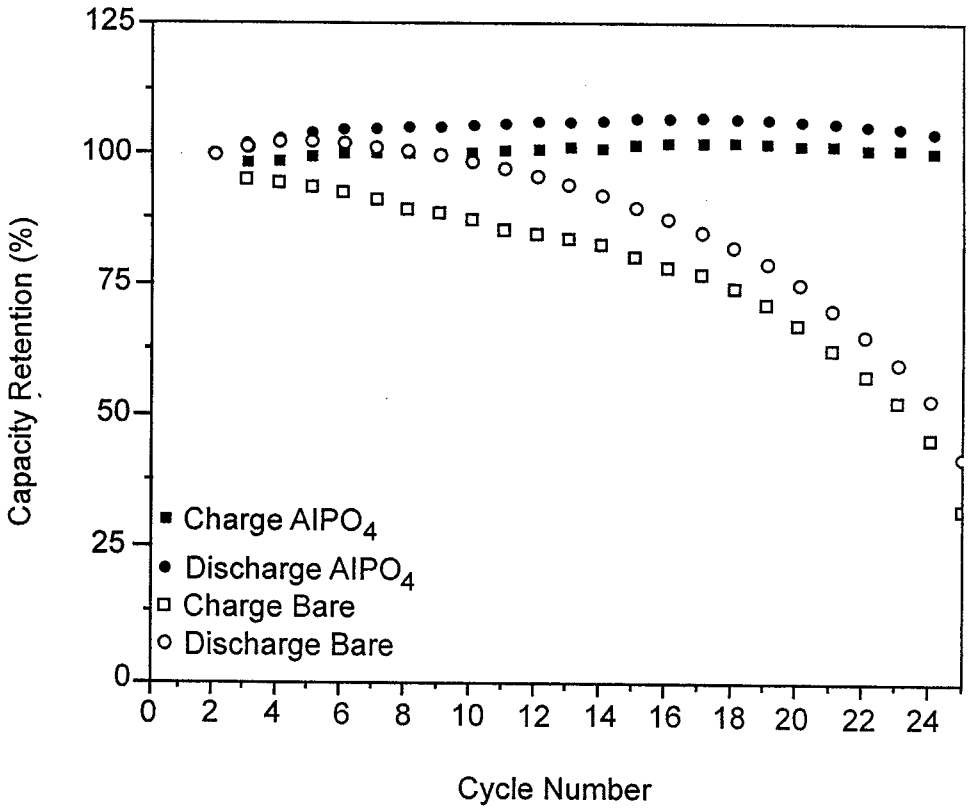
125
100
75
50
25
0
Capacity Retention (%)
0 2 4 6 8 10 12 14 16 18 20 22 24
Cycle Number
Charge AlPO4
Discharge AlPO4
Charge Bare
Discharge Bare

