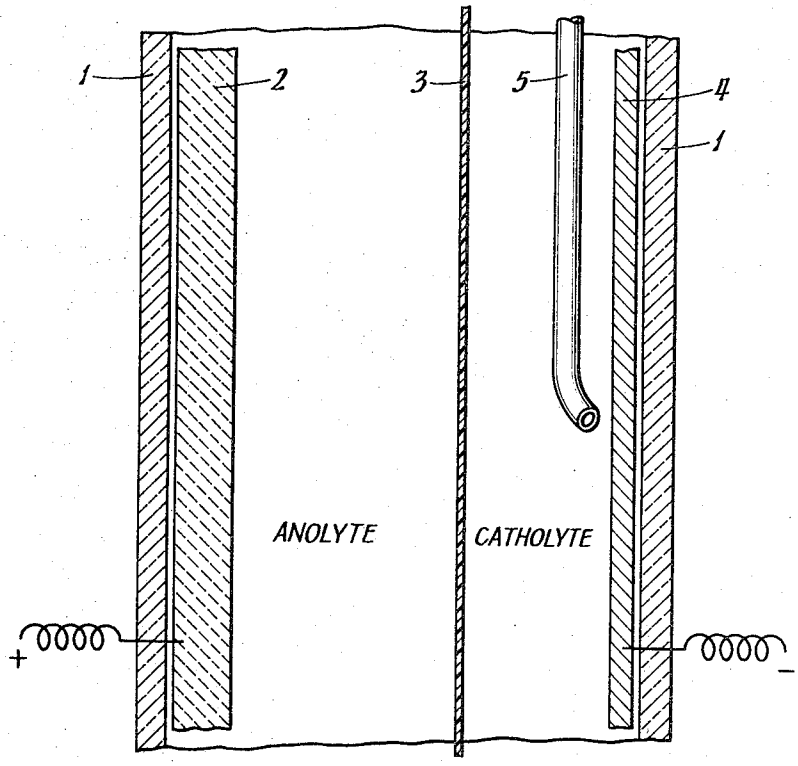
Oct. 31, 1967 J. R. HALL ET AL 3,350,294

ELECTRODES

Filed Nov. 21, 1963



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United States Patent Office 3,350,294
Patented Oct. 31, 1967

3,350,294

ELECTRODES

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Filed Nov. 21, 1963, Ser. No. 325,279
Claims priority, application Australia, Nov. 21, 1962, 24,574/62
10 Claims. (Cl. 204—290)

This invention relates to electrodes for use in electrolytic cells.

In the electrolytic cells for the electrolysis of brine or in direct current generators such as fuel cells, the cathodes most commonly used at present are made from iron or steel. Such electrodes, because of their low corrosion resistance in acidic media, impose limitations on the cell design; thus e.g. they must not come into direct contact with the anolyte because of the rapid attack of halogens on iron in aqueous medium.

Furthermore, it is well-known that the voltage drop between the anode and the cathode in an electrolytic cell in which gases are generated at the electrodes is made up of a number of components one of which is the overvoltage for the particular gases and for the particular electrodes concerned.

In industrial applications of electrolytic cells it is very important from the point of view of operating costs to reduce to a minimum the voltage drop for an electrolytic process and this therefore leads to the use of electrodes having the lowest overvoltage potentials in the system employed. For example, it is customary in alkaline cells involving evolution of hydrogen and oxygen to use a nickel anode and an iron cathode.

In certain cells it is important for reasons other than operating cost to reduce the voltage drop to a minimum. Thus in certain cases the constructional design of the cell may be materially simplified by reducing the voltage drop by even as little as 0.1 volt.

It is known that finely divided platinum or palladium coatings deposited on the iron support of the electrode overcome the disadvantages associated with steel electrodes by reducing the hydrogen overvoltage, but such deposits are very expensive and not always durable enough to be economical.

In U. S. Patent No. 3,291,714, patented Dec. 13, 1966, we have disclosed that certain alloys may be deposited on suitably pretreated titanium core electrodes to provide composite cathodes of a lower hydrogen overvoltage. In Patent No. 3,291,714, we have also disclosed that certain of these alloys can be deposited on metallic, particularly steel, electrodes which have a reduced hydrogen overvoltage when used as cathodes in electrolytes.

