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ASTIA DOCUMENT No. AD
Contract AF 61 (052) - 260

Technical Final Report :

"BASIC RESEARCHES IN METAL CORROSION -
- ELECTROCHEMICAL BEHAVIOUR OF OXYGEN AND HYDROGEN PEROXIDE"

by

G. BIANCHI

University of Milano (Italy)

Laboratory of Electrochemistry and Metallurgy.

March 30, 1962

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The researches reported in this document have been sponsored by
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ABSTRACT

In this report the scientific, practical and indirect results are summarized, which were obtained during researches carried out to explain the mechanism of corrosion processes involving oxygen cathodic reduction.

The experimental results concerning oxygen and hydrogen peroxide cathodic reduction are of interest also in the field of fuel cells.

The researches carried out from April 1, 1958 to March 31, 1959 under the Contract AF 61(052)-85, were pursued from April 1, 1959 to March 31, 1962 under the Contract AF 61(052)-260.

The results of these researches have been published in the following Scientific Notes :

CONTRACT AF 61(052)-85

- (1) Giuseppe BIANCHI and Giovanni CAPRIOGLIO - Influence of surface preparation of platinum electrodes on cathodic processes of hydrogen peroxide (April 1959)
- (2) Giuseppe BIANCHI and Francesco MAZZA - The electrochemical behaviour of hydrogen and oxygen mixtures on platinum electrodes (April 1959)
- (3) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO, Franco GASPERINI and Francesco MAZZA - Electrochemical behaviour of graphite electrodes in solutions of various pH containing oxygen and hydrogen peroxide (April 1959)
- (4) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO, Franco GASPERINI and Francesco MAZZA - Anodic behaviour of hydrogen peroxide on platinum electrodes (April 1959)
- (5) Giuseppe BIANCHI - Basic Research in Metal Corrosion - (Technical Final Report) (April 1959)

CONTRACT AF 61(052)-260

- (1) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Stefano MALAGUZZI, Francesco MAZZA and Torquato MUSSINI - Electrochemical behaviour of oxygen and hydrogen peroxide on silver electrodes. AFOSR TN 60-299 (May 1960)
- (2) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Stefano MALAGUZZI, Francesco MAZZA and Torquato MUSSINI - Electrochemical behaviour of oxygen and hydrogen peroxide on titanium electrodes. AFOSR TN 60-859 (August 1960)

- (3) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO, Francesco MAZZA and Torquato MUSSINI - Electrochemical behaviour of oxygen and hydrogen peroxide on magnetite electrodes. AFOSR TN 60-1209 (October 1960)
- (4) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Francesco MAZZA and Torquato MUSSINI - Electrochemical behaviour of oxygen and hydrogen peroxide on Aluminum, Tantalum and Zirconium electrodes. AFOSR TN 60-1468 (December 1960)
- (5) Giuseppe BIANCHI, Francesco MAZZA and Torquato MUSSINI - Oxygen and hydrogen peroxide electrochemical behaviour on gold electrode. AFOSR TN 2054 (December 1961)
- (6) Giuseppe BIANCHI, Francesco MAZZA and Torquato MUSSINI - Cathodic reduction of oxygen and hydrogen peroxide on Pt, Pd and Ir electrodes. AFOSR TN 2050 (December 1961)
- (7) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Francesco MAZZA and Torquato MUSSINI - Oxygen and hydrogen peroxide electrochemical behaviour on Copper electrodes. AFOSR TN 2051 (January 1962)
- (8) Giuseppe BIANCHI, Francesco MAZZA and Torquato MUSSINI - Oxygen and Hydrogen Peroxide Electrochemical Behaviour on Chromium, Nickel, Cobalt and Stainless Steel Electrodes. AFOSR TN 2052 (February 1962)
- (9) Giuseppe BIANCHI - Basic Researches in Metal Corrosion : Electrochemical Behaviour of Oxygen and Hydrogen Peroxide (Technical Final Report). AFOSR TN 2053 (March 1962)

The following papers have been published with the most significant results of the researches :

- (1) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO, Franco GASPERINI e Francesco MAZZA - Comportamento elettrochimico dell'acqua ossigenata e dell'ossigeno su elettrodi di grafite. *Chimica e Industria* 40, 822 (1958).