FIG. 3

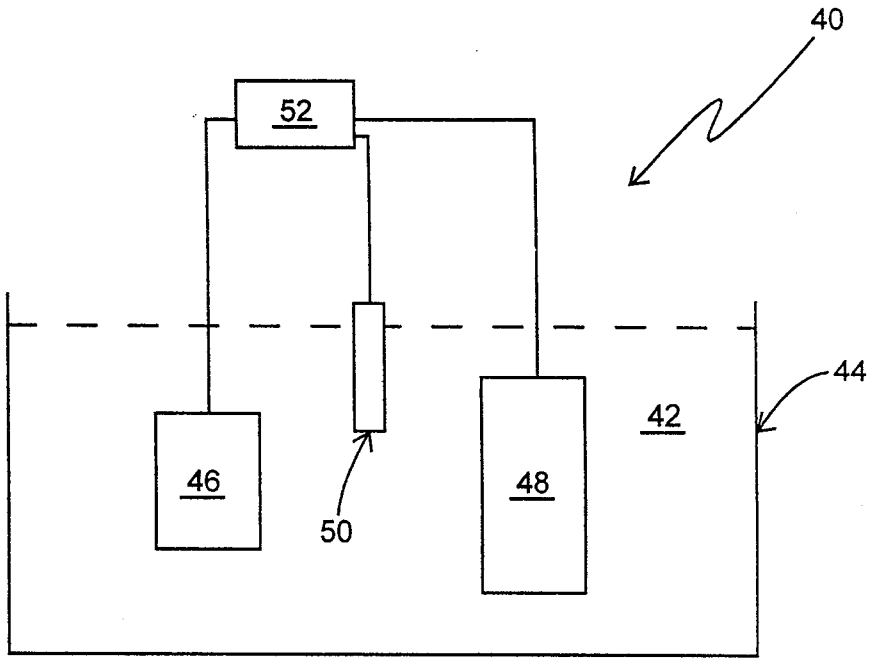

FIG. 4

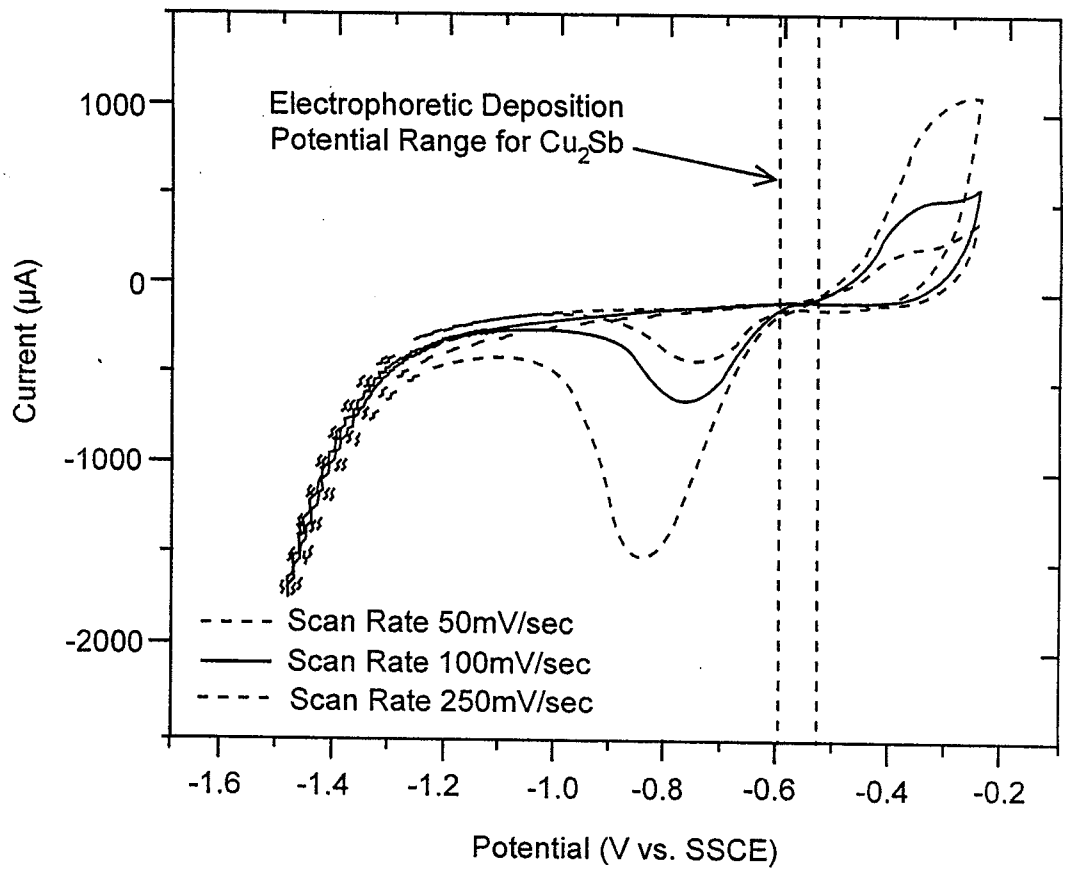
Electrophoretic Deposition
Potential Range for Cu2Sb
1000
0
-1000
-2000
Current (μA)
Scan Rate 50mV/sec
Scan Rate 100mV/sec
Scan Rate 250mV/sec
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
-0.4
-0.2
Potential (V vs. SSCE)

