May 13, 1969 E. J. HELLUND 3,444,061

METHOD OF CONDUCTING CHEMICAL REACTIONS IN A GLOW DISCHARGE

Filed Aug. 22, 1966

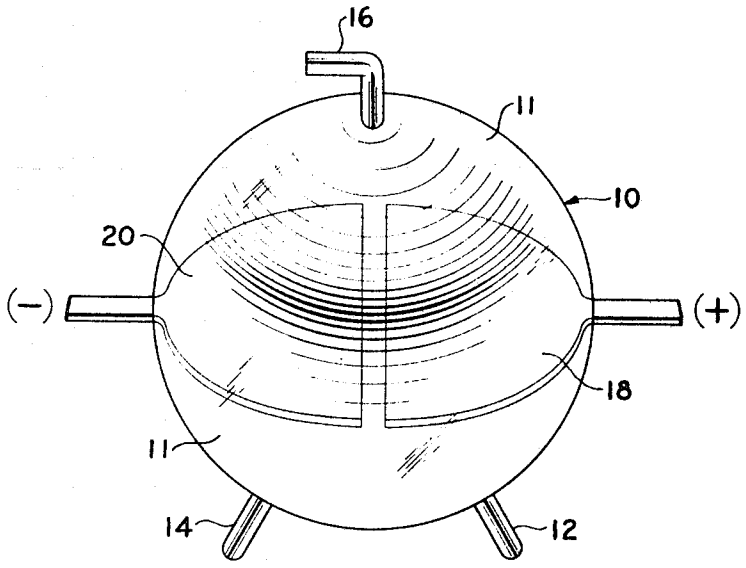


Fig. 1

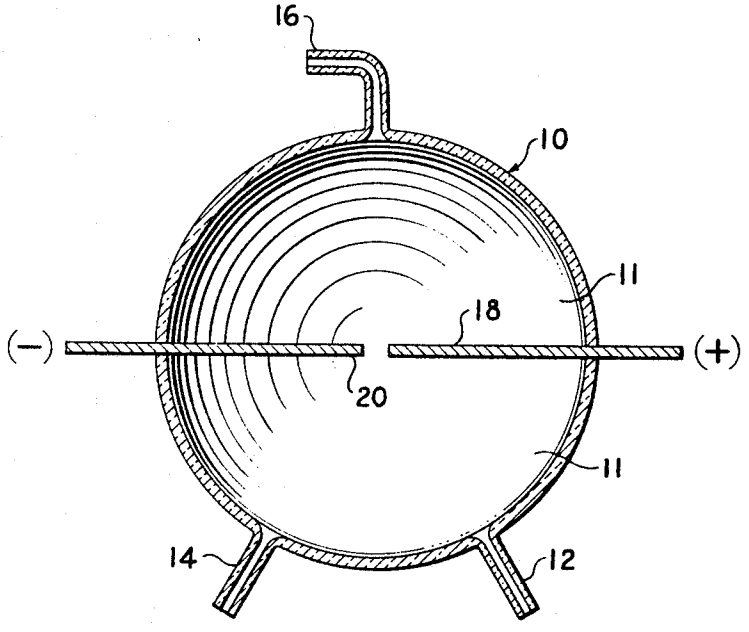


Fig. 2

United States Patent Office 3,444,061 Patented May 13, 1969

3,444,061

METHOD OF CONDUCTING CHEMICAL REACTIONS IN A GLOW DISCHARGE

Emil J. Hellund, South Laguna, Calif., assignor to Hooker Chemical Corporation, Niagara Falls, N.Y., a corporation of New York

Filed Aug. 22, 1966, Ser. No. 573,928
Int. Cl. B01k 1/00
U.S. Cl. 204—164 9 Claims

This invention relates to a glow discharge reactor particularly suited for electrochemical reactions, and more particularly to a high capacity glow discharge reactor, particularly suited for subjecting large volumes of gases to an electrical glow discharge.

Glow discharge reactions have been previously known and used for the synthesis of various desirable chemicals which may be more difficult or expensive to prepare by normal chemical or electrochemical means. As interest in large scale production of the various chemicals produced by these methods has increased, the need for apparatuses capable of subjecting large volumes of gases to a glow discharge to produce the chemicals in quantity has also increased.

It is an object of this invention to provide a glow discharge reactor particularly suited for subjecting large volumes of gaseous reactants to a glow discharge. It is another object of this invention to provide a glow discharge reactor particularly suited for operation at widely varying temperatures, pressures and electrical capacities. These and other objects will become apparent to those skilled in the art from a description of the invention which follows.

