

### Thermoelectric Power of Binary Solid Solutions on a Palladium Base

T. F. TARASOVA, I. L. ROGEL'BERG and I. S. GIL'DENGORN, *Tr. Gos. Nauch.-Issled. Proekt. Inst. Splavov Obrab. Tsvet. Metal.*, 1969, (29), 5-23

Thermoelectric powers were measured at temperatures from 100 to 1200°C for alloys of Pd with Ag, Al, Au, Co, Cr, Fe, Ir, Mn, Mo, Nb, Ni, Pt, Re, Rh, Ru, V, and W. Most additions increase the thermoelectric power of Pd; Au, Ag, Cu, Al, and Mn decrease it.

### Thermocouples of Palladium-containing Alloys

T. F. TARASOVA, I. L. ROGEL'BERG and I. S. GIL'DENGORN, *Ibid.*, 140-150

Thermoelectric properties are described for Pallaplat (5% Rh-Pt : 2% Pt - 46% Pd - Au), TB 19-29 (10% Rh-Pt : 10% Pt - 30% Pd - Au), Baker 417 (10% Rh-Pt : 40% Pd-Au), Pallador I (10% Rh-Pt : 40% Pd-Au), Platinel I (3% Au-14%Pt-Pd : 35% Pd-Au), Platinel II (14% Au-31%Pt-Pd : 35% Pd-Au), PIP (15% Ir-Pt : Pd).

## NEW PATENTS

### METALS AND ALLOYS

#### Palladium-Vanadium Resistance Alloys

JOHNSON MATTHEY & CO. LTD

*British Patent 1,171,674*

Pd-V alloys having high specific resistance and reduced temperature coefficient of resistance contain 74 to 98.5 wt.% Pd, 1 to 15 wt.% V and 0.5 to 11 wt.% in total of one or more of the elements Au, Mo or Al.

#### Manufacture of Titanium Dioxide

LAPORTE TITANIUM LTD *British Patent 1,173,593*  
TiCl<sub>4</sub> may be preheated in a tube constructed of refractory material. This is preferably SiO<sub>2</sub> or a suitable metal e.g., Pt, a Pt alloy or Pt-lined Inconel.

#### Constant Conductivity Alloys

TRW INC.

*British Patent 1,173,703 U.S. Patent 3,463,636*

The alloys consist of: 70-90 wt% Pt, Rh, Ir, Au or Ag, 7-23 wt% W, 2-8 wt% Re; e.g., 70 wt% Pt, 22.5 wt% W, 7.5 wt% Re.

#### Sparking Plug Alloy

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,466,158*

A bonded compound article, e.g., a sparking plug, comprises a Ag component and a high melting point component of Ir, Ru or an Ir-rich or Ru-rich alloy. They are connected by a junction made of a Ag-Pd alloy.

#### Platinum Metal Ball Bearings, Pivots, Etc.

INTERNATIONAL NICKEL CO. INC.

*U.S. Patent 3,466,165*

The difficulty of producing very small balls, pivots for instruments, porous metal filter raw materials from these metals and their alloys are overcome in a matrix system. Small spheres and spheroid-like articles which are predominantly

of Ru, Ir, Os or Rh are formed in a molten matrix of other metal and the matrix is then solidified and leached to recover spheres or spheroids. In the examples Pd and Ag form the matrix.

#### Hydrogen-permeable Membrane

JAPAN GAS-CHEMICAL CO. INC.

*U.S. Patent 3,469,372*

A H<sub>2</sub> permeable membrane consists of a Pd or a Pd alloy, the surface of the membrane having a wavy configuration as a result of being stamped with the surface of a plain dutch weave wire netting of 20-200 meshes.

#### Stabilised Group VIII Metal Alloys

JOHNSON MATTHEY & CO. LTD

*French Patent 1,570,312*

The high temperature properties of Group VIII noble metal alloys are stabilised by the presence of up to 20% of a lanthanide, Sc, Y, Ti, V, Zr, Nb, Hf and/or Ta.

#### Bonding Two Different Metals

JOHNSON MATTHEY & CO. LTD

*German Patent 1,521,335*

In bonding metals, e.g., Pt or its alloys to stainless steels, interdiffusion is reduced by interposing a layer of a metal/ceramic mixture. The metal in the layer is insoluble in one of the metals being bonded but is virtually soluble in the other. Mo, W, Nb, Ta and Ti are suitable metals. This corresponds to *British Patent 1,093,136*.