FIG. 5

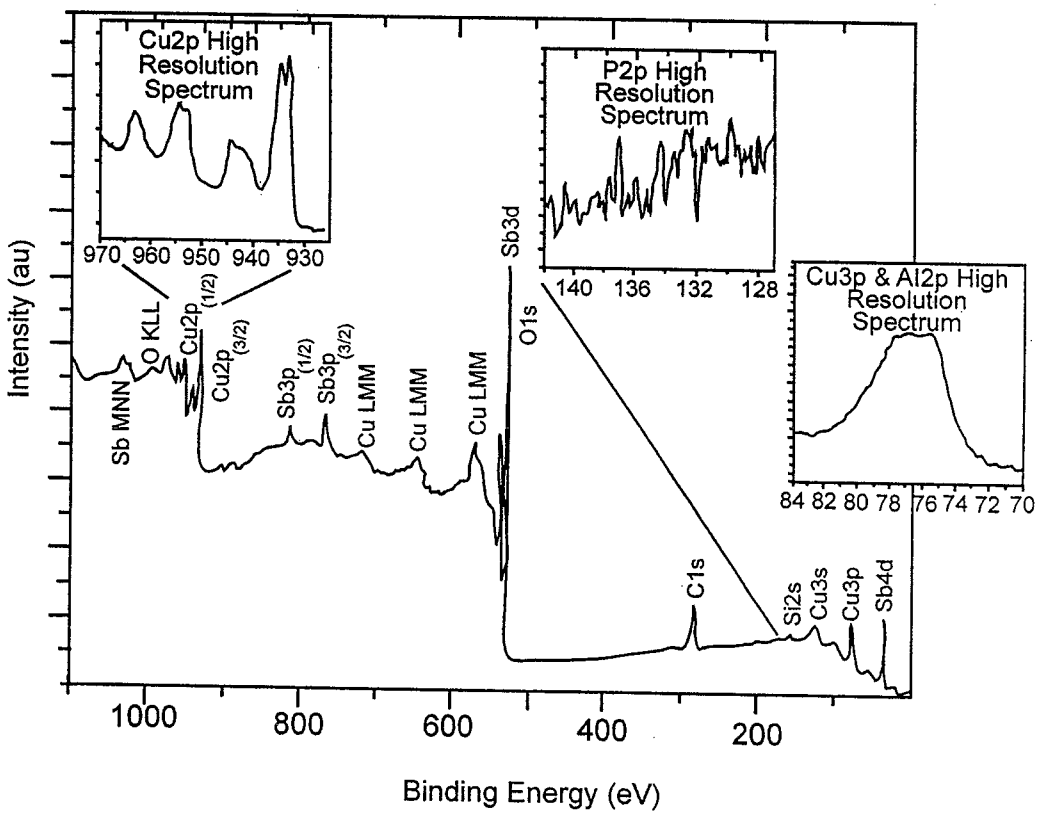
Cu2p High Resolution Spectrum
970 960 950 940 930
P2p High Resolution Spectrum
140 136 132 128
Cu3p & Al2p High Resolution Spectrum
84 82 80 78 76 74 72 70
Intensity (au)
Sb MNN
O KLL
Cu2p(1/2)
Cu2p(3/2)
Sb3p(1/2)
Sb3p(3/2)
Cu LMM
Cu LMM
Cu LMM
Sb3d
O1s
C1s
Si2s
Cu3s
Cu3p
Sb4d
1000
800
600
400
200
Binding Energy (eV)

FIG. 6

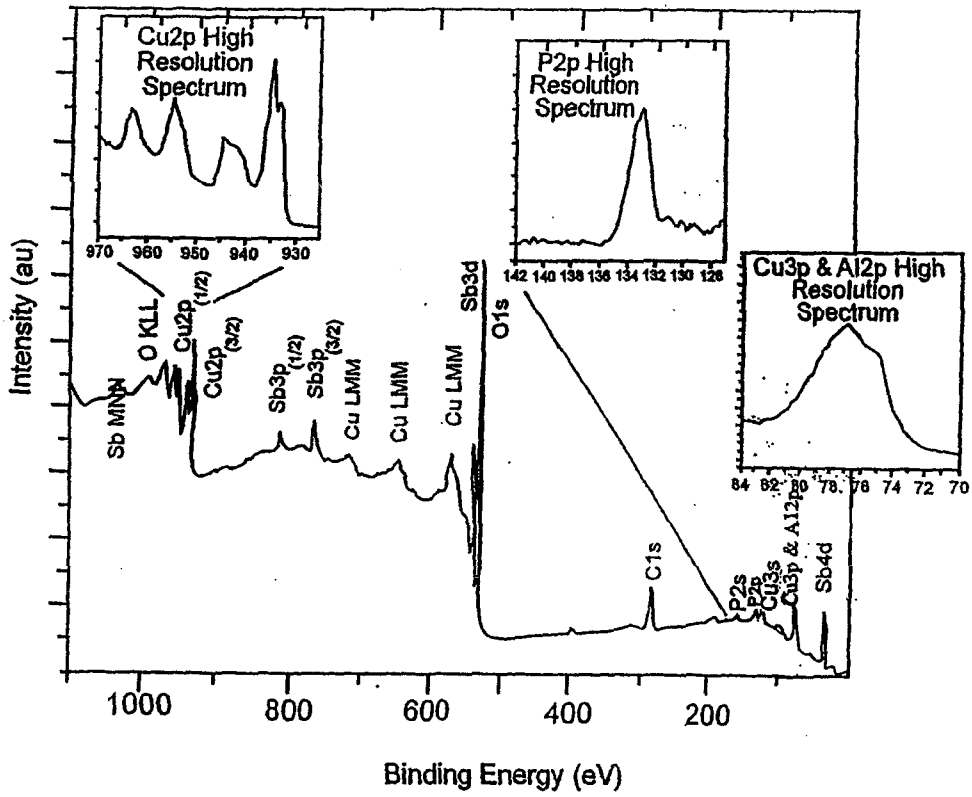
Cu2p High Resolution Spectrum
970 960 950 940 930
P2p High Resolution Spectrum
142 140 138 136 134 132 130 128
Cu3p & Al2p High Resolution Spectrum
84 82 80 78 76 74 72 70
Intensity (au)
Sb MNN
O KLL
Cu2p(1/2)
Cu2p(3/2)
Sb3p(1/2)
Sb3p(3/2)
Cu LMM
Cu LMM
Cu LMM
Sb3d
O1s
C1s
P2s
P2p
Cu3s
Cu3p & Al2p
Sb4d
1000
800
600
400
200
Binding Energy (eV)