In accordance with the invention, a glow discharge reactor for electrochemical reactions is provided comprising a reaction chamber having a reactant inlet means and a reactant outlet means separated by electrode means, said electrode means, comprising a pair of substantially flat conductive sheets lying in the same plane with an edge of each sheet in a spaced relationship with respect to an edge of the other, said edges comprising major straight line edges of said electrodes and being positioned substantially parallel and equidistant from each other over substantially the entire opposing lengths thereof.

The invention will be described more fully with reference to the drawing in which:

FIG. 1 is a perspective view of an apparatus constructed in accordance with the present invention; and

FIG. 2 is a sectional view of the apparatus of FIG. 1 further illustrating the apparatus of the present invention.

The glow discharge reactor **10** of the present invention comprises a chamber **11** which is preferably spherical or ellipsoidal in shape or of other similar configuration, substantially divided into two portions by electrode means **18** and **20**. Reactant inlet means **12** and **14** are positioned at one end of chamber **11** with reactant outlet means **16** positioned at the other end of chamber **10**. The inlet means may be one or a multitude of inlets depending on whether separate feed streams are to be utilized in the desired reaction or whether a premixed gaseous reactant is supplied as a single stream. Thus, if a mixture of gases is utilized, only one inlet means need be provided. In a like manner, if separate reactant feeds are desired for a number of gaseous reactants, a corresponding number of inlet means can be provided.

Reactant chamber **11** is substantially divided into two parts by electrode means **18** and **20**. During operation, one electrode means serves as the anode and the other electrode means serves as the cathode when the current supply is direct current and when alternating current is used, the electrode means each function as both anode and cathode. The electrodes are planer structures shaped

to conform substantially to the inside curvature of reaction chamber **11** and preferably to extend completely across the chamber from wall to wall thereby completely separating the inlet side of the chamber from the outlet side of the chamber with the exception of the spacing between the electrodes. Thus, opposing edges of electrode means **18** and **20** form a slit or channel through which gases flowing into the chamber from the inlet means pass between the electrode edges and subsequently are exhausted from the chamber through the outlet means.

The distance between electrode means **18** and **20** is preferably about 0.1 millimeter to about 5 centimeters and more preferably about 0.5 to 10 millimeters. The particular electrode distance can be made to suit the particular reactant and reactant conditions desired in the glow discharge.

The length of the opposing electrode edges is preferably greater than the distance between the electrodes and more preferably the length of the discharging edges is about 2 to 100 or more times the distance between opposing electrode edges.

The electrodes may be of any conductive metal but preferably a metal resistant to the reactants and reaction products formed during the glow discharge. When the reactant is a corrosive material such as chlorine, inert metals, such as titanium, platinum, gold, silver, tantalum, and the like are preferably used. When other less corrosive reactants are contemplated, the inert metals as well as other metals, such as low carbon steel, chromium, nickel, copper, and the like and alloys thereof are suitable conductive materials. Stainless steel has been found to be a very suitable electrode material for numerous reactants and reactant conditions.

The thickness of the electrodes can be varied within wide limits, for instance, a minimum thickness equal to that sufficient to provide structural support for the electrode to a thickness of about 1 centimeter depending on the particular metal used, its conductivity and the like. An electrode thickness of about 0.1 millimeter to about 5 millimeters is preferred. The electrode edge from which the glow discharge originates can be of the same thickness as the remainder of the electrode or tapered to a point similar to that of a knife edge.

Cooling of the electrode can be carried out by including a cavity within the electrode and providing the same with inlet and outlet ducts so as to permit a continuous flow of coolant therethrough. Temperature control means to control the temperature of the coolant can also be provided in association therewith.

The reactant chamber **11** is preferably constructed of a nonconductive material resistant to the environment encountered in the particular glow discharge reaction contemplated. Particularly suitable materials are glass, quartz, ceramic and the like. With certain reactants and reaction conditions, various non-conductive inert plastic materials can also be used. Because glow discharges are often characterized by low pressures, but not necessarily of high vacuum, the structural material utilized is of sufficent strength to contain the reaction under the particular reaction conditions contemplated. Thus, the present apparatus is capable of sustained operation under pressures as low as about 0.5 micron of mercury to about atmospheric pressure and, as is sometimes desirable, under superatomospheric conditions. Depending on the operating conditions contemplated, a structure of corresponding strength is provided.

