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(54) **METHOD OF FORMING A POROUS NICKEL COATING, AND RELATED ARTICLES AND COMPOSITIONS**

(75) **Inventors:** **Larry Steven Rosenzweig**, Clifton Park, NY (US); **Grigorii Lev Soloveichik**, Latham, NY (US); **Guillermo Daniel Zappi**, Niskayuna, NY (US)

Correspondence Address:
GENERAL ELECTRIC COMPANY
GLOBAL RESEARCH
PATENT DOCKET RM. BLDG. K1-4A59
NISKAYUNA, NY 12309

(73) **Assignee:** **General Electric Company**

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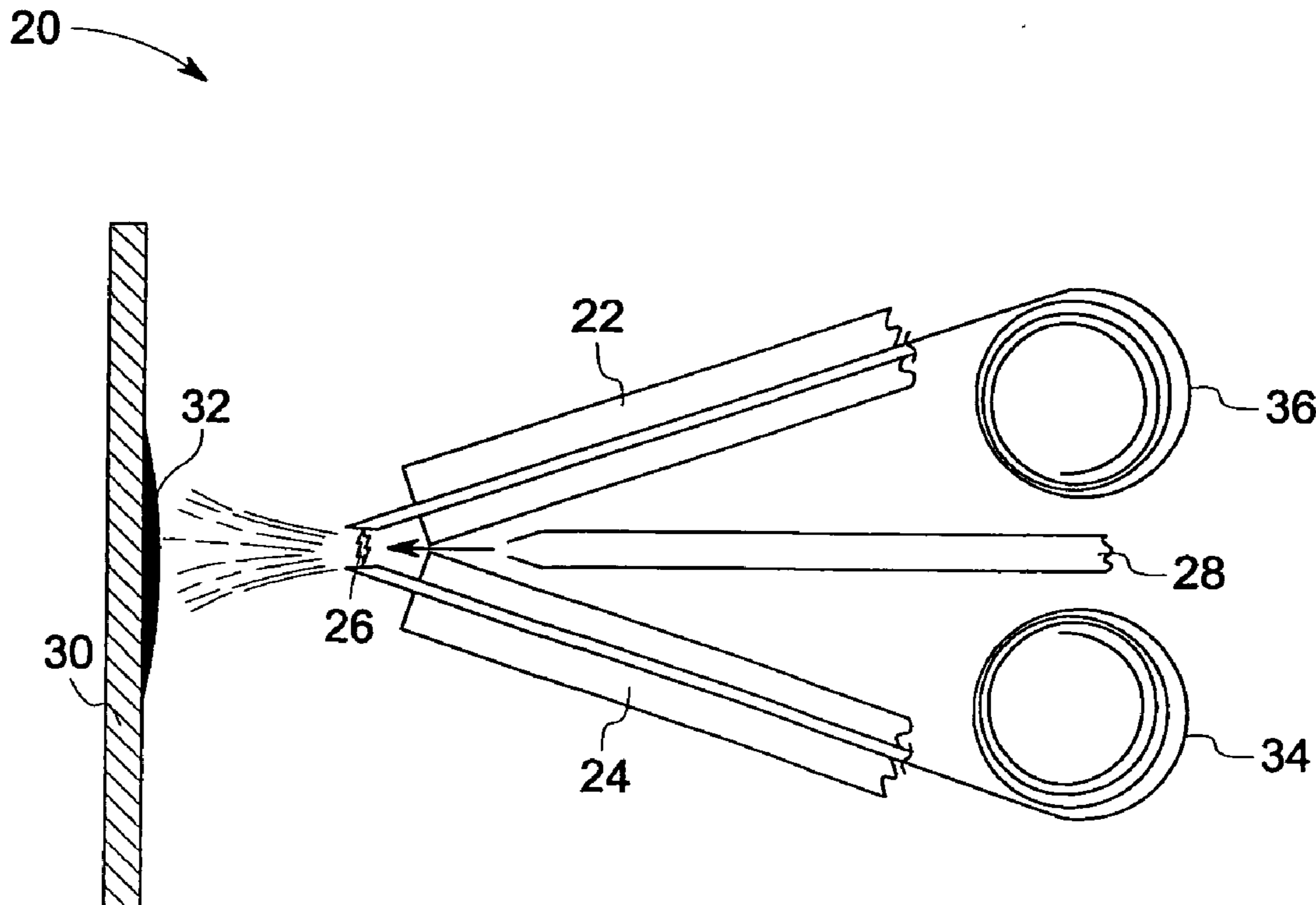
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(57) **ABSTRACT**

A method of forming a porous nickel coating is provided. The method includes the steps of: depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit; the selected composition including nickel and a sacrificial metal; and then dissolving at least a portion of the sacrificial metal from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating. An electrolytic cell that includes a porous nickel coating is also described.