## ELECTRODEPOSITION AND SURFACE COATINGS

### Electrodeposition of Palladium

SEL-REX CORP.

*British Patent 1,171,734*

A plating bath consists of a solution of a urea complex of Pd, adjusted to a pH >8. It is claimed that this prevents porosity previously found in thin (2.5 to 5 μm) Pd coatings.

## Plating Platinum Metals on Chromium

E. H. LYONS

*U.S. Patent 3,467,584*

A process for plating a Cr surface to provide a corrosion resistant adherent precious metal coating by (a) depassivating the Cr surface by cathodising it in an acid bath, (b) rinsing the depassivated surface with a weak acid bath, (c) plating the depassivated surface from an aqueous acidified solution of an alkali iodide containing PtI<sub>2</sub>, PdI<sub>2</sub>, PdCl<sub>2</sub>, RhCl<sub>3</sub> and/or RhI<sub>3</sub>.

## Platinum Coating Compositions

MATTHEY BISHOP INC.

*U.S. Patent 3,470,019*

A colloidal dispersion of Pt for use in forming Pt by reaction with a lower alcohol-HCHO mixture is made to contain minor amounts of other Pt group metal, in addition to Pt. When this dispersion is coated on substrates and dried out, adherent, catalytically active Pt deposits are formed. This corresponds to *British Patent 1,147,563*.

## Improved Method of Coating and Inlaying

JOHNSON MATTHEY & CO. LTD

*French Patent 1,550,563*

Phosphor bronze strip inlaid with Pd may be produced by rolling processes including an intermediate layer of Ni, Fe, Co, Mo or V. This corresponds to *Italian Patent 822,094*.

## LABORATORY APPARATUS AND TECHNIQUE

### Combustion Detector for Gas Chromatography

U.S. ATOMIC ENERGY COMMISSION

*U.S. Patent 3,460,909*

A thermal conductivity compensation device for a catalytic combustion detector has means for dividing the input gas flow to the detector into two equal portions. The first portion of the gas is passed over a heated active Pt filament and the second over a heated deactivated (i.e., V<sub>2</sub>O<sub>5</sub>-poisoned) Pt compensation filament.

### Electrochemical Cell

BECKMAN INSTRUMENTS INC.

*U.S. Patent 3,468,781*

A polarographic cell for determining H<sub>2</sub> comprises a pair of electrodes joined by an electrolyte and separated from the test medium by a H<sub>2</sub> permeable barrier. The barrier is a gas permeable plastic membrane having a coating of Pd or Ag-Pd alloy of a thickness not greater than 500 Å.

## HETEROGENEOUS CATALYSIS

### Selective Catalytic Reduction

JOHNSON MATTHEY & CO. LTD

*British Patent 1,159,967*

Reduction of a ketone or of an aromatic aldehyde

to the corresponding alcohol uses H<sub>2</sub> and Pd/charcoal catalyst in the presence of a primary aromatic amine, e.g., C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub>, *p*-toluidine or benzylamine, or of a heterocyclic tertiary amine, e.g., C<sub>6</sub>H<sub>5</sub>N or quinoline. This corresponds to *Italian Patent 787,791*.

### Aliphatic Dinitriles Production

RHONE-POULENC S.A.

*British Patent 1,168,958*

Dicyanobutenes and/or adiponitrile are formed from acrylonitrile by heating under pressure in the presence of a Group VIII metal, oxide or hydroxide, e.g., Ru(OH)<sub>3</sub>.

### I.C.E. Exhaust Gas Combustion Catalyst

H. BERGER

*British Patent 1,169,719*

The catalyst contains Pt and/or Pd (amongst other metals) on refractory supports where the support is ball-milled with catalyst metal solution and the paste coated on a fabric. The layer is dried and calcined to burn away the fabric.

### Catalytic Reforming

TEXACO DEVELOPMENT CORP.

*British Patent 1,170,206*

Reforming to give aromatic enrichment is effected in two zones containing Pt metal catalysts with intermediate removal of a lower fraction.

### Activation of Hydrocracking Catalysts

ESSO RESEARCH & ENGINEERING CO.

