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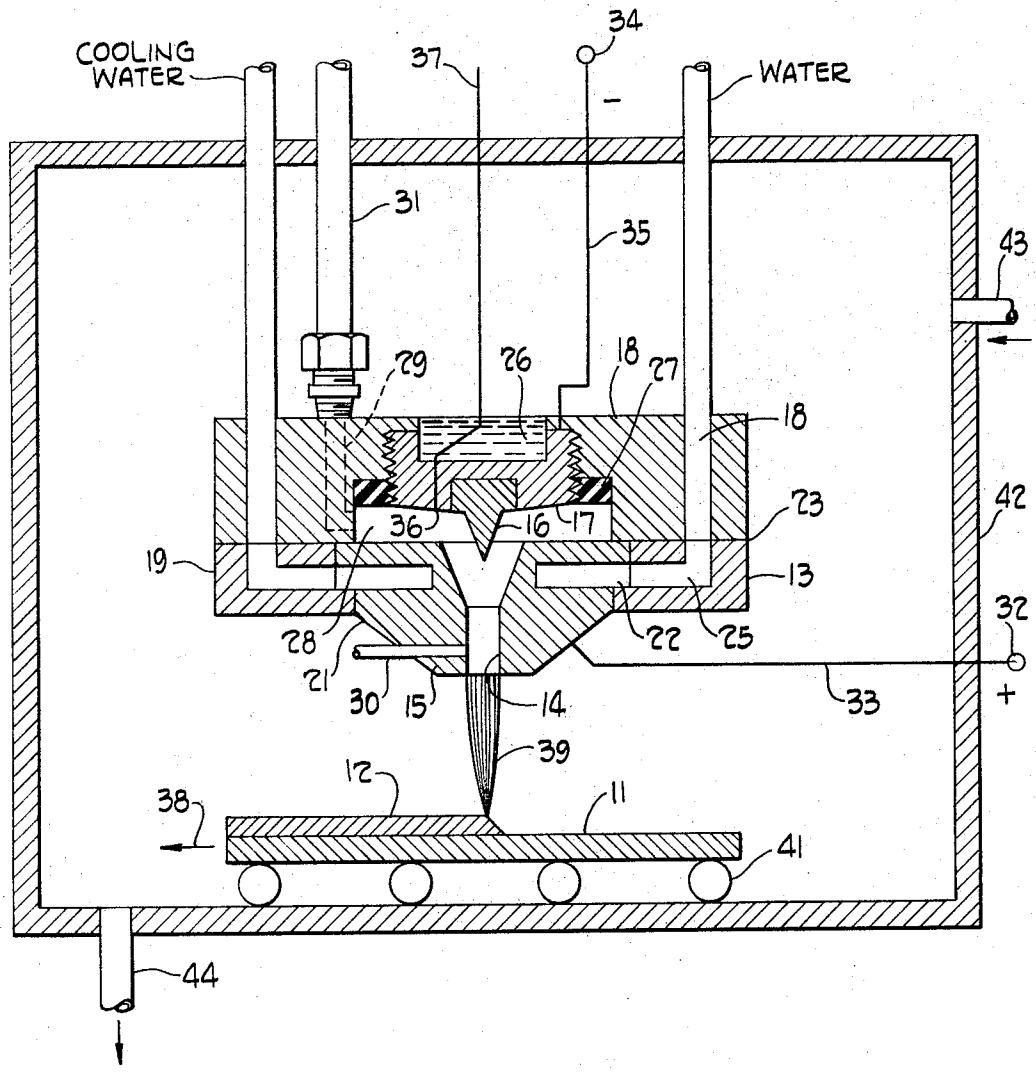

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FORMATION OF CATALYTIC OXIDE SURFACE ON AN ELECTRODE

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This invention relates to oxide coating, and concerns particularly the formation of oxide coatings on supporting substrate surfaces.

Electrochemical reaction devices using an oxygen electrode require a hard thermally resistant oxide coating, especially a catalytic coating with a variable oxidation state. High melting point refractory oxide coatings are desired.

In certain devices such as electric storage devices and fuel cells, the valence exchange feature of metals with variable oxidation states such as molybdenum, vanadium, tungsten and chromium is employed to enhance the rate or quantum of electron generation.

This application, accordingly, is concerned with the provision of electrodes with coatings of variable oxidation state which may be employed in electrodes for electrochemical reaction processes, particularly for fuel cells, capacitors, electric storage devices, electrochemical reaction apparatus for selective oxidation-reduction of certain chemical compounds, and other devices where oxygen chemisorption-desorption is desired.

In carrying out the invention in a preferred form thereof, a suitable medium such as the flame of an oxy-hydrogen or oxyacetylene torch or a plasma arc torch is employed for spraying on to a suitable substrate, in an oxygen rich atmosphere, a substance which forms an effective oxidation catalyst having the properties of the oxides of molybdenum, vanadium, tungsten and chromium. The oxides in accordance with one embodiment are applied directly in the powder form, or the oxides are formed in situ while spraying by fluidizing the parent metal powder in an oxygen carrier before feeding to the flame or arc, thus oxidizing the metal at the temperature of the coating process. In accordance with another embodiment a suitable compound is decomposed in the vapor phase in an oxygen rich flame or arc to form the oxide.