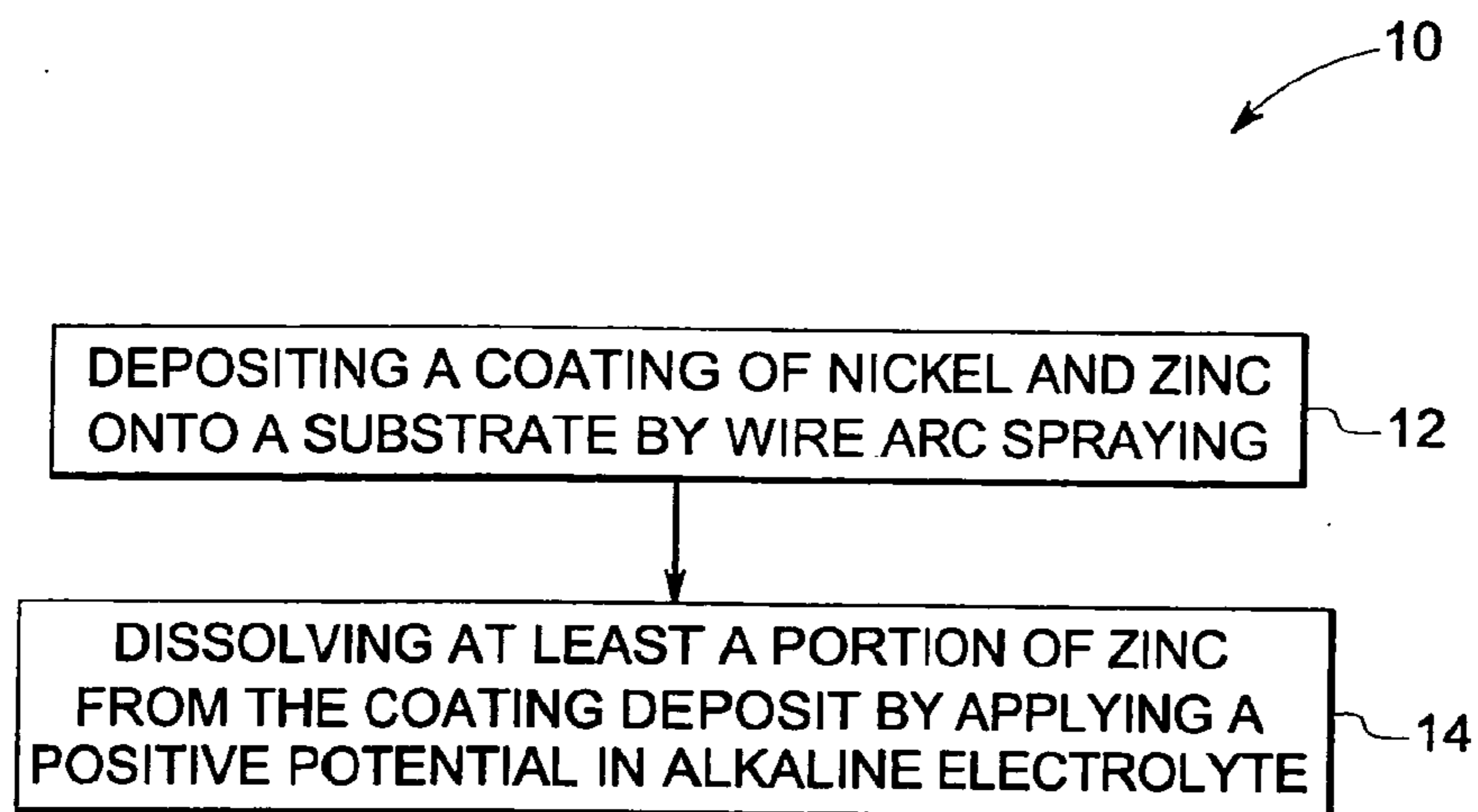


FIG. 1

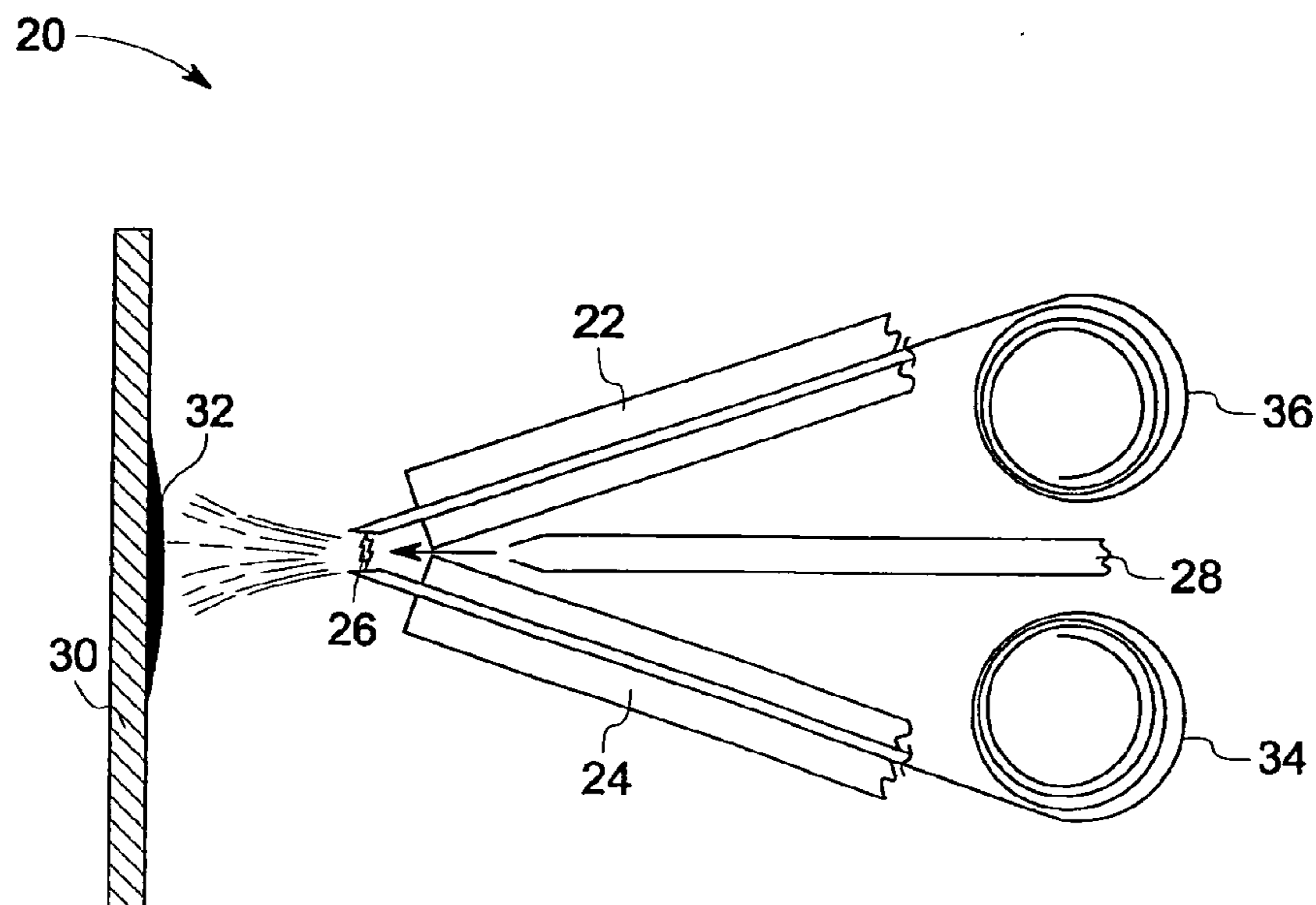


FIG. 2

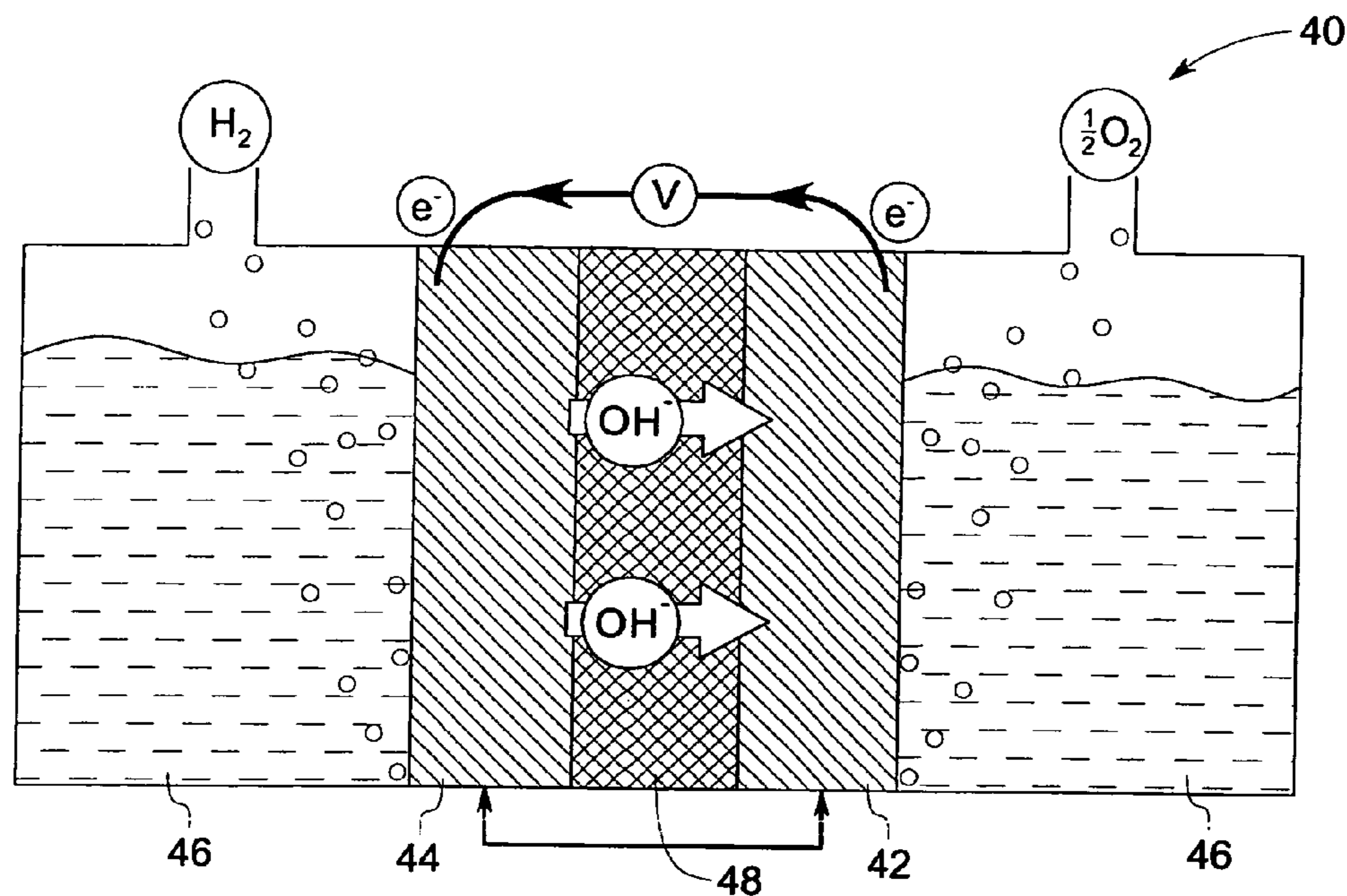


FIG. 3

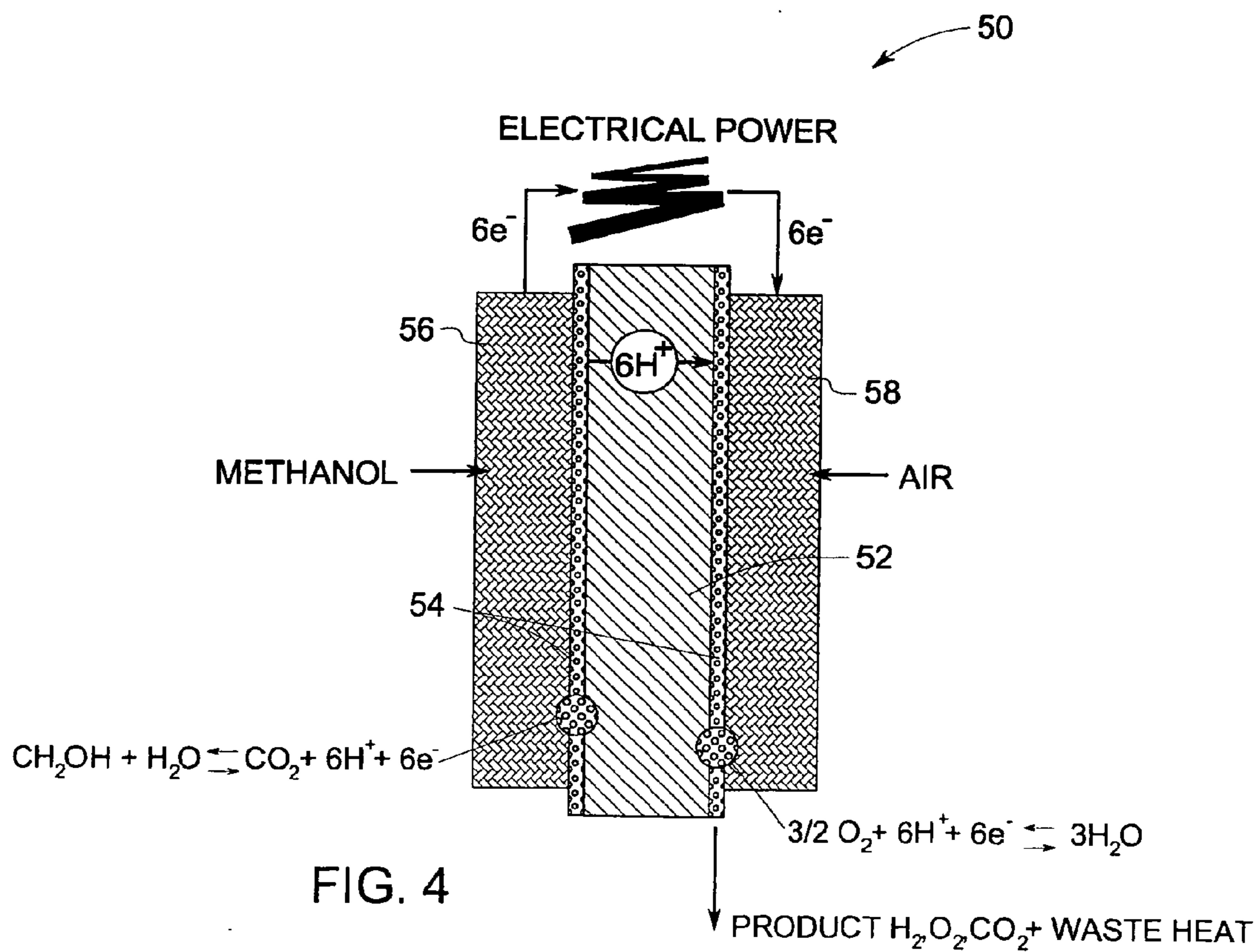


FIG. 4

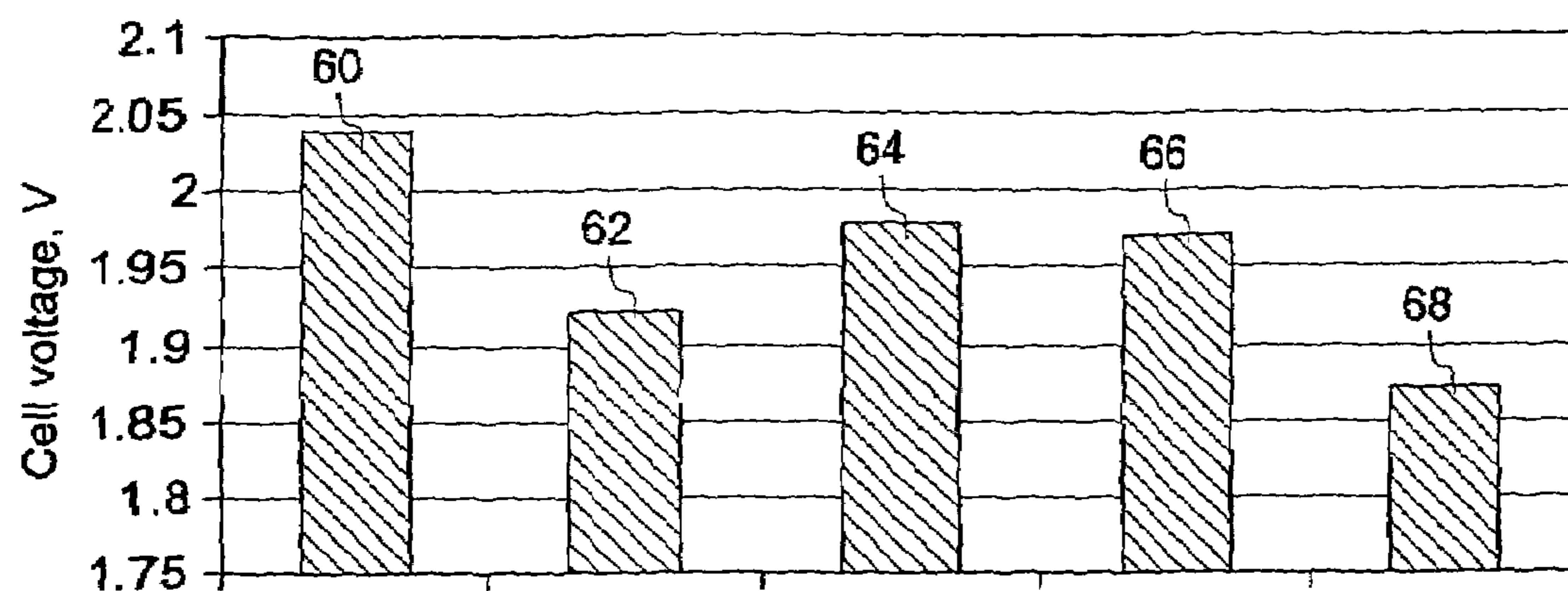


FIG. 5

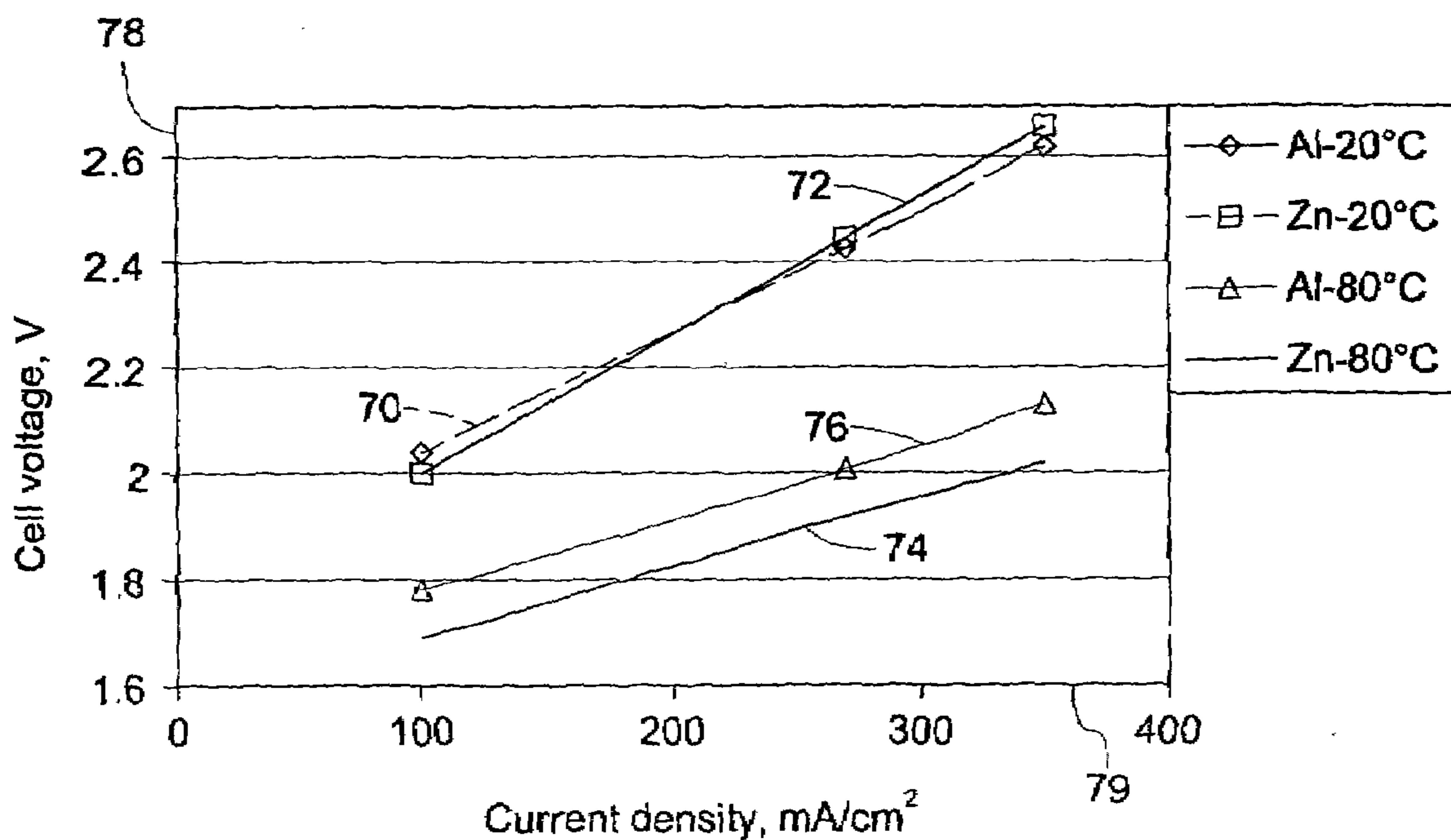


FIG. 6

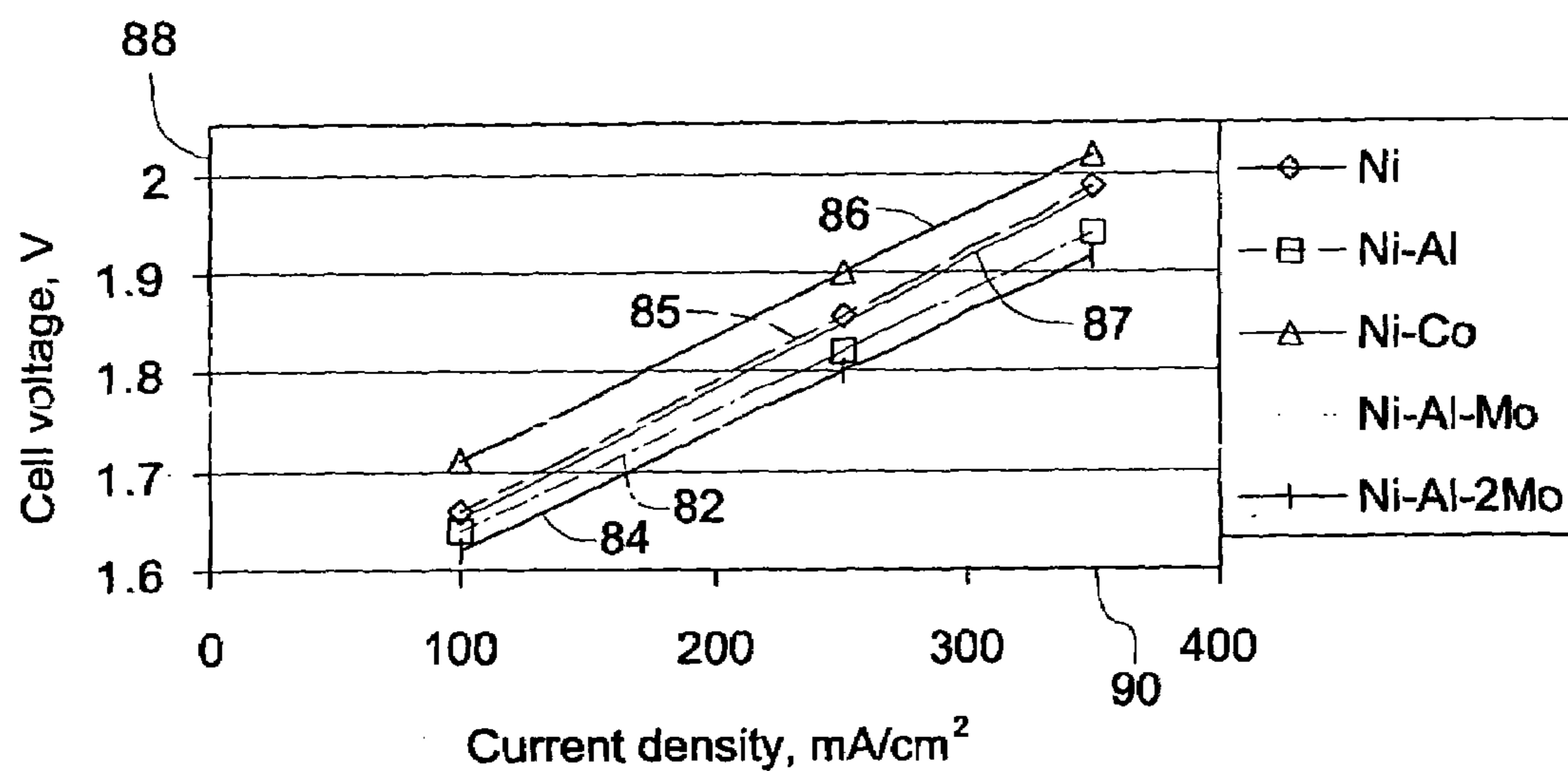


FIG. 7

METHOD OF FORMING A POROUS NICKEL COATING, AND RELATED ARTICLES AND COMPOSITIONS

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH & DEVELOPMENT

[0001] This invention was made with Government support under contract number DE-FC36-04GO14223 awarded by DOE. The Government has certain rights in the invention.

BACKGROUND OF THE INVENTION

[0002] The invention is related to a method of forming a nickel coating. More particularly, the invention is related to a wire-arc spray coating method of making a porous nickel coating, e.g., a coating which comprises Raney nickel. The invention is also related to an electrode, comprising a porous nickel coating.

[0003] Electrocatalysts are extensively used in alternative fuels production (e.g., hydrogen): production of crude oil and gas from non-conventional sources such as tar sands and heavy oil reservoirs: synfuels production (e.g., coal liquefaction/gasification, shale oil). Electrocatalysts are also useful in oil recycling, and other emerging energy technologies such as fuel cells and photovoltaic cells. They are also employed in various other chemical processes. Electrocatalysts are indispensable to many types of environmental remediation, from vehicle emission control systems to industrial effluent and municipal waste treatment. Electrocatalysts also contribute indirectly to reducing pollution and other adverse environmental impacts, e.g., through cleaner-burning fuels (hydrogen production) and the production of products such as refrigerants, which pollute less than the substances they replace.