We have now found that it is also possible to co-deposit tungsten and molybdenum together with one or more metals selected from the group of iron, cobalt and nickel on metallic electrodes, particularly titanium and steel electrodes, to form electrodes of considerable durability which have a very low hydrogen overvoltage when used as cathodes in aqueous electrolytes.

Accordingly we provide an electrode comprising a support formed from a metal suitable for the construction of solid electrodes, portion or the whole of the surface of which is conductively covered by a coating of an alloy consisting of the primary metals molybdenum and tungsten alloyed with one or more secondary metals selected from the group of cobalt, nickel and iron.

We also provide an electrode comprising a support formed from a metal suitable for the construction of solid electrodes, portion or the whole of the surface of which is conductively covered by a coating of a co-deposit consisting of molybdenum and tungsten and one or more metals selected from the group of cobalt, nickel and iron.

We furthermore provide an electrolytic cell having a cathode formed from a metal suitable for the construction of solid electrodes, portion or the whole of the surface of which is conductively covered by a coating of an alloy consisting of molybdenum and tungsten alloyed with one or more metals selected from the group of cobalt, nickel and iron.

One preferred metal of the electrode supporting the alloy coating is iron, conveniently in the form of mild steel.

Another preferred metal of the electrode supporting the coating is titanium.

The electrodes of the invention may be in the form of wire, tube, rod, planar or curved sheet, perforated sheet, expanded metal, foraminous metal, gauze, porous, compacted or fused metal powder.

While the electrodes of this invention can be used as cathodes generally they are particularly useful as hydrogen cathodes i.e. when hydrogen is deposited on or evolved from them.

When the electrodes of the present invention are used as cathodes in fuel cells a higher operating voltage, faster reaction rate, improved capacity and better energy efficiencies are attained.

Accordingly we also provide a process of producing electric current from a fuel cell characterised in that the cathode of the fuel cell is an electrode according to the present invention.

The preferred use of the invention is in electrolytic processes for the production of hydrogen from aqueous electrolytes.

Accordingly we provide a process of electrolysing an aqueous electrolyte characterised in that hydrogen is evolved electrolytically from a cathode according to the present invention.

The cathodes of our invention are particularly useful for the electrolysis of alkali chloride solution to produce hydrogen, alkali hydroxide and chlorine or, alternatively, to produce alkali chlorate. When hydrogen, sodium hydroxide and chlorine are produced from brine using the cathodes of this invention, a considerably reduced operating voltage and improved energy efficiency and corrosion resistance are attained.

A preferred embodiment of this invention comprises an electrolytic cell suitable for electrolysis of aqueous sodium chloride solution characterised in that the cathode is an electrode according to this invention.

The preferred range of composition for the molybdenum/tungsten alloys is shown at the top of Table I. If the composition is kept within the most preferred range shown at the bottom of Table I, the maximum reduction in hydrogen overvoltage is achieved.

All percentages in this specification are given by weight.

It has been established that electro-deposited layers contain varying amounts, up to 10%, of non-metallic constituents such as oxide. It is, however, convenient to express results as a percentage of the metallic constituents only. The analysis of very thin layers of alloys is fraught

with difficulties; consequently the figures stated are thought to be accurate to within ±2% of the amount present.

TABLE I

Alloy			Preferred range of metallic constituents (weight percent) in electrode coating		
A	B	C	Primary Constituent A	Secondary Constituent B	Tertiary Constituent C
Mo	W	Fe	2-60% Mo	2-70% W	100%(A+B) Fe
			Where (A+B) is between 10 and 72%		
Mo	W	Ni	2-60% Mo	2-45% W	100%(A+B) Ni
			Where (A+B) is between 10 and 62%		
Mo	W	Co	2-60% Mo	2-70% W	100%(A+B) Co
			Where (A+B) is between 10 and 72%		
			Most preferred range of metallic constituents (weight percent) in electrode coating		
Mo	W	Fe	30-55% Mo	2-35% W	100%(A+B) Fe
			Where (A+B) is between 32 and 65%		
Mo	W	Ni	30-55% Mo	2-35% W	100%(A+B) Ni
			Where (A+B) is between 32 and 62%		
Mo	W	Co	35-55% Mo	2-30% W	100%(A+B) Co
			Where (A+B) is between 37 and 65%		

The cathodic alloy surfaces of the present invention may be applied to the surface of the metal support by a number of methods known "per se." They may be deposited by electroplating, by sintering a mixture of the powdered alloy metals under the application of heat, with or without pressure, by roll-bonding, vacuum depositing, metal spraying or rolling the powdered alloy or a mixture of the powdered metals on to the metal sheet, or by painting metallising solution of the alloy on to a metal sheet and subsequent firing, where the metals of the alloy coating are applied in a finely divided form in an organic slovent resin system.