*British Patent 1,170,647*

Hydrocracking catalysts consisting of a Pt group metal on a zeolite are activated with dry H<sub>2</sub> (containing less than 10 p.p.m. H<sub>2</sub>O) and then with an undried gas. Both stages are carried out at elevated temperatures.

### Hydrogen Peroxide Production

DEUTSCHE GOLD-UND SILBER-SCHNEIDANSTALT

*British Patent 1,171,485*

The selectivity of Pd catalysts in the hydrogenation stage is increased by introducing up to 50% of one or more of the other five Pt metals, e.g., 70% Pd - 30% Ir.

### Palladium Hydrogenation Catalyst

BRITISH PETROLEUM CO. LTD

*British Patent 1,173,469*

The catalyst, which retains its activity in the presence of S, consists of Pd (preferably 0.1 to 5 wt%) incorporated by ion-exchange into a zeolite.

### Catalyst for Carbonylation

NATIONAL DISTILLERS & CHEMICAL CORP.

*British Patent 1,174,747*

$\alpha$ ,  $\beta$ -Unsaturated acyl halides are produced by reaction of a vinylic halide with CO at elevated temperatures and pressures in the presence of a noble metal catalyst, e.g., Pd, Pt, Ru, Rh, Os, Ir or Pd with a minor amount of Au.

### Low Pressure Reforming

CHEVRON RESEARCH CO.

*British Patent 1,175,022*

New catalyst for naphtha reforming consists of 0.01-1% Pt promoted with 0.01-2% Re on an inorganic oxide support.

### Alkali-moderated Ruthenium Catalyst

E. I. DU PONT DE NEMOURS & CO.

*British Patent 1,176,336*

An alkali-moderated Ru metal catalyst on an  $Al_2O_3$ ,  $BaSO_4$  or kieselguhr support, suitable for use in hydrogenation reactions, is obtained by mixing a supported Ru catalyst with at least 1 wt% of a basic alkali metal compound. See also *British Patent 1,176,337*.

### Ammonia-oxidation Catalyst

SOC. BELGE DE L'AZOTE ET DES PRODUITS CHIMIQUES DU MARLY S.A.

*British Patent 1,176,697*

A Pt or Pt alloy mesh is used as catalyst for the conversion of  $NH_3$  to the oxides of  $N_2$ .

### Noble Metal Condensation Catalysts

MONTECATINI EDISON S.p.A.

*British Patent 1,177,233*

Alcohols are dimerised in the presence of an alkaline condensing agent and a finely-divided noble metal catalyst (optionally supported). The catalyst may be Rh, Pd, Pt or Ru. The particle size range is: at least 80% less than  $150\mu$ ; at least 20% less than  $50\mu$ .

### Catalyst for Manufacture of Vinyl Acetate

B.P. CHEMICALS (U.K.) LTD

*British Patent 1,177,515*

Vinyl acetate is produced by vapour phase reaction of  $C_2H_4$ ,  $O_2$  and  $CH_3COOH$  in the presence of a catalyst. The catalyst is a Pt-group metal or Pt group metal compound together with Au or a Au compound. A support of Sn oxide is used.

### Isoocyanate Production

AMERICAN CYANAMID CO.

*U.S. Patent 3,461,149*

The aromatic nitro-compound-CO reaction is catalysed by a supported noble metal and a Lewis acid, e.g.,  $Pd/Al_2O_3-FeCl_3$ .

### Preparation of Dicarboxylic Acids

E. I. DU PONT DE NEMOURS CO.

*U.S. Patent 3,461,160*

Oxidation of cyclic olefines to carboxylic acids is effected by contacting the olefines with a liquid phase reaction system comprising aqueous  $HNO_3$  and an Os-V catalyst, e.g., comprising 10-70 parts of  $HNO_3$ , 0.01-0.7 part of V, 0.01-5.0 parts of Os, and 24-90 parts of  $H_2O$ .

### Removal of Ammonia from Gases

UNIVERSAL OIL PRODUCTS CO.

*U.S. Patent 3,467,491*

$NH_3$  is removed from  $NH_3$ -containing gases by its conversion to  $N_2$  and  $H_2O$  without the production of harmful  $N_2$  oxides by contacting the gases and air with a  $Pt/Al_2O_3$  catalyst at 400-450°F.