[0004] Platinum-based materials are extensively used as electrocatalysts in many of these applications. However, the high cost of these materials encourages researchers to find alternative electrocatalysts with efficiency comparable to the efficiency of platinum-based electrocatalysts. For many of these applications, in addition to high catalytic activity and low cost, the catalyst materials should be corrosion-resistant in a strong alkaline solution. Such electrocatalysts would find additional uses as absorbents to remove toxic waste from the environment, as catalysts for organic synthesis, as catalysts in fuel cells, and in sensors. In spite of large research efforts concentrated on the development of such electrocatalysts, there is a need for new high-efficiency electrocatalysts.

[0005] Hydrogen made from renewable energy resources provides a clean and abundant energy source, capable of meeting most of the future's high-energy needs. When hydrogen is used as an energy source in a fuel cell, the only emission is water, which can then be electrolyzed to make more hydrogen—the waste product supplies more fuel. This continuous cycle of energy production has the potential to replace the traditional energy sources in every aspect. The only drawback of hydrogen-based fuels is that hydrogen is still more expensive than other energy sources, such as coal, oil and natural gas. Researchers are helping to develop technologies to tap into this natural resource and generate hydrogen in mass quantities, and less expensively, in order to compete with the traditional energy sources.

[0006] Water is an abundant and inexpensive source of hydrogen. Hydrogen can be produced from the splitting of

water through various processes, including water electrolysis, photo-electrolysis, photo-biological production, and high temperature water decomposition. Water electrolysis is a process where water is split into hydrogen and oxygen through the application of electrical energy. Three types of water electrolysis processes are being considered for hydrogen generation: alkaline electrolysis, PEM (proton exchange membrane) electrolysis, and SOEC (solid oxide electrolytic cell) processes. Alkaline water electrolysis is a mature technology allowing unmanned remote operation, and is thus suited for large-scale production. The major challenges involved in reducing the cost of hydrogen production by alkaline electrolysis are to reduce the amount of electrical energy required for the process, and to increase the efficiency of the system. These requirements necessitate the operation of the system at high current densities and low over-potential for achieving economic generation of hydrogen. By utilizing electrocatalysts at the electrodes, it is possible to achieve high current density and/or low cell voltage. Although the art has suggested various non-platinum based electrocatalysts, most of them suffer from insufficiently low cell voltage and mechanical weakness. Improvements in the performance of known electrocatalyst materials, as well as the development of inexpensive methods for their preparation, would be welcome in the art.

BRIEF DESCRIPTION OF THE INVENTION

[0007] The present invention meets these and other needs by providing an efficient method for the production of a high performance porous nickel electrocatalyst.