Still another embodiment would include the deposition of an oxide of an inactive metal upon a sub-strate, by the use of a flame or arc followed by a post-impregnation of deposited oxide with a solution of a compound of a catalytically active metal.

A better understanding of the invention will be afforded by the following detailed description considered in conjunction with the accompanying drawing constituting a schematic diagram of a plasma arc torch being employed to form a variable oxidation state surface on a substrate.

Coating may be accomplished by the utilization of a plasma-stream torch **13** of the type described in Patent No. 2,922,869 and illustrated therein.

The plasma coating torch **13** comprises a nozzle **14** formed in a copper anode **15** cooperating with a cathode **16** mounted in a copper cathode holder **17**. The cathode **16** is composed of thoriated tungsten. The cathode holder **17** is secured in a suitable manner as by means of threading it into a non-conducting body **18** to which the copper anode **15** is removably secured. The anode **15** is secured by a body **19** having a lip **21** engaging a shoulder **22** in the copper anode **15**.

Suitable means such as bolts (not shown) and a ring gasket (not shown) are provided for securing the bodies

18 and **19** together with a water proof seal **23**. Aligned passageways **24** and **25** are provided in the bodies **18** and **19** for cooling water. Likewise, a pocket or well **26** for a body of cooling water is formed in the cathode holder **17**. A water proof joint between the cathode holder **17** and the body **18** is formed by means of an insulating gasket **27**.

The body **18** is so formed as to provide an arc chamber **28** therein surrounding the cathode **16** and a passageway **29** is formed in the body **18** for injecting material to be fed into the chamber **28** for feeding into the jet **39**. An inlet tube **31** is connected to the passageway **29** for supplying the arc operating inert gas, such as argon.

For feeding in certain types of materials which must be fed to the arc after it has been formed an alternate injection port **30** may be provided in the anode **15** adjacent the nozzle **14**. The injection port **30** is close to the outlet of the nozzle **14**.

The anode **15** is connected to a positive current supply terminal **32** by a diagrammatically indicated conductor **33** and the cathode holder **17** is connected to a negative current supply terminal **34** through a diagrammatically indicated conductor **35**. Preferably a starter electrode **36** is also provided which is adapted to be connected through a conductor **37** to a source of starting or ignition voltage.

As indicated schematically by the arrow **38**, the substrate **11** is adapted to be moved as the coating **12** is applied by the plasma jet or stream **39**. As shown, the substrate **11** is mounted upon a roller table indicated schematically by rollers **41**, driven by suitable means (not shown).

The jet-maintaining gas is applied through the tube **31**. If desired, refractory material in the form of powder may be suspended in the gas jet and introduced through the tube **31**. In cases where the material is of such a nature as to make it most feasible to entrain it in the arc at the nozzle **14**, the alternate injection port **30** is employed for entraining the powdered refractory material.

When the substrate **11** is an oxidizable metal or composed of a material capable of reacting with oxygen such as carbon or graphite, the coating is preferably carried out in an inert atmosphere stream or by enclosing the entire assembly in a housing **42**. An inert gas such as argon is in this case introduced through an inlet **43**. The housing **42** is provided with an outlet **44** for gas from the plasma jet **39** and for any other substances or reaction products.

The gas supplied in the inlet tube **31** may comprise an inert gas such as argon, helium or nitrogen which, however, is rich in oxygen to prevent thermal dissociation of oxygen atoms from a high oxide to a lower oxide state resulting from the vaporized entrained powder.

The powder employed is one which will produce an effective oxidation catalyst having catalytic properties similar to tungsten, molybdenum, vanadium or chromium oxides. One of these parent metals may be employed in powdered form and is fluidized in the oxygen carrier brought through the injection port **30** into the oxygen rich arc. The high temperature causes conversion to the oxide which is sprayed by the plasma jet **39** against the surface of the substrate **11** to form the oxide coating **12**.

Instead of the parent metal powder, a suitable compound may also be employed which is decomposed by vapor phase decomposition in the oxygen rich flame or arc to the desired oxide. Among the compounds which may be used for this purpose are ammonium metatungstate, $(NH_4)_2W_4O_{13}\cdot 8H_2O$, ammonium vanadate,

NH_4VO_3

a complex hydrated ammonium molybdate,

$$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$$

chromium carbonyl, Cr $(CO)_6$, or many other compounds of similar nature.

The gas flow into the inlet **31** is regulated to permit a current of the order of 300 to 800 amperes to flow with a potential difference between terminals **32** and **34** not exceeding 50 volts, in the case of argon, and not exceeding 175 volts in the case of nitrogen or helium, and to maintain a temperature between 7000° F. and 14,000° F. in the arc **39**.

The process of the invention may be illustrated by the following specific example of a process of depositing a vanadium oxide coating on steel.