The preferred method of deposition of the alloy is by electroplating. The surface of the metal sheet may be subjected to pretreatments to facilitate the depositing of the alloy layer and its surface area may be increased by surface treatment or by manufacturing the metal sheet by rolling metal in powder form to produce a compacted sheet of vast surface area. A number of methods of pretreatment and of increasing the surface area of the metal sheet are known "per se." Compared with platinised titanium cathodes the cathodes of the present invention have the advantage of considerably lower capital cost; compared with conventional iron or steel cathodes they have the advantage that they are more corrosion resistant and have a lower hydrogen overvoltage and consequently a lower operating voltage and energy consumption. A particular advantage of this invention is that the electrodes can be prepared from existing mild steel electrodes by plating the steel electrodes after descaling pickling treatment. Thus no large capital expenditure is required for converting existing electrolytic cells into cells having the reduced cathode overvoltage of the present invention.

The lowering of the overvoltage on the cathodes of the present invention may be demonstrated in pure alkali chloride and iodide solutions or in the solutions normally encountered in the electrolyte of diaphragm cells and in chlorate and iodate cells.

The reduced hydrogen overvoltage of the cathodes of the present invention under practical operating conditions compared with the mean attainable cathode potential of "aged," i.e. well rusted steel electrodes is apparent from Table II. It is well known and was confirmed during these experiments that rusted steel electrodes have the lowest cathode potential which can, in practice, be attained from steel electrode.

The voltages stated in Table II include liquid junction potentials and the small ohmic potential drop of the column of electrolyte between the cathode and the tip of the Luggin capillary and the potential arising from the concentration polarisation at the cathode surface and hence are not indicative of overvoltages in the strictly scientific sense, but the measurements are strictly comparable between experiments.

TABLE II

Temperature—60° C.
Electrolyte—100 g./l. NaOH, 200 g./NaCl.

Surface composition of plated mild steel cathode	Example No.	Metal content in coating (wt. percent)	Cathode potential versus standard hydrogen electrode in volts	Current density A./cm.²
Rusted mild steel	1	No coating	1.05	1
			1.20	10
			1.28	30
Titanium sheet	2	do	1.12	1
			1.27	10
			1.36	30
Tungsten-molybdenum-cobalt alloy	3	W, 10.1	0.87	1
		Mo, 39.3	0.92	10
		Co, 42.9	0.94	30
Tungsten-molybdenum-iron alloy	4	W, 14.9	0.93	1
		Mo, 32.2	0.99	10
		Fe, 44.3	1.02	30
Tungsten-molybdenum-nickel alloy	5	W, 2.8	0.91	1
		Mo, 33.6	0.98	10
		Ni, 53.4	1.01	30
Tungsten-molybdenum-cobalt alloy	6	Mo, 38.1	0.87	1
		Co, 43.6	0.93	10
		W, 10.4	0.95	30
Tungsten-molybdenum-iron alloy	7	Mo, 14.4	0.93	1
		Fe, 44.4	0.98	10
		W, 33.1	1.02	30
Molybdenum-nickel-tungsten alloy	8	Mo, 33.0	0.92	1
		Ni, 53.0	0.97	10
		W, 3.1	1.01	30

The laboratory experiments 1 to 8 were carried out on a model diaphragm cell of the vertical submerged cathode type. The cell was a glass vessel the ratio of height to width (cross section through cell) to length (plane of electrodes and diaphragm) being approximately 2:1:1 The figure is a schematic sketch of a vertical cross section through the centre of the cell. The cell walls 1 consisted of glass; all liquid-tight joints were made by silicone rubber gaskets. A graphite anode 2 and the interchangeable cathode 4, insulated from each other were connected to the opposing electrodes of a source of direct current. Anode and cathode compartment were separated from each other by a permeable porous, polyethylene diaphragm 3. To prevent back diffusion of anode products a relatively large flow of electrolyte through the cell compartment was maintained. Inlets and outlets for feed of electrolyte and discharge of catholyte, hydrogen and chlorine not shown in the sketch were arranged in the manner usual with diaphragm cells of the submerged vertical cathode type and known to those skilled in the art.