[0008] One embodiment of the invention is a method of forming a porous nickel coating, including the steps of: depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit; the selected composition comprising nickel and zinc; and then dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

[0009] Another embodiment is an electrolytic cell comprising at least one electrode which includes a porous nickel coating. The porous nickel coating is formed by a process including the steps of: depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit; the selected composition comprising nickel and zinc; and then dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

DESCRIPTION OF THE DRAWINGS

[0010] These and other features, aspects, and advantages of the present invention will become better understood when the following detailed description is read with reference to the accompanying drawings in which like characters represent like parts throughout the drawing, wherein:

[0011] FIG. 1 is a flow diagram of a method according to one embodiment of the present invention;

[0012] FIG. 2 is a schematic view of a twin-arc spray device according to one embodiment of the present invention;

[0013] FIG. 3 is a schematic view of an electrolytic cell comprising the porous nickel coating according to one embodiment of the invention;

[0014] FIG. 4 is a schematic view of a direct methanol fuel cell comprising the porous nickel coating according to one embodiment of the invention;

[0015] FIG. 5 is a plot indicating the influence of leaching on cell performance, according to one embodiment of the invention;

[0016] FIG. 6 is a plot of cell voltage vs. current density for nickel-zinc and nickel-aluminum coatings, according to one embodiment of the invention; and

[0017] FIG. 7 is a plot of cell voltage vs. current density for nickel-zinc coatings with different alloying additives, according to some embodiments of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] Various embodiments of this invention have been described in fulfillment of the various needs that the invention meets. It should be recognized that these embodiments are merely illustrative of the principles of various embodiments of the present invention. Numerous modifications and adaptations thereof will be apparent to those skilled in the art without departing from the spirit and scope of the present invention. Thus, it is intended that the present invention cover all suitable modifications and variations as come within the scope of the appended claims and their equivalents.

[0019] Advances and novelties in fields such as energy conversion (batteries, fuel cells), electronics, communication technologies, nanotechnology, biocompatibility, etc. are to a large extent related to new and improved electrocatalytic materials. Intense research efforts are concentrated on the development of non-platinum based catalysts with high efficiency. Nickel-based coatings are explored for these applications. Porous nickel coatings have shown promising results. However, obtaining an electrocatalyst with high efficiency and low cost has proven to be a very challenging task. Many methods have been described in the art, such as electrodeposition, sintering of nickel and aluminum and then selective removal of aluminum, and plasma spraying. Most of these efforts are concentrated on forming a coating of nickel with aluminum, and then selective leaching of the aluminum. In some cases (although not all), aluminum-based coatings are undesirable, as they are expensive, and can present handling problems. Furthermore, aluminum deposits can sometimes contaminate the deposition chambers. Moreover, most of these coatings suffer from insufficiently low cell voltage, short life-time, and mechanical weakness. Despite such efforts, there is no simple method to produce, on an industrial scale, porous nickel coatings having an engineered porous structure and high catalytic activity. Moreover, there is a need for a method to fabricate porous nickel coatings capable of low over-potential for hydrogen production.

[0020] Disclosed herein is a versatile method for making porous nickel coatings with controlled porosity and superior catalytic properties. In accordance with aspects of the present invention, it has been determined that it is possible to wire arc spray a coating of nickel with zinc, and then

selectively leach out zinc to obtain a highly porous and robust nickel coating. The details of the process are described in the subsequent embodiments. The performance of nickel-zinc-based coatings of the embodiments of the invention is found to be superior to the nickel-aluminum-based coatings known in the art.

[0021] As used herein, the term “wire” means a wire of any practical diameter, e.g., from several microns (a thin wire or a fiber) to several centimeters (a thick rod). For the purposes of understanding the invention, “coating deposit” is interchangeable with coating, deposit, and a film. As used herein, “nickel coating” predominantly comprises nickel (at least about 70 weight percent) and may comprise a small amount of other components. As used herein, “Raney nickel” is meant to describe a porous nickel material. Porous nickel may comprise predominantly nickel, or may comprise any other component such as aluminum or other metals along with nickel.

[0022] One exemplary, non-limiting processing route is disclosed for forming a porous nickel coating through twin wire-arc spray process. The flow chart of the method 10 is shown in FIG. 1. The method involves the steps of: depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition, comprising nickel and zinc, in a wire-arc spray device (in step 12), so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit; and then dissolving at least a portion of zinc from the coating deposit by applying a positive potential in an alkaline electrolyte (in step 14), so as to obtain a porous nickel coating.

[0023] Twin wire arc spray processes are well known in the art. The wire arc spray process is one of the most economical ways of manufacturing large-scale coatings. A schematic of a wire-arc spray device is shown in FIG. 2. In a wire-arc spray process, a DC electric current is utilized to directly melt two consumable electrode wires 22 and 24. Thus the thermal efficiency of the wire-arc spray process is higher than that of a thermal spray process, in which the particles are indirectly heated through a jet gas. In wire-arc spraying, current is carried by the two consumable wires. An electric arc 26 is formed between the wire tips in the gap where the two wires are continuously being converged. A high velocity gas jet 28 blows behind the two wires to atomize the molten metal, which continuously forms as the wires are melted by the electric arc. Then the atomizing gas accelerates the particles away from the electrode tips to the substrate surface 30, to form a coating 32.

[0024] Typically, the wires 22 and 24 are carried forward at a speed of from about 1 to about 10 inches (about 2.54 cm to about 25.4 cm) per second by motor driven rollers 34 and 36. The wires 22 and 24 may be of any practical diameter. As will be described more fully herein below, the wires may be cored. A cored wire in our case, may consist of a nickel sleeve filled with powders of any mixture of metals (Mo, Al, Co, etc.) or alloys. The electric arc created during the wire arc process is sufficient to melt all the materials in the wires, cored or solid. It is generally from about 3 kilowatts to about 24 kilowatts, i.e., from about 20 volts and 150 Amperes to about 40 volts and 600 amperes. In this way, an arc temperature is provided that is hot enough to melt both nickel and zinc, and to maintain the metals (including alloys and

intermetallic compositions thereof), in a molten state. These conditions will allow the formation of the desired composition on substrate **30**.

[0025] The molten metal may be carried from the arc to the substrate as a fine spray, using compressed air. In some embodiments, an inert gas or a reducing gas is chosen to prevent oxidation of the metals. Examples of suitable gases include, but are not limited to, nitrogen, argon, krypton, xenon, helium, and neon.

[0026] The total, selected composition of the consumable electrode wires comprises at least about 40 weight percent of zinc. According to one exemplification, at least one consumable electrode wire, the first consumable electrode wire **22**, comprises zinc, and the second consumable electrode **24** comprises nickel. In certain embodiments, the first consumable electrode wire consists essentially of zinc. In another embodiment, the first consumable electrode wire comprises at least about 90 weight percent of zinc, based on the total weight of the wire. In another embodiment, the first consumable electrode wire comprises at least about 75 weight percent of zinc, based on the total weight of the wire. In one embodiment, at least one of consumable electrode wires **22**, **24** comprise both nickel and zinc. According to one embodiment, both of the consumable electrode wires **22**, **24** comprise both nickel and zinc.

[0027] In certain embodiments, the second consumable electrode consists essentially of nickel. In other embodiments, the second consumable electrode wire comprises at least one alloying additive. Some suitable examples of alloying additives include, but are not limited to, Al, Mo, Co, and combinations thereof. The alloying additives are found to advantageously improve the performance of the porous nickel coatings by further decreasing cell over-potential. Typically, the second consumable electrode wire comprises the alloying additive at less than about 30%, based on the total weight of the wire. In other embodiments, the second consumable electrode wire comprises the alloying additive in the range from about 0.05 weight percent to about 30 weight percent, based on the total weight of the wire.

[0028] In certain embodiments, pre-formation of an alloy of two metals is avoided by providing a wire comprising a powder filled core and a solid metal shell. In such embodiments, at least one of the consumable electrode wires comprises a powder filled core and a solid metal shell. In this way, ease of wire feed to the arc is enhanced.

[0029] Generally, the substrate **30** is electroconductive. The substrate may be a perforated sheet, a perforated plate, metal mesh, expanded metal mesh, metal rods or the like. In one embodiment, the substrate comprises iron or an iron alloy. Examples of such alloys include carbon steel or an alloy of iron with manganese, phosphorous, cobalt, nickel, chromium, molybdenum, vanadium, palladium, titanium, zirconium, niobium, tantalum, tungsten, graphite, carbon, or various combinations thereof. Alternatively, the substrate may be cobalt, nickel, molybdenum, tungsten other alkali metal hydroxide-resistant metals, or combinations of any of the foregoing. In an exemplary embodiment, the substrate comprises stainless steel.

[0030] Prior to being coated, the surfaces of the substrate to be coated are cleaned to remove any contaminants that could diminish adhesion of the coating to the substrate. Illustrative cleaning techniques are vapor degreasing, chemical etching, sand or grit blasting, and the like, or combinations of such techniques. Good adhesion and low

hydrogen over-voltage using steel substrates has been obtained with grit and sand blasting, and is generally used.

[0031] All or only part of the substrate surface may be coated, depending upon the type of electrolytic cell in which the coating is to be employed. For example, when the coating is employed in halo-alkali cells wherein a diaphragm is deposited directly upon the side of the cathode facing the anode, then only the non-facing side will normally be electrolytically active and, hence, need be coated. Conversely, when the cathode is used in halo-alkali cells having a diaphragm or membrane spaced apart from the cathode, both sides of the substrate may be coated. When used as a cathode for water electrolysis, or as a bipolar electrode, both sides of the substrate are also typically coated. The coating may be applied either before or after formation of the desired cathode configuration, depending upon the accessibility of the cathode surfaces to be coated; the type of metal spraying equipment; and the procedures for spraying and leaching.