### Nitrogen Oxides Removal from Gases

CHEMICAL CONSTRUCTION CO.

*U.S. Patent 3,467,492*

Tail gases from  $HNO_3$  production are mixed with  $CH_4$  and treated over a series of beds of supported Pt group metal, e.g., usual  $HNO_3$  catalysts on  $Al_2O_3$  or  $SiO_2$  gel.

### Hydrogenation of Adiponitrile

E. I. DU PONT DE NEMOURS & CO.

*U.S. Patent 3,471,563*

Hexamethylene diamine is prepared by reducing adiponitrile in the presence of  $NH_3$  and 0.001-10% of Ru catalyst (calculated as metallic Ru on the weight of adiponitrile). The Ru is supported on an inert carrier and is alkali moderated with 0.1-15% of an alkali metal compound (calculated as alkali metal).

### Palladium Catalysts

CATALYSTS AND CHEMICALS INC.

*U.S. Patent 3,471,583*

$Pd-Al_2O_3$  catalysts are known to be useful as selective hydrogenation catalysts. However, it is difficult to prepare low surface area  $Pd/Al_2O_3$  catalysts because their tensile properties are partially destroyed by the necessary heating. Catalysts having superior tensile properties can be made if the  $Al_2O_3$  matrix is modified with 1-5%  $Ni-Al_2O_3$  spinel.

### Saturated Hydrocarbon Dehydrogenation

INSTITUT FRANCAIS DE PETROLE, DES CARBURANTS ET LUBRIFIANTS

*French Patent 1,567,900*

The dehydrogenation catalyst consists of 0.1-2% Pt and 0.01-0.5% Ir deposited on  $SiO_2$ .

### Unsaturated 3C Hydrocarbon Fraction Hydrogenation

FARBENFABRIKEN BAYER A.G.

*German Patent 1,518,827*

3C hydrocarbon fractions containing unsaturated compounds are treated by trickling them over noble metal catalysts in a virtually stationary  $H_2$  atmosphere. A suitable catalyst is 0.5%  $Pd/Al_2O_3$ .

### Noble Metal Gas Purification Catalysts

VEB LEUNA-WERKE WALTER ULBRICHT

*German Patent 1,667,348*

An oxidic support is impregnated with a solution of a reducing agent (e.g.,  $HCHO$ ), the surface film is evaporated and then the support is immersed in a solution of a noble metal salt.

Pd/Al<sub>2</sub>O<sub>3</sub> for purifying protective gas atmospheres can be obtained in this way.

### Unsaturated Ester Production

STAMICARBON N.V. *Dutch Appln* 68.06,541

The olefine-O<sub>2</sub>-acid reaction is catalysed by a material formed by depositing on a support, such as SiO<sub>2</sub> gel, first Pd and then one or more of Pt, Rh and/or Ru. The Pd : Pt group metal (s) ratio is from 300 : 1 to 3 : 1. Subsequently the catalyst is impregnated with a Group IV, VI or VIII metal, e.g., FeCl<sub>3</sub>.

### Oxidation of Ferrous Compounds and Reduction of Ferric Compounds

JOHNSON MATTHEY & CO. LTD

*Canadian Patent* 828,669

A feedstock containing Fe<sup>2+</sup> or Fe<sup>3+</sup> is reacted with O<sub>2</sub> or H<sub>2</sub> respectively in an acid solution in the presence of a catalyst comprising at least one Pt group metal (Pt, Pd or a Pt-Pd alloy) on an inert support (charcoal) in a trickle column reactor. The feedstock may be obtained from a steel-pickling liquor by extracting Fe ore with H<sub>2</sub>SO<sub>4</sub> or HCl.

## HOMOGENEOUS CATALYSIS

### Polysiloxane Copolymer Production

RHONE-POULENC S.A. *British Patent* 1,169,290

Excellent yields of polysiloxane-polyoxyalkylene co-polymers are obtained using a Ru carbonyl or diketone as catalyst.

### Platinum Catalyst

UNION CARBIDE CORP. *British Patent* 1,173,570

A catalyst for the production of organosilicon compounds is a nitrile complex of a Pt halide. Examples are: bis(acetonitrile)dichloroplatinum, bis(4-chlorobenzonitrile)dichloroplatinum and bis(lauronitrile)dichloroplatinum.