The cathode potential was measured by means of a Luggin capillary 5 which penetrated the glass cell wall at the top of the cell to extend to a position slightly spaced from, or touching, the centre of the cathode. The Luggin capillary was connected by a salt bridge to an individual calomel reference electrode (not shown) in the usual manner. The electrolyte discharged from the cell contained 100 g. NaOH and 200 g. NaCl per litre. The interchangeable cathodes were prepared as set out in the examples and a series of determinations was carried out at each selected current density after careful equilibration of experimental conditions. The results shown in Table II are the means of the replicate determinations.

Our invention is now illustrated by, but is not limited to the following examples:

Example 1

Twenty mild steel plates of ⅛ in. thickness were subjected to a pretreatment consisting of degreasing with trichlorethylene, drying and treating for 10 minutes at room temperature (20±2° C.) with 17% w./v. hydrochloric acid. The samples were then rinsed with distilled water and dried in the oven at 110° C.

After the pretreatment they were allowed to "age" by exposure to the open atmosphere in a chlorine producing factory for 4 weeks. A fine surface of rust was formed on the steel during this period. Each aged sample in succession was then made the cathode of an electrolytic cell for the production of sodium hydroxide and chlorine and the cathode potential was measured at three current densities. The potential of the aged electrodes was lower than that of bright steel untreated or acid treated.

Each of the three results given in Table II is the means of these twenty determinations and was used subsequently as a basis for calculation of the lowering of overvoltage in Examples 3 to 8 inclusive.

Example 2

A piece of rolled titanium sheet was treated for a period of 5 minutes at a temperature of 60° C. in a solution of the following composition: 200 mls. conc. HCl, 56 g. NaF, 142 g. H_3BO_3 per litre of aqueous solution. After rinsing with distilled water, the sample was made the cathode of an electrolytic caustic/chlorine diaphragm cell. Details of cathode potentials measured are shown in Table II where they are used as a basis of comparison for alloys according to the present invention.

Example 3

A mild steel plate was degreased, dried and pickled in 20% hydrochloric acid for five minutes at room temperature. After rinsing with water it was immediately transferred to a plating solution of the following composition: 32.2 g./l. $NaMoO_4.2H_2O$, 11.9 g./l. $CoCl_2.6H_2O$, 67.0 g./l. $Na_4P_2O_7.10H_2O$, 80.0 g./l. $NaHCO_3$, 69.4 g./l.

$Na_2WO_4.2H_2O$

and 1.5 g./l. $N_2H_4.H_2SO_4$. The sample was made the cathode is this electrolyte and plated at a current density of 4 amps./dm.² for 30 minutes. Bagged graphite anodes were used and an electrolyte temperature of 60° C. was maintained during the electrodeposition. The electroplated sample was then made the cathode in a caustic/chlorine diaphragm cell and cathode potentials were measured. Results are shown in Table II. An analysis of the electrodeposit is also shown in Table II.

Example 4

A mild steel sample, after degreasing and pickling as in Example 3, was made the cathode in an electroplating bath of the following composition: 40.0 g./l. of

$Na_2MoO_4.2H_2O$

9.0 g./l. of $FeCl_3.6H_2O$, 45.5 g./l. of $Na_4P_2O_7.10H_2O$, 75.0 g./l. of $NaHCO_3$ and 69.4 g./l. of $Na_2WO_4.2H_2O$. Electro-deposition was continued for a period of 30 minutes at a current density of 3.5 amps/dm.². Mild steel anodes were used with a bath temperature of 60° C. The electroplated sample was made the cathode in a caustic/chlorine diaphragm cell and cathode potentials and analytical data for the electrodeposit are shown in Table II.