[0032] As herein contemplated, layer or coating **32** is adherent to the electroconductive substrate **30**. The coating thickness is typically from about 50 microns thick to about 250 microns thick. In one embodiment, the coating thickness is from about 100 microns to about 230 microns, and in another embodiment, from about 100 microns to about 175 microns thick.

[0033] In the embodiments discussed herein, nickel acts as the catalytic metal and zinc acts as a sacrificial metal. By "sacrificial metals" are meant those metals that can be removed from the metallized deposit while leaving behind the catalytic metal. Under the metallizing conditions herein contemplated, nickel and zinc may form alloys such as NiZn_3 , Ni_2Zn_3 , and NiZn . These alloy systems provide an easily leachable deposit, having high activity. The zinc and nickel may also be deposited as individual pure elements, not alloyed. After the coating is deposited, at least a portion of the zinc is leached out from the coating to obtain a highly active porous nickel coating. The amount of zinc leached out or removed depends on the required porosity and activity. In certain embodiments, dissolving at least a portion of the zinc comprises dissolving an amount of zinc in the range from about 70 weight percent to about 100 weight percent of zinc compared to the total amount of zinc that was present in the deposit. In other embodiments, dissolving at least a portion of the zinc comprises dissolving an amount of zinc in the range from about 50 weight percent to about 100 weight percent of zinc.

[0034] At least a portion of zinc is removed from the deposit after the coating is formed, to obtain a porous nickel coating. By itself, conventionally used chemical leaching is not very efficient in removing zinc from the coatings. The inventors have discovered that, by using an anodization process to remove the zinc, it is possible to obtain a highly active porous nickel coating. In cathode anodization, a positive potential is applied to the coating which is immersed in an alkaline electrolyte. It has been discovered that anodization in an alkaline electrolyte such as KOH or NaOH is very efficient in dissolving the zinc content from the coating. Therefore, it is possible to produce highly active porous nickel coatings by this process. The typical concentration of electrolyte is from about 20 to about 35 wt %, and a typical electrolyte temperature is from about room temperature to about 90° C. Anodization time is determined by applied current density, and the desired level of zinc removal. Typically, the positive potential applied is sufficient

for dissolving the zinc in the chosen electrolyte. Generally, the positive voltage applied is higher than the electrochemical potential of zinc in the selected electrolyte. Accordingly, the exact potential needed for dissolving out zinc depends on the type of electrolyte, and the temperature. In one embodiment, the positive potential is at least about 1.2 V vs. standard hydrogen electrode (SHE). In another embodiment, the positive potential is at least about 1.5 V vs. standard hydrogen electrode (SHE).

[0035] In certain embodiments, dissolving at least a portion of zinc may optionally include an additional chemical leaching of the coating deposit prior to the anodization step. A strong base, and in some cases an acid, may be used in the leaching step. In an exemplary embodiment, zinc is removed by a strong base. The electrolyte may be any strong aqueous base (or basic solution) which is capable of leaching or dissolving the sacrificial metal. Non-limiting examples are sodium hydroxide or potassium hydroxide. The concentration of the basic solution may generally be from about 1 to about 50 weight percent. The leaching may be done at room temperature (cold leaching) or at an elevated temperature from about 50 to 90° C. (hot leaching). The leaching of zinc is carried out by means well known in the art, i.e., by immersion of the deposit in the alkaline medium, prior to cell assembly; by immersion of the deposit in alkaline media during diaphragm deposition; by immersion of the diaphragm in alkaline media after cell assembly and prior to commencing electrolysis; by contacting the deposit with alkaline electrolyte during electrolysis; or by a combination of any of the above steps. The leaching conditions and durations are optimized to obtain the desired porosity and activity.

[0036] After leaching out zinc from the deposit, an active porous nickel coating is obtained, i.e., one having an active porous surface. As used herein, the term “active porous nickel coating” refers to a coating that has high electrochemical activity compared to the substrate. That is, the coating has a low over-potential as compared to the substrate. The resulting porous coating has a porosity of from about 35 to about 80 percent, and usually, from about 50 to about 75 percent. The resulting coating may exhibit pyrophoric properties. That is, when exposed to air, the coating may increase in temperature. Therefore, the activated coating may be immersed in an electrolyte, maintained under an inert gas, or coated with a protective film, i.e., a wax or polymeric film, when not in an electrolytic cell.

[0037] The porous nickel coatings of the embodiments of the invention are suitable for use in an electrochemical cell. An electrochemical cell is a device, which has at least one anode and cathode, and an electrolyte. The cell may use electrical energy to achieve a chemical reaction, such as the oxidation or reduction of a chemical compound, as in an electrolytic cell. Alternatively, it can convert inherent chemical energy present in a conventional fuel into low voltage, direct-current electrical energy, as in a fuel cell.

[0038] The porous nickel coatings of the invention are suitable for cathodes, especially as hydrogen-evolution cathodes of cells intended for the electrolysis of brine, water or the like. The porous nickel coatings are suitable for halo-alkali cells that have either a diaphragm or a membrane separator. These cells are used to electrolyze aqueous alkali metal halide solutions to the corresponding alkali metal hydroxide and halogen, according to conventional procedures known to the art. While useful for any alkali metal

halide, as a practical matter, they will normally be employed in the electrolysis of sodium or potassium chloride. Also, the porous nickel coatings are well adapted for use as a cathode and/or an anode in a unipolar water electrolyzer, or as a bipolar electrode in a bipolar water electrolyzer. Such devices employ advantageously an alkali metal hydroxide as the electrolyte, because of their decreased hydrogen over-potential and/or low oxygen over-potential for prolonged periods of service. Such water electrolyzers and processes are, in other respects, conventional and known to the art. See, for example, “Water Electrolysis”, in *Industrial Electrochemistry*, second edition, by D. Pletcher and F. C. Walsh, Chapman and Hall (1990), pp. 256-269.

[0039] The electrolytic decomposition of water in an alkaline electrolyte has long been practiced for the production of hydrogen gas. An exemplary electrolytic cell comprising at least one electrode comprising the porous nickel coating of embodiments of the invention is shown in FIG. 3. The cell includes an anode **42** and a cathode **44**, which are in contact with an electrolytic solution **46**. A diaphragm or membrane separator **48** in the cell separates the anode and cathode, and their reaction products. The exemplary cell employs a hydroxyl ion-conductive membrane to achieve a decreased electrolyte resistance. During operation, the selected electrolyte, such as NaOH or KOH, is continually fed into the cell, and a voltage is applied across the anode and cathode. This produces electrochemical reactions, which take place at the anode and cathode to form oxygen and hydrogen gas, respectively.

[0040] The particular materials utilized for the anode and cathode are important, since they provide the necessary catalysts for the reactions taking place at each site. For example, the catalyst plays a critical role in evolving oxygen/hydrogen at the electrodes. In addition to allowing the desired reactions to take place, the catalytic efficiency of the catalytic materials is a very important consideration, since an efficient catalytic material reduces the operating energy requirements of the cell. The applied voltage necessary to produce the anode and cathode reactions in an electrolytic cell is the sum of the decomposition voltage (thermodynamic potential) of the compounds in the electrolyte being electrolyzed, the voltage required to overcome the resistance of the electrolyte and the electrical connectors of the cell, and the voltage required to overcome the resistance to the passage of current at the surface of the anode and cathode (charge transfer resistance). The charge transfer resistance is referred to as the “over-potential”. The over-potential represents an undesirable energy loss, which adds to the operating costs of the electrolytic cell. The high catalytic activity of the porous nickel coatings of the embodiments of the invention makes them attractive for use as anodes and cathodes. These coatings are found to yield lower over-potential as compared to the porous nickel coatings known in the art, as will be discussed in more detail below.

[0041] In such embodiments, the coatings may be deposited on any suitable substrate, depending on the end-use application. When the porous nickel coating is intended for use in a brine-electrolysis diaphragm cell, the diaphragm may be applied directly to the porous nickel surface of the coating. In some cases (zero gap arrangement), the electrode coating is directly applied on the diaphragm. For example, the coating may be made in the form of a tubular screen, and may be immersed in an aqueous dispersion of polytetrafluoroethylene fibers and asbestos fibers. The fibers are drawn

onto the outer surface of the screen until a diaphragm of the desired thickness is formed. As is known in the art, the satisfactory operating lifetime of such diaphragms is not nearly as long as that of the cathodes of the brine electrolysis cells. Economics dictates that the diaphragms must be changed several times during the operating life of the cathode. With nickel coatings of the present invention, the diaphragms may be readily stripped from the porous nickel surface and replaced many times with insignificant detriment to the electrochemical activity or mechanical properties of the electrode.