- (2) Giuseppe BIANCHI and Giovanni CAPRIOGLIO - Influence of surface preparation of platinum electrodes on cathodic processes of hydrogen peroxide - *Electrochimica Acta* 1, 18 (1959)
- (3) Giuseppe BIANCHI and Francesco MAZZA - The electrochemical behaviour of hydrogen and oxygen mixtures on platinum electrodes. *Electrochimica Acta* 1, 198 (1959)
- (4) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO, Francesco MAZZA e Torquato MUSSINI - Comportamento anodico del platino nel sistema $H_2O - H_2O_2 - O_2$. *Chimica e Industria* 43, 146 (1961)
- (5) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Francesco MAZZA e Torquato MUSSINI - Comportamento elettrochimico di O_2 e H_2O_2 su elettrodi di Zirconio, Tantalio ed Alluminio. *Chimica e Industria* 43, 867 (1961)
- (6) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Francesco MAZZA and Torquato MUSSINI - The electrochemical behaviour of oxygen and hydrogen peroxide on silver electrodes. *Electrochimica Acta* 4, 232 (1961)
- (7) Giuseppe BIANCHI and Stefano MALAGUZZI - Cathodic reduction of oxygen and hydrogen peroxide on titanium - Proceedings of the 1st International Congress of Metallic Corrosion, p. 503, London 1961
- (8) Giuseppe BIANCHI, Giovanni CAPRIOGLIO, Giovanni DAVOLIO und Torquato MUSSINI - Ueber das elektrochemische Verhalten von Sauerstoff und Wasserstoffsperoxyd auf Magnetit-Elektroden. *Werkstoffe und Korrosion* (under press)
- (9) Giuseppe BIANCHI, Francesco MAZZA and Torquato MUSSINI - Catalytic Decomposition of Acid Hydrogen Peroxide Solutions on Platinum, Iridium, Palladium and Gold Surfaces. (Submitted for publication on *Electrochimica Acta*)

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The results of the researches were presented to the following Congresses :

- 1) VIII Congresso Nazionale di Chimica - Torino, May 1958 : Note (1)
- 2) X Meeting CITCE - Amsterdam, September 1958 : Notes (2) and (3)
- 3) Meeting of the CITCE Commission 4 - Bruxelles, September 1960 : Note (6)
- 4) 1st International Congress on Metallic Corrosion -
- London, April 1961 : Note (7)
- 5) Achema Tagung 1961 - Frankfurt M. : Note (8)
- 6) XVIII International Congress of Pure and Applied Chemistry -
- Montreal, August 1961: Note (9)
- 7) Spring Meeting of Electrochemical Society
- Los Angeles, May 1962

SCIENTIFIC RESULTS

- a) The decomposition of hydrogen peroxide acid solutions involves the intervention of the adsorbed oxides of the metal acting as catalyst.
- b) During the oxygen cathodic reduction, hydrogen peroxide is formed only as long as the H_2O_2 concentration in the solution has reached a steady value which, in acid solutions, is of the order of 10^{-3} moles/liter.
- c) Oxygen cathodic reduction is a two or four-electron process depending on the nature of the metal, the electrode potential at which the reduction occurs, and the H_2O_2 concentration in the solution.
- d) Hydrogen peroxide formation does not occur with such metal as Iron, Nickel, Cobalt, Chromium for which the oxygen cathodic reduction occurs indirectly through the compounds of the metal concerned.
- e) Hydrogen peroxide cathodic reduction in acid solutions is an indirect process occurring through the formation and reduction of adsorbed oxides of the metal acting as electrode.
- f) Hydrogen peroxide anodic oxidation to oxygen in acid solutions is an indirect process occurring between ^{the} anodically formed oxides and hydrogen peroxide, with oxygen evolution.

PRACTICAL RESULTS

The results so achieved are of practical interest for the foreseeing and interpretation of galvanic corrosion phenomena in neutral media.

Less dangerous metals are Aluminum, Zirconium and Tantalum which form oxide layers not able to act as electrodes, without giving compounds realizing the indirect cathodic reduction of oxygen. The less dangerous of all is Chromium, on which the O_2 cathodic reduction in neutral solutions occurs at a very low potential (about - 200 mV, NHE) through the metal compounds of surface. Titanium may give rise to galvanic corrosion because the oxide layer formed on the metal surface may be stoichiometrically unbalanced and act as an electrode.

When an anodic protection is to be realized e. g. , of stainless steel, oxygen cathodic reduction must occur at the highest possible potential. The metal better satisfying this condition is platinum; palladium is efficient as well, while poorer is the action of iridium and gold.

INDIRECT RESULTS

Many interesting results have been obtained for the problem of the realization of an oxygen electrode for fuel cells.

Whilst in alkaline solutions silver and cobalt (this latter result being not previously known) are very efficient, in acid solutions the highly efficient metal is platinum in sulphuric acid solution. This result enables to consider again the problem of the realization of hydrogen-oxygen fuel cells with acid electrolytes.

PERSONNEL

The following persons have contributed to the above mentioned researches, Of these persons the present position is indicated :

- Dr. Giovanni CAPRIOGLIO - has been employed by General Atomic, San Diego, Cal. , for researches on primary batteries and fuel cells.
- Dr. Giovanni DAVOLIO - carries out researches on corrosion at the Istituto Sperimentale Metalli Leggeri, Novara, Italy.
- Dr. Stefano MALAGUZZI - employed by the Laboratory of the Società Italiana Alluminio, Bolzano, Italy.
- Dr. Franco GASPERINI - carries on researches on metal finishing with Soc. Montecatini, Milano, Italy.
- Dr. Francesco MAZZA, }
 Dr. Torquato MUSSINI, } are still Assistants at the Institute of
 Dr. Sergio TRASATTI } Electrochemistry, Milan University, Italy.

REMARKS

The significance of the problems connected with the electrochemical processes concerning oxygen and hydrogen peroxide is considerably increased in connection with the problem of fuel cells.

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