### Platinum Catalysts for SiH addition

GENERAL ELECTRIC CO. *British Patent* 1,175,224

SiH addition to olefines is catalysed by Pt(CH<sub>3</sub>)<sub>3</sub>I or Pt(CH<sub>3</sub>)<sub>6</sub>.

### Palladium Oxidation Catalyst

IMPERIAL CHEMICAL INDUSTRIES LTD

*British Patent* 1,176,664

An unsaturated organic compound (e.g. C<sub>2</sub>H<sub>4</sub>) is oxidised, (e.g. to vinyl acetate) by reaction with a nucleophilic compound in the presence of a Pd compound. These are preferably a palladous halide or carboxylate, and an ionisable cyanate.

### Ruthenium Catalyst for Dimerisation of Acrylonitrile

MITSUBISHI PETROLEUM CO. LTD

*British Patent* 1,177,059

Acrylonitrile is dimerised by the action of a Ru

halide and a metal e.g., Ag in an alcoholic medium.

### Catalyst for Condensation of Alcohols

MONTECATINI EDISON S.P.A.

*British Patent* 1,177,423

Two molecules of primary alcohol are condensed to give a primary alcohol branched at position 2, in the presence of a soluble compound of Rh, Ir, Ru, Os, Pd or Pt.

### Platinum Catalyst for Organosilicons

DEUTSCHE GOLD- & SILBER-SCHNEIDANSTALT

*U.S. Patent* 3,470,225

The SiH-olefine addition reaction is catalysed by PtX<sub>2</sub>(RCOCR'COR'')<sub>2</sub> where X is halogen, R is alkyl, preferably, lower alkyl, R' is H or alkyl, preferably lower alkyl, and R'' is alkyl or alkoxy, preferably lower alkyl or alkoxy.

### Palladous Chloride-Acetylene Reaction Product

AIR REDUCTION CO.

*U.S. Patent* 3,474,118

A complex of PdCl<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> is prepared by reacting PdCl<sub>2</sub> with liquefied C<sub>2</sub>H<sub>2</sub>. The complex is useful as a catalyst for the polymerisation and cyclisation of C<sub>2</sub>H<sub>2</sub>.

### Hydrogenation Catalysts

INSTITUT FRANCAIS DU PETROLE, DES LUBRIFIANTS

ET CARBURANTS

*French Patent* 1,568,741

New catalysts for hydrogenation contain Rh complexed to an amino-derivatives of a phosphine, arsine or stibine.

### Acetic Acid Production

INSTITUT FRANCAIS DU PETROLE, DES CARBURANTS

ET LUBRIFIANTS

*French Patent* 1,568,742

Olefines are oxidised to CH<sub>3</sub>COOH in the vapour phase and over a Pd-V<sub>2</sub>O<sub>5</sub> catalyst.

### Platinum Metal Catalyst

JOHNSON MATTHEY & CO. LTD

*German Patent* 1,543,078

A catalyst for the isomerisation of olefines consists of RhCl<sub>3</sub>.3H<sub>2</sub>O, PdCl<sub>2</sub>, RuCl<sub>3</sub>, IrCl<sub>4</sub> and/or H<sub>2</sub>PtCl<sub>6</sub> dissolved in a thermally stable solvent of high viscosity such as polyethylene-glycol, propylene glycol, glycerol or pinacol. This corresponds to *British Patent* 1,116,943.

## FUEL CELLS

### Hydrogen-permeable Membrane

ATLANTIC RICHFIELD CO.

*British Patent* 1,177,265

In a fuel cell, means are provided to maintain the Pd membrane in the anode negative to the cathode during periods of lowered H<sub>2</sub> supply, so that the membrane is not corroded by the electrolyte.

### Fuel Cell Electrode

GENERAL ELECTRIC CO. (NEW YORK)  
U.S. Patent 3,461,044

An intimately blended codeposit of a Pt metal and a wet-proofing polymer is formed from a bath containing from 0.1 to 10% Pt metal and 0.1-50% of polymer. A substrate is immersed in the plating bath and a current of 10-25 mA/cm<sup>2</sup> is applied to the substrate with polarity being reversed at 10-60 second intervals. The coated substrate may be used as an electrode in a cell such as a fuel cell.