[0042] In certain embodiments, the above process may involve a chlor-alkali process, potassium permanganate production, potassium perchlorate production, potassium bichromate production, or oxidation of organic compounds, depending on the electrolyte used in the electrolytic cell. These electrochemical processes are well known in the art and hence, need not be described in detail herein. In these processes, the products of interest are typically produced at the anode, while the main cathodic process is hydrogen evolution. Therefore, these processes can benefit from the reduction in the hydrogen over-potential provided by the invention.

[0043] The porous nickel coatings of the embodiments of the invention may form a part of a fuel cell. They are suitable for use as electrodes (anodes/cathodes) in a fuel cell. Fuel cells are electrochemical energy conversion devices that generate electricity and heat by converting the chemical energy of fuels. Fuel cells can accept almost any kind of fuel, including natural gas, coal gas, gaseous fuels from biomass (plant materials and animal waste), and liquid fuels (gasoline, diesel), although some fuels may require preprocessing and purification. Once connected to a fuel supply, a fuel cell will produce electricity until its fuel supply is removed or exhausted.

[0044] In one exemplary embodiment, the fuel cell is a direct methanol fuel cell (DMFC), which can utilize the porous nickel coatings. DMFC's use liquid methanol directly as a fuel, to generate energy. DMFC's are promising candidates for portable power sources, because methanol has high energy density, is easy to handle, and can be purchased at a relatively low price. In order to enhance the activity for methanol oxidation, intense research efforts are directed towards development of improved catalytic materials.

[0045] When providing current, methanol is electrochemically oxidized at the anode electrocatalyst to produce electrons, which travel through the external circuit to the cathode electrocatalyst, where they are consumed together with oxygen in a reduction reaction. The circuit is maintained within the cell by the conduction of protons in the electrolyte. In modern cells, electrolytes based on proton conducting polymer electrolyte membranes are often used, since these allow for convenient cell manufacture, and for high temperature and pressure operation. A schematic description of the components in a direct methanol cell **50** is shown in FIG. **4**. The typical overall reaction is as follows:



[0046] The heart of the direct methanol fuel cell is the proton exchange membrane **52**: a thin membrane covered on both sides with the catalyst coating **54**. In an exemplary embodiment, coating **54** is the porous nickel coating described previously, sandwiched between two electrodes **56** and **58**. A methanol/water solution is introduced to a negatively charged electrode **56** that spontaneously reacts by breaking the methanol molecules apart. Once broken up, the

carbon atom combines with the oxygen atoms from the methanol and water at the negative electrode **56**, to form carbon dioxide.

[0047] The hydrogen atoms are further separated, while the protons pass through the membrane to the positively charged electrode **58**. Meanwhile, the electrons are forced to go around the membrane, forming an electric current. The two parts of the hydrogen atom are reunited at the positive electrode, and combine with oxygen to produce water. Because it readily frees its hydrogen to react in the fuel cell, methanol is an ideal hydrogen carrier.

[0048] In one embodiment, the fuel cell is a solid-oxide fuel cell (SOFC). SOFCs are made from solid-state materials, namely ceramic oxides. SOFCs consist of three components: a cathode, an anode, and an electrolyte sandwiched between the two. Oxygen from air is reduced at the cathode and is converted into negatively charged oxygen ions. These ions travel through the electrolyte to the anode, where they react with fuel that has been delivered to the anode. The fuel is oxidized by the oxygen ions, and releases electrons to an external circuit, thereby producing electricity. The electrons then travel to the cathode, where they reduce oxygen from air, thus continuing the electricity-generating cycle. The porous nickel coating of the embodiments of the invention is characterized by high porosity and high catalytic activity, and may be used as an anode in a solid state fuel cell.

[0049] The nickel catalyst may also be used in hydrogenation and dehydrogenation reactions, for example in halogen-hydrogen exchanges, or the reduction of nitro, nitrile and oxo groups. These coatings may be used in the cracking reaction of petroleum, involving the hydrogenation of heavy oil to gasoline or kerosene, or hydrogenation of tar to a liquid, so that it is more suitable for further applications. Furthermore, hydrogenation, utilizing the nickel catalyst, may be used to convert unsaturated hydrocarbon to a corresponding saturated hydrocarbon. In particular, the porous nickel catalyst may be used in reducing a carbon-carbon double bond. A typical example is the catalytic hydrogenation of cyclohexane. The substance to be hydrogenated may either be an inorganic compound or an organic compound. Any inorganic or organic compound without particular limitation can be subjected to a hydrogenation reduction in accordance with the invention, whether it is liquid or gaseous. Thus, no supporting electrolyte is required.

[0050] In certain embodiments, the porous nickel is used as a catalyst or reagent in an organic synthesis. For example, the nickel may be used as a catalyst in the hydrogenation of compounds that have multiple carbon-carbon bonds, such as alkynes, alkenes, dienes, and aromatic hydrocarbons with hydrogen. Additionally, the nickel catalyst may be used in the reduction of carbon-heteroatom bonds such as nitriles and carbonyls, and the reduction of heteroatom-heteroatom bonds such as nitro groups. The nickel catalyst of the embodiments of the invention may be used in the reductive alkylation of amines and the amination of alcohols. Alternatively, the nickel catalyst may act as a reagent to desulfurize organic compounds.

[0051] The method of the present invention is designed to meet fundamentally different design requirements from those applied to conventional methods used for making porous nickel coatings. Typically-used methods to make porous nickel coatings, such as sintering of nickel and aluminum, and then selective leaching of aluminum, or plasma spraying processes, have not been successful in providing coatings suitable for large-scale production and desirable over-potential. Conventionally used processes to make porous nickel coatings from nickel-aluminum depos-

its/films suffer from a number of drawbacks. Aluminum is more expensive than zinc, and can sometimes be an explosion hazard when it is present as a fine particulate dust. Nickel-zinc based coatings have been examined less frequently, because of the problems associated with the leaching of zinc from the coatings. The rate of zinc reaction with the base (leaching) is much slower than the same reaction with aluminum, and the reaction stops when zinc content is still high (about 25%). Therefore, porous coatings based on nickel-zinc coatings have shown poor activity. However, the inventors have discovered a method of efficient leaching of zinc from the coatings. In addition, the method of the present invention provides porous nickel coatings with superior catalytic properties.

EXAMPLES

[0052] The following examples are presented to further illustrate certain embodiments of the present invention. These examples should not be read to limit the invention in any way.

Example 1

[0053] Sample Preparation: Porous Ni-Based Coatings by Twin Arc Spray Process

[0054] A wire arc coating of Ni based alloys on Microcell cathodes cut from stainless steel 304 sheet with thickness of about 1.6 millimeters was formed, using a SmartArc-350PP Electric Arc Spray System manufactured by Sulzer Metco. Zinc was co-sprayed with Ni and Ni-based alloys by feeding two wires made of these materials into the spray system. For comparison, a set of samples was prepared by co-spraying nickel along with aluminum. The coating thickness was about 114 microns to about 228 microns after 3 passes.

[0055] Zinc Leaching:

[0056] To determine optimal conditions for leaching, different procedures were tested: hot leaching included leaching at 80° C., and cold leaching included leaching at 25° C. Leaching outside the cell included leaching overnight in a beaker with 30% KOH, while cold in-cell leaching included leaching overnight at 25° C. in an assembled cell, and hot in-cell leaching, included leaching for 4-5 hours at 80° C. in an assembled cell. To improve zinc removal from the initial coating, electrochemical oxidation (anodization) was used on the samples. It was found that for zinc-based wire arc coatings, anodization significantly improves electrode performance, and the best cathode preparation procedure was cold in-cell leaching, followed by anodization at a current density of about 110 mA/cm², for a duration of 30 minutes. All of the anodizations were carried out under these conditions.

[0057] Electrochemical Measurements:

[0058] Standard 4-dram glass vials equipped with a Teflon cap with 2 or 3 drilled holes (for 3-electrode experiments) for electrodes, and 1 or 2 drilled holes for sampling and gas release, were used as undivided electrochemical cells in batch experiments. The same batch cells with two electrodes and one sampling hole were used in high throughput experiments. A Hg/HgO electrode (CH Instruments) in 6 molar KOH was used as the reference electrode. Metal and graphite rods of about 6 millimeters and about 5 millimeter in diameter were used as electrodes for batch cells. The working surface area of these electrodes was in the range of 2.1 cm²-2.5 cm². To provide a fair comparison, the charge accumulation and current were measured at 6000 sec.

[0059] A commercial ElectroCell AB Microflow® cell with metal electrodes and PTFE gaskets by Electrolytica,

Inc., with a working electrode surface of 8.8 cm², was used in flow cell experiments. The cell was used in undivided form, or was divided with a porous diaphragm. The electrolyte was placed in two glass vessels or round bottom flasks equipped with a condenser for elevated temperature experiments, and had been recirculated, using MasterFlex L/S peristaltic pump. All hoses and connectors were made from PTFE. The electrolyte temperature was maintained using a heating tape with a regulator. Gas analyses were performed using Varian Micro GC.