FIG. 7

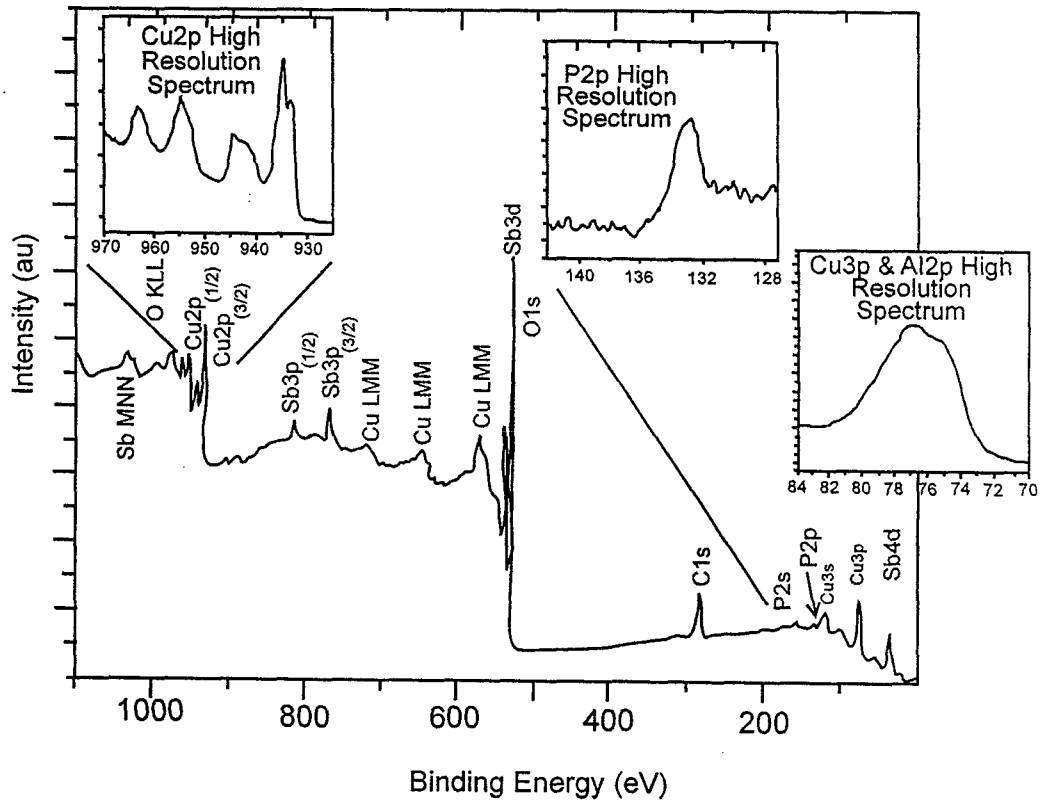
Cu2p High Resolution Spectrum
970 960 950 940 930
P2p High Resolution Spectrum
140 136 132 128
Cu3p & Al2p High Resolution Spectrum
84 82 80 78 76 74 72 70
Intensity (au)
Sb MNN
O KLL
Cu2p(1/2)
Cu2p(3/2)
Sb3p(1/2)
Sb3p(3/2)
Cu LMM
Cu LMM
Cu LMM
Sb3d
O1s
C1s
P2s
P2p
Cu3s
Cu3p
Sb4d
1000 800 600 400 200
Binding Energy (eV)

FIG. 8

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/30224

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C07K 1/28 (2011.01)
USPC - 204/548
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC(8)- C07K 1/28 (2011.01);
USPC- 204/548

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC- 204/644; 239/79, 81; 427/446
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
PubWest (US Pat, PgPub, EPO, JPO), GoogleScholar (PL, NPL), FreePatentsOnline (US Pat, PgPub, EPO, JPO, WIPO, NPL); search terms: isoelectric, pH, point, measure, determine, analyze, disc, disk, plate, turntable, circular, annular, rotate, potential, difference, rest, potential, reference, electrode, self-assemble, coat, deposit, Cu2Sb...