Example 5

A mild steel sample, after degreasing and pickling as in Example 3, was made the cathode in an electroplating bath of the following composition: 20.0 g./l. of

$Na_2MoO_4.2H_2O$

6.1 g./l. of triammonium citrate $(NH_4)_3C_6H_5O_7$, 3.3 g./l. of $NiSO_4.6H_2O$, 5.9 g./l. of $NiCl_2.6H_2O$, 41.6 g./l. of $Na_4P_2O_7.10H_2O$, 40.0 g./l. of $NaHCO_3$, 16.5 g./l. of $Na_2WO_4.2H_2O$. Electro-deposition was continued for a period of 30 minutes at a current density of 3.5 amps/dm.² with a bath temperature of 60° C. Platinized titanium anodes were used. The electroplated sample was made the cathode in a caustic/chlorine diaphragm cell and cathode potentials and analytical data for the electrodeposit are shown in Table II.

Example 6

A piece of titanium sheet was treated for a period of 5 minutes at a temperature of 60° C. in a solution of the following composition: 200 mls. conc. HCl, 56 g. of NaF, 142 g. of H_3BO_3 per litre of aqueous solution. After rinsing with water the sample was transferred immediately to an electroplating bath of the following composition: 32.3 g./l. of $Na_2MoO_4.2H_2O$, 11.9 g./l. of $CoCl_2.6H_2O$, 67.0 g./l. of $Na_4P_2O_7.10H_2O$, 37.0 g./l. of $NaHCO_3$, 24.0 g./l. of Na_2CO_3, 69.4 g./l. of $Na_2WO_4.2H_2O$ and 1.5 g./l. of $N_2H_4.H_2SO_4$. The sample was plated at a current density of 4.5 amps/dm.² for 30 minutes at 60° C. using platinised titanium anodes. The sample was made the cathode of an electrolytic caustic/chlorine diaphragm cell and cathode potentials were measured. The results are shown in Table II, together with analytical data for this alloy.

Example 7

A piece of titanium sheet was etched as described in Example 6 and made the cathode in an electroplating bath of the following composition: 40 g./l. of

$Na_2MoO_4.2H_2O$

9.0 g./l. of $FeCl_3.6H_2O$, 4.5 g./l. of $Na_4P_2O_7.10H_2O$, 75.0 g./l. of $NaHCO_3$ and 69.4 g./l. of $Na_2WO_4.2H_2O$. Electrodeposition was continued for a period of 30 minutes at a current density of 3.5 amps/dm.². Mild steel anodes were used with a bath temperature of 60° C. The electroplated sample was made the cathode in a caustic/chlorine diaphragm cell and cathode potentials and analytical data for the electrodeposit are shown in Table II.

Example 8

A piece of titanium sheet was etched as described in Example 6 and electroplated in a solution of the following composition: 20.0 g./l. of $Na_2MoO_4.2H_2O$, 6.1 g./l. of triammonium citrate $(NH_4)_3C_6H_5O_7$, 3.3 g./l. of $NiSO_4.6H_2O$, 5.9 g./l. of $NiCl_2.6H_2O$, 41.6 g./l. of $Na_4P_2O_7.10H_2O$, 40.0 g./l. of $NaHCO_3$ and 16.5 g./l. of $Na_2WO_4.2H_2O$. Electrodeposition was continued for a period of 30 minutes at a current density of 3.5 amps/dm.^{2} with a bath temperature of 60° C. Platinized titanium anodes were used. The electroplated sample was made the cathode in a caustic/chlorine diaphragm cell and cathode potentials and analytical data for the electrodeposit are shown in Table II.

Example 9

A cathode element from a commercial caustic/chlorine diaphragm cell consisting of two mild steel wire meshes welded on a steel frame was treated in the following way. The mesh was woven such that wire thickness and the spaces between wires were equal, and there were seven wires and seven spaces per inch in each direction. The whole assembly was pickled in 20% HCl solution for 5 minutes at room temperature, followed by a water spray rinse. The cell cathode was transferred to a nickel plating bath of the following composition: 240 g./l. of $NiSO_4.6H_2O$, 45 g./l. of $NiCl_2.6H_2O$, 30 g./l. of N_3BO_3. The pH of the bath was adjusted to within the range 4.5 to 6.0 by addition of 2.5 g./l. of nickel carbonate, followed by heatinng of the solution to 80°–90° C. for 30 to 60 minutes to facilitate the reaction. After filtration, impurities were removed from this bath by the normal "plating out" procedure well known to electroplating technique. The cathode sample was plated in this nickel bath for 30 minutes at an apparent cathode current density of 4.5 amps/dm.^{2}. The projected area of the cathode was used in calculating the apparent current density. The bath temperature during plating was 60° C. and bagged nickel anodes were used. A matt grey electrodeposit of nickel was produced in this manner.