The cold rolled steel sub-strate surface **11** to be coated was sand blasted, washed with solvent to remove grit and grease, and air dried. This optional pretreatment improves the quality of adhesion of the oxide coating to the steel. The plasma spraying of the oxide powders was carried out with a Giannini Plasmadyne Corporation Model L–40 plasma generating system with an N–4 head. The vanadium oxide (V_2O_5) powder of −150 to+325 mesh particle size was fed to the arc **39** by means of a feed hopper (adapted from the "Flame Ceramic" spray equipment of Continental Coating Corporation) for entraining the finely divided powder in the stream of argon carrier gas supplied through the inlet tube **31**.

Four Miller Electric Company rectifiers capable of producing forty-eight kilowatts supplied the electrical power for the arc. In this case, the arc gas rate was 1.0 standard cubic feet per minute of argon, and the powder-carrier gas rate also was 1.0 standard cubic feet per minute of argon at an arc current of 500 amperes and 40 volts. The area of the substrate sheet to be coated was passed rapidly back and forth across the nozzle exit of the plasma arc at a distance of three inches from the arc anode while being cooled on the reverse side at the same time by a stream of air.

The coating produced was a VO_2 blue coating which could be dissolved off in acid to produce the typical vanadyl blue solution. The VO_2 blue coating could be converted to orange-brown V_2O_5 upon mild heating in air.

Another specific example, under exactly the same condition with the exception that the carrier gas was air instead of argon, produced an orange-brown coating of V_2O_5 directly. As other examples, ammonium heptamolybdate sprayed in an oxyhydrogen flame gave a molybdenum blue coating when the hydrogen to oxygen ratio was greater that two to one and gave a white coating of molybdenum trioxide when the hydrogen to oxygen ratio was less than two to one.

In another example, the cold rolled steel substrate, in the form of a 1⅞ inch diameter by ⅛ inch thick disc, was pretreated with a Pangborn type "AY" grit blasting machine using No. G–40 angular iron grit. The grit blasted disc was washed with solvent to remove grit and grease and then air dried. The disc was then immediately plasma-sprayed with alumina using the Giannini Plasmadyne Corporation Model L–40 plasma generating system with an N–4 head and applying techniques similar to those previously described for the plasma spraying of the catalytically active materials. However, in this case, the powder which is sprayed is Davison High Purity Beta Trihydrate Alumina (screened to −140 to +325 mesh) using argon as the carrier gas.

The weight of the alumina coating was determined to be 0.4177 gram. Approximately 0.08 milliliter of a sixty-two percent aqueous solution of chromium nitrate [$Cr(NO_3)_3$] was distributed evenly over the surface of the alumina deposit by means of a one hundred microliter syringe. A few minutes were allowed for the liquid to become completely absorbed, and then the disc was dried in an electric oven for twenty-five minutes at a temperature of 120 degrees C. This process was repeated until five approximately equal increments (a total of 0.392 milliliter) of the chromium nitrate solution had been added. After the last incremental addition of chromium nitrate solution had been dried, the disc was placed in an electric furnace and heated for one hour at 1000 degrees C. to decompose the nitrate. This resulted in a coating composition containing 19.3 percent of chromic oxide (Cr_2O_3) on alumina.

Certain embodiments of the invention and certain methods of operation embraced therein have been shown and particularly described for the purpose of explaining the principle of operation of the invention and showing its application, but it will be obvious to those skilled in the art that many modifications and variations are possible, and it is intended, therefore, to cover all such modifications and variations as fall within the scope of the invention.

What is claimed is:

1. The method of producing electrodes for use in an electrochemical apparatus, said electrodes having variable oxidation state surfaces and produced by the steps of suspending in an oxygen-rich plasma torch arc a dry, free-flowing material selected from the group consisting of ammonium metatungstate $(NH_4)_2W_4O_{13}.8H_2O$, ammonium vanadate, NH_4VO_3, ammonium molybdate,

$$(NH_4)_6Mo_7O_{24}.4H_2O$$

and vanadium pentoxide, V_2O_5, and projecting a plasma jet containing suspended decomposition products thereof against a substrate, said surface consisting essentially of said decomposition products.

2. The method of producing electrodes for use in an electrochemical apparatus, said electrodes having variable oxidation state surfaces and produced by the steps of suspending in an oxygen-rich flame of an oxy-hydrogen torch a substance selected from the group consisting of ammonium metatungstate, $(NH_4)_2W_4O_{13}.8H_2O$, ammonium vanadate, NH_4VO_3, ammonium molybdate,

$$(NH_4)_6Mo_7O_{24}.4H_2O$$

and vanadium pentoxide, V_2O_5 and projecting the flame and the resulting decomposition product against a substrate, said surface consisting essentially of said decomposition product.

3. The method of forming an electrode for use in an electrochemical apparatus said electrode having a variable oxidation state surface and produced by the steps of thermodecomposition of a compound selected from the group consisting of ammonium metatungstate,

$$(NH_4)_2W_4O_{13}.8H_2O$$

ammonium vanadate, NH_4VO_3, and ammonium molybdate, $(NH_4)_6Mo_7O_{24}.4H_2O$, in a flame spray process and spraying the medium onto the substate, said sufrace consisting essentially of said decomposition product.

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