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,298,143 A (IVORY et al.) 29 March 1994 (29.03.1994), Figs. 16-19; col 3, ln 21-27; col 4, ln 18-24; col 8, ln 5-36; col 9, ln 61-66; col 11, ln 4-10; col 11, ln 55 to col 12, ln 2; col 13, ln 61 to col 14, ln 2; col 17, ln 60 to col 18, ln 37; col 21, ln 9 to col 22, ln 6	1-10
Y	US 4,165,242 A (KELLY et al.) 21 August 1979 (21.08.1979), col 2, ln 40 to col 3, ln 34; col 4, ln 13-29; col 6, ln 67 to col 7, ln 58; col 13, ln 5-24	1-22
Y	US 2005/0014151 A1 (TEXTOR et al.) 20 January 2005 (20.01.2005), para [0025]-[0030], [0042], [0072], [0078], [0168], [0170], [0194]	11-22
Y	US 2007/0163884 A1 (STRAND et al.) 19 July 2007 (19.07.2007), para [0171]-[0172]	1-22
Y	US 2007/0020400 A1 (CHANG) 25 January 2007 (25.01.2007), para [0008]-[0129]	1-22
Y	TANG et al. "Electrophoretic deposition of aqueous nano-sized zinc oxide suspensions on a zinc electrode." Materials Research Bulletin [online], 25 January 2003 (25.01.2003), Vol. 38, Iss. 2, pp. 207-212, Retrieved from the Internet: <URL: http://www.sciencedirect.com/science/article/pii/S0025540802010292>, esp. pg 209	11-22
Y	US 5,290,408 A (LEWANDOWSKI et al.) 01 March 1994 (01.03.1994), col 4-9	1-10
Y	US 4,673,483 A (MANDLE) 16 June 1987 (16.06.1987), col 2-6	1-10
Y	US 4,588,492 A (BIER) 13 May 1986 (13.05.1986), Fig. 1; col 3-5	1-10

☒ Further documents are listed in the continuation of Box C. ☐

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
25 July 2011 (25.07.2011)	02 AUG 2011
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/30224

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4,234,404 A (SATOH) 18 November 1980 (18.11.1980), col 2-5	1-22
Y	US 3,664,939 A (LUNER et al.) 23 May 1972 (23.05.1972), col 3-5	1-22
A	MOSBY et al. "Direct Electrodeposition of Cu2Sb for Lithium-Ion Battery Anodes." Journal of the American Chemical Society [online], Publication date (Web): 16 July 2008 (16.07.2008) [Retrieved on 2011-07-25], Vol. 132, No. 32, pp. 10656-10661, Retrieved from the Internet: <URL: http://www.chem.colostate.edu/alprieto/Publications_files/Mosby%202008%20(13)%20pdf%20w%20links.pdf>, esp. pg 10656	5, 6, 13, 18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/30224

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 11/30224

Box No. III, Observations where unity of invention is lacking:

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: claims 1-10: directed to an apparatus/method of determining the isoelectric pH of a material.

Group II: claims 11-22: directed to a method for depositing a coating material onto a substrate.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Group I does not include the inventive concept of a determining the isoelectric pH of a coating material, preparing a solution of the coating material having a pH between an isoelectric pH of a substrate and the isoelectric pH of a coating material, and immersing the substrate into the solution for a time sufficient for selfassembly of the coating material onto the substrate.as required by Group II.

Group II does not include the inventive concept of a first chamber comprising a circular disk, a shaft, reference electrode, hollow tube and a second chamber comprising a rotory means and means for measuring a potential gradient, as required by Group I.

Groups I and II share the technical feature of determining an isoelectric pH of a material. However, this shared technical feature does not represent a contribution over the prior art of US 2007/0163884 A1 to Strand et al. (19 July 2007), which teaches a method of determining an isoelectric pH of a material (Abstract and para [0171]-[0172]). As the above method of determining isoelectric pH of a material was known at the time, as evidenced by the teaching of Strand, this cannot be considered a special technical feature that would otherwise unify the groups.

Groups I and II therefore lack unity under PCT Rule 13 because they do not share a same or corresponding special technical feature.