After removal from the nickel plating bath, the assembly was transferred to a second plating bath of the following composition: 40.0 g./l. of $Na_2MoO_4.2H_2O$, 9.0 g./l. of $FeCl_3.6H_2O$, 45.5 g./l. of $Na_4P_2O_7.10H_2O$, 75.0 g./l. of $NaHCO_3$ and 69.4 g./l. of $Na_2WO_4.2H_2O$. Plating was carried out at an apparent current density of 5.2 amps/dm.^{2} for 30 minutes at 60° C. Bagged graphite anodes were used. The assembly was removed from the plating bath and rinsed with water. The composition of the plating expressed as percent of the total metallic constituents only was 16.8% W, 35.0% Mo, 48.1% Fe.

This cathode element and others identcially treated were assembled into 3 comercial chlorine/caustic diaphragm cells. Voltage performance data compared with 3 standard control cells having conventional mild steel cathodes as described in Example 1 are shown in Table III.

TABLE III

Time in days after current switched on	Experimental Cell Voltage (mean of 3 cells)	Control Cells Mean (corroded iron as Ex. 1, mean of 3 cells)	Apparent Current Density,* Amp/cm.^{2}
6	2.81	2.94	2.5
23	2.84	3.02	3.0
30	2.83	3.01	3.0

*Cathode current density calculated on cathode area projected onto a vertical plane.

We claim:

1. An electrode comprising a support formed from a metal suitable for the construction of solid electrodes, at least a portion of the surface of which is conductively covered by a coating of an alloy or co-deposit consisting of the metals molybdenum and tungsten and of at least one further metal selected from the group consisting of cobalt, nickel and iron, said coating containing 2 to 60% of molybdenum, 2 to 70% of tungsten and the balance to 100% of the said further metal, wherein the sum of molybdenum and tungsten is between 10 and 72%, said percentages being by weight of the metallic constituents in the coating.

2. An electrode according to claim 1 wherein the metal of the electrode support is mild steel.

3. An electrode according to claim 1 wherein the metal of the electrode support is titanium.

4. An electrode according to claim 1 wherein the coating contains 2–60% of molybdenum 2–45% of tungsten and the balance to 100% of nickel, where the sum of molybdenum and tungsten is between 10 and 62% and where the percentage is expressed by weight and on the basis of the metallic constituents in the coating only.

5. An electrode according to claim 1 wherein the coating contains 30–55% of molybdenum 2–35% of tungsten and the balance to 100% of iron, where the sum of molybdenum and tungsten is between 32 and 65% and where the percentage is expressed by weight and on the basis of the metallic constituents in the coating only.

6. An electrode according to claim 1 wherein the coating contains 30–55% of molybdenum 2–35% of tungsten and the balance to 100% of nickel, where the sum of molybdenum and tungsten is between 32 and 62% and where the percentage is expressed by weight and on the basis of the metallic constituents in the coating only.

7. An electrode according to claim 1 wherein the coating contains 35–55% of molybdenum, 2–30% of tungsten and the balance to 100% of cobalt, where the sum of molybdenum and tungsten is between 37 and 65% and where the percentage is expressed by weight and on the basis of the metallic constituents in the coating only.

8. The electrode of claim 1 wherein the said further metal is iron.

9. The electrode of claim 1 wherein the said further metal is cobalt.

10. An electrolytic cell having a cathode formed from a metal suitable for the construction of solid electrodes, at least a portion of the surface of which is conductively covered by a coating of an alloy consisting of molybdenum and tungsten and of at least one metal selected from the group consisting of cobalt, nickel and iron, said coating containing 2 to 60% of molybdenum, 2 to 70% of tungsten and the balance to 100% of the said further metal, wherein the sum of molybdenum and tungsten is between 10 and 72%, said percentages being by weight of the metallic constituents in the coating.

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