### Magnesium Anode Primary Cell

UNITED STATES SECRETARY OF THE NAVY  
U.S. Patent 3,462,309

A primary cell has a Mg anode and an inert metal cathode which is a metal wire screen of from 8-40 mesh having an outer surface of granular Pd plating which may be deposited in an intervening stage of electroless Ni plating.

### Fuel Cell Electrode

LEESONA CORP. U.S. Patent 3,467,554

An electrochemical cell uses an electrode which contains a Pd-Au alloy having from 35 to 82 at.% Au and the remainder Pd, as the catalytic material. The alloy in black form is mixed with hydrophobic polymer particles to provide improved results.

### Fuel Cell Electrode

ATLANTIC RICHFIELD CO. U.S. Patent 3,470,031

A process for the preparation of a fuel electrode for a fuel cell by intimately mixing PtO<sub>2</sub> and Ag powder in a weight ratio of 0.1-5 : 1, pressing the mixture between two Ag screens to form an electrode body and reducing the body to a stage of reduction between 50%-95% relative to the stoichiometrically calculated stage where the theoretical value for the formation of PtH is 125.2%.

## CATHODIC PROTECTION

### Reference Electrodes

CONTINENTAL OIL CO. U.S. Patent 3,462,353  
Electrodes, for instance for cathodic protection systems, are made of a metal-metal oxide system, e.g., Pt-Pt oxide and Rh-Rh oxide.

## CHEMICAL TECHNOLOGY

### Hydrogen Separation Foil or Tube

VARTA A.G. British Patent 1,168,457

Non-porous bodies for H<sub>2</sub> separation and purification are made by forming an alloy of a hydrogen-absorbing metal (e.g., Pd) and a less noble metal. The latter is leached out from the powdered alloy to leave the hydrogen-absorbing metal in the form of a non-pyrophoric powder. This is compacted with a binder to form the body.

### Electrolytic Cell Construction

IMPERIAL METAL INDUSTRIES (KYNOCHE) LTD  
British Patent 1,168,558

The electrode assemblies consist of a plurality of parallel electrodes, e.g., Pt-coated Ti, with steel, Cu or Al spacers clamped together to give electrical contact.

### Palladium Electrode for Electrolytic Production of Hydrogen

MILTON ROY CO. British Patent 1,177,219

The cathode in an electrolytic cell consists of a tube (closed at one end) of Pd or a H<sub>2</sub>-permeable Pd alloy. The surface of the tube is activated to increase H<sub>2</sub> permeability so that virtually all of the gas generated is recovered in ultra-pure form. The activation process consists of contacting the clean surface with a molten alkali or alkaline earth metal hydroxide and then exposing the treated surface at not less than 450°C to an O atmosphere.

### Activation of Platinum Metal Electrodes

JOHNSON MATTHEY & CO. LTD  
Japan Patent 554,329

Particularly active electrodes for brine electrolysis are produced by exposing a Ti electrode plated with Pt group metal or alloy, in particular Pt, Pt-Rh or Pd-Ag, to the action of Hg vapour or alkali metal amalgam vapour, the Hg coating being distilled off after it has been deposited to leave the surface in a highly active state. This corresponds to British Patent 957,703.

## ELECTRIC AND ELECTRONIC ENGINEERING

### Metal Contact on a Semiconductor

INTERNATIONAL BUSINESS MACHINES CORP.  
British Patent 1,174,832

The contact consists of three layers. These are (outwards from the semiconductor): (1) vacuum-deposited Pt, (2) electroless-plated Pd, and (3) Al or Mo.

### Semiconductor Mounting

BENDIX CORP. U.S. Patent 3,460,241

A method is described of mounting Si semiconductor elements on a thick film circuit using a mixture of Pt and Au to form a Au-Si eutectic bond.

### Piezoelectric Ceramic

NIPPON ELECTRIC CO. LTD U.S. Patent 3,461,071

Piezoelectric ceramic has the general formula Pb(Zr<sub>x</sub>Ti<sub>y</sub>Sn<sub>z</sub>)O<sub>3</sub> where the subscripts are molar fractions and x=0-0.9, y=0.1-0.6, z=0-0.65, and x+y+z=1.00, and is improved by two additives, the first being 0.01-50-wt% MnO and the second 0.01-30 wt% IrO<sub>2</sub> and 0.01-50 wt% Cr<sub>2</sub>O<sub>3</sub>.