[0060] Power potentiostats (CHI 1100) were used for cyclic voltammetry experiments, and for bulk electrolysis with coulometry runs. Power source Sorensen DCS40-13E and HP 6296A were used for bulk electrolysis in a controlled current regime for flow cell experiments, which were designed and analyzed using Design-Expert 6.0.1 program.

[0061] The batch glass cell, equipped with a stirring bar, was charged with a 30 wt. % solution of KOH (typically 21 g). Bulk electrolysis was performed at constant potential. Hydrogen produced on the cathode and oxygen produced on the anode were vented through the sampling hole. The typical time of experiment was 2 hours. After that, a I-V curve was obtained for each set of electrodes.

[0062] In a typical flow experiment, two glass storage/gas-liquid separation vessels were connected to a peristaltic pump, and to the Microflow cell with about 6 millimeter diameter PTFE tubes, forming a closed loop. Before each experiment, all connections and the flow cell were checked for leaks, and the cell and electric connections were checked for electrical shorts. The vessels were charged with 500-600 mL of KOH electrolyte. The cell was filled with electrolyte, using a priming regime, and again checked for leaks. Constant current was applied during electrolysis. The temperature of the electrolyte was maintained using silicon heating tapes, and controlled by a thermometer. The electrolyte level in gas-liquid separators was maintained at the same level. The amount of hydrogen produced was measured using a Cole-Parmer digital flow meter with a totalizer.

[0063] Over-potentials for hydrogen and oxygen evolution reactions are different, but both can be described in simplified form by the Tafel equation (2). The intercept at $h=0$ gives the exchange current density i_0 . $\eta=a+b*\log i$ (2)

$$U_{cell}=U_{rev}+b*\log(i/i_0)+i*R_{cell} \quad (3)$$

In this case, Eq. 3 describes the cell potential. Usually the Tafel slope increases with temperature. However, exceptions are also known. It was observed that for the hydrogen evolution reaction (HER), I-V curves are often better described by two different Tafel slopes, due to the change in reaction mechanism. At low current densities the slope was usually smaller than that for higher current densities. According to the Tafel equations (2,3), the over-potentials increase logarithmically with current density. However, for high current densities (typically from 0.3 to 1 A/cm²) these values can be very well linearized to give Eq. 7.

$$U_{cell}=U_{rev}+DU_h+iR_h+iR_{cell} \quad (7a)$$

$$U_{cell}=U_h+i(R_h+R_{cell}) \quad (7b)$$

[0064] The parameters a and b were calculated for different coatings. The cell voltages were measured for samples leached under different conditions at current density of 270 mA/cm² at 80° C. (9 cm² flow cell and SS304 anode), and the data is plotted in FIG. 5. Plot 60 indicates the cell voltage measured on a sample, which was leached in hot KOH outside the cell, 62 indicates the cell voltage measured on a sample, which was leached in hot KOH inside the cell, 64 indicates the cell voltage measured on a sample, which was

leached in cold KOH outside the cell, **66** indicates the cell voltage measured on a sample, which was leached in cold KOH inside the cell, and **68** indicates the cell voltage measured on a sample which was leached in cold KOH followed by anodization. It was found that the cathode performance increased in the order: hot out of cell < cold out-of cell > cold in cell < hot in-cell. With anodization followed by cold leaching, there was a significant improvement of about 150-170 mV in the over-potential. The best cathode preparation procedure was the cold (room temperature) treatment with a KOH solution, either outside or inside the cell, followed by anodization in the assembled cell.

[0065] FIG. 6 shows the plot of cell voltage vs. current density for nickel-zinc and nickel-aluminum samples at 20° C. and at 80° C. The plots **70** (Ni—Al at 20° C.), **72** (Ni—Zn at 20° C.), **74** (Ni—Zn at 80° C.) and **76** (Ni—Al at 80° C.) indicate that the cell voltage of the nickel-zinc-based coating is generally less than the cell voltage of the nickel-aluminum-based coating. The difference is especially significant at 80° C., implying that the performance of a nickel-zinc-based coating is substantially better than the nickel-aluminum-based coatings.

[0066] FIG. 7 shows the plot of cell voltage vs. current density for nickel-zinc and nickel alloy-zinc samples at 80° C. Plot **82** is associated with Ni—Al—Mo, plot **84** is associated with Ni—Al—2Mo, plot **85** is associated with Ni, and plot **86** is associated with Ni—Co. Ni—Al—2Mo samples showed the best cathode performance. Microphotographs (not shown) of the most active fresh, leached, and tested wire arc coatings made from Ni-5Al-15Mo alloy and zinc wires indicated the presence of two phases (zinc and nickel-based alloy) in fresh samples, and voids formed during leaching were clearly seen for the tested sample, implying that a porous coating has formed on leaching.

[0067] While the invention has been described with reference to exemplary embodiments, it will be understood by those skilled in the art that various changes may be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from the essential scope thereof. Therefore, it is intended that the invention not be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the appended claims.

What is claimed is:

1. A method of forming a porous nickel coating, comprising the steps of:

depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit;

wherein the selected composition comprises nickel and zinc; and then

dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

2. The method according to claim **1**, wherein the total, selected composition of the consumable electrode wires comprises at least about 50 weight percent of zinc.

3. The method according to claim **1**, wherein a first consumable electrode wire comprises zinc.

4. The method according to claim **3**, wherein the first consumable electrode wire comprises at least about 90 weight percent of zinc, based on the total weight of the wire.

5. The method according to claim **1**, wherein a second consumable electrode wire comprises nickel.

6. The method according to claim **5**, wherein the second consumable electrode wire comprises at least one alloying additive selected from the group consisting of Al, Mo, Co, and combinations thereof.

7. The method according to claim **6**, wherein the amount of the alloying additive for the second consumable electrode wire is no greater than about 30%, based on the total weight of the wire.

8. The method according to claim **7**, wherein the second consumable electrode wire comprises the alloying additive in the range from about 0.05 weight percent to about 30 weight percent, based on the total weight of the wire.

9. The method according to claim **1**, wherein at least one of the consumable electrode wires comprises a powder-filled core and a solid metal shell.

10. The method of claim **1**, wherein dissolving at least a portion of the zinc comprises dissolving an amount of zinc in the range from about 70 weight percent to about 100 weight percent of zinc.

11. The method of claim **1**, wherein the positive potential is at least about 1.2 V vs. standard hydrogen electrode (SHE).

12. The method of claim **11**, wherein the positive potential is at least about 1.5 V vs. standard hydrogen electrode (SHE).

13. The method of claim **1**, wherein dissolving at least a portion of the zinc further comprises chemical leaching of the coating deposit prior to applying the positive potential.

14. A porous nickel coating formed by the process of:
depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit;
wherein the selected composition comprises nickel and zinc; and then

dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

15. An electrolytic cell comprising at least one electrode which itself comprises the porous nickel coating obtained by the method of claim **1**.

16. A direct methanol fuel cell comprising at least one electrode which itself comprises the porous nickel coating obtained by the method of claim **1**.

17. A method of generating hydrogen from a cathode in an electrolytic cell by passing an electric current between an anode and the cathode, wherein the cathode comprises a porous nickel coating formed by:

depositing coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit;

wherein the selected composition comprises nickel and zinc; and then

dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

18. The method according to claim **17**, wherein at least one of the consumable electrode wires comprises at least about 40 weight percent of zinc.

19. The method according to claim **18**, wherein at least one of the consumable electrode wires comprises at least about 80 weight percent of zinc.

20. An electrochemical process using the electrolytic cell of claim **15**, wherein the electrochemical process comprises at least one process selected from the group consisting of a chlor-alkali process, potassium permanganate production, potassium perchlorate production, potassium bichromate production, and oxidation of organic compounds.

21. A method of making a porous nickel catalyst, comprising the steps of:

depositing a coating onto a substrate by melting and atomizing two consumable electrode wires of a selected composition in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit;

wherein the selected composition comprises nickel and zinc; and then dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel catalyst.

22. A chemical process of hydrogenation of unsaturated chemical bonds, in which the porous nickel catalyst formed in claim **21** is used to catalyze at least one step of the process.

23. The chemical process of claim **22**, wherein the porous nickel catalyst reduces a carbon-carbon double bond.

24. A chemical process in which the porous nickel catalyst made in claim **21** is used as a reagent.

25. A method of forming a porous nickel coating, comprising the steps of:

depositing a coating onto a substrate by melting and atomizing a first consumable electrode wire comprising nickel and at least one alloying additive selected from the group consisting of Al, Mo, Co, and a second consumable wire comprising zinc in a wire-arc spray device, so as to form a molten, atomized material, and directing the material to the substrate to form a coating deposit; and then

dissolving at least a portion of the zinc from the coating deposit by applying a positive potential in an alkaline electrolyte, so as to obtain a porous nickel coating.

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