The flow rate of gases through the reactor can be adjusted to suit the particular reaction being performed, but preferably are such that the dwell time in the glow discharge is less than one second, and more preferably less than 0.5 second.

The term "glow discharge" is used herein in its normal technical sense to mean an electrical discharge between an anode and a cathode wherein the cathode function is carried out by ion and/or photon bombardment of the cathode. The discharge is at ambient temperatures with little heating effect. As was stated previously, the glow discharge is often characterized in that it is normally of low pressure, but not necessarily of high vacuum. The discharge is normally sustained in the pressure range of about 1 micron to about 300 millimeters of mercury pressure for a normal glow. Higher pressures can be utilized particularly when external ionizing means are employed. Such a discharge is of a self-sustaining type having flat voltage over amperage characteristics. By this is meant that small variations in voltage effect large variations in current. A further description of glow discharges and other types of plasmas can be found in the book, The Plasma State, by E. J. Hellund, (1961), Reinhold Publishing Corporation.

The present reactor can be operated at ambient temperatures or as may be desired in certain reactions, at low temperatures approaching the condensation temperature of the particular gaseous reactants at the particular reaction pressure, such as —100 degrees centigrade, or at elevated temperatures up to about 500 degrees centigrade. Because glow discharge reactions are normally carried out near room or lower temperatures wherein the stability of the reaction products is best maintained, the present reactor is particularly suited for such reactions. Of course, when higher or lower temperatures are required, suitable cooling and heating means can be provided.

The present apparatus is operated by connecting the electrodes to a source of electrical current, applying a voltage to the electrodes and adjusting the power level to obtain a diffused glow. The voltage employed is a function of the reactants fed to the reactor, the temperature, the length of the electrodes, the particular metal used for the electrodes, the distance between the electrodes and the pressure in the discharge zone. Normally, the voltage imposed between the electrodes is of a field gradient of about 100 to 300 volts per centimeter in a pressure range of about 5 to 25 millimeters of mercury pressure. It is recognized that the voltage can vary widely with the particular pressure used, the distance between the electrodes and the length of the electrodes, being generally within the range of about 100 volts per centimeter of distance between electrodes at a pressure of about 5 millimeters of mercury and about 10,000 volts per centimeter of distance between electrodes at pressures approaching atmospheric.

When alternating current is utilized, the alternating current supply is normally 60 cycles per second, but can be of a lesser or higher rate. Alternating current rates of 20 to 100 kilocycles and more can be used with the preferred range being of about 50 to 1,000 cycles per second.

In commercial or semi-commercial operation of the present apparatus, a multitude or bank of reactors can be used. The reactors can be of increased size and/or have an increased length of opposing electrode edges to thereby provide an increased area of glow discharge with a corresponding increase in production capacity.

The following example illustrates certain preferred embodiments of the present invention. Unless otherwise indicated, all parts and percentages used herein are by weight and all temperatures in the example and claims are in degrees centigrade.

EXAMPLE

A spherical glow discharge reactor was constructed in accordance with FIGS. 1 and 2 having therein 2 silver electrodes of a flat, semi-circular configuration with a straight line edge for the discharge zone of the electrode. The electrodes are positioned with the flat thin edges of the sheets facing each other at a distance of about 2 millimeters from each other. The semi-circular configuration substantially conforms to the interior diameter of the spherical reactor. The opposing edges of the electrode are about 5 centimeters in length. The thickness of the electrodes at the opposing edges is about 0.2 millimeter thick. Opposite the electrode major surfaces are two separate inlets for gaseous reactants. On the other side of the major electrode surfaces is an outlet for the reaction product.

The reactor described is used for the production of chlorine oxides by connecting the electrodes to a source of direct current and the gas inlets to a source of oxygen and chlorine gas. The gas outlet is connected to a cold trap and a gas withdrawal means, such as a vacuum pump, capable of reducing the pressure within the reactor to the desired level of about 0.1 to 30 millimeters of mercury pressure. The reactor is prepared for operation by evacuating to about 0.1 millimeter of mercury pressure absolute and then flushing with oxygen. The reactor pressure is subseqeuntly adjusted to about 3.5 millimeters of oxygen pressure. A source of direct current is applied to the electrodes to obtain a glow discharge. Chlorine gas is then admitted to the reactor to increase the pressure to about 4.0 millimeters of mercury absolute while adjusting the molar feed ratio of the gases to about 10 moles of oxygen to 1 mole of chlorine. The voltage is increased until a magenta glow discharge is obtained. This discharge is obtained at a current of about 20 milliamperes. The pressure within the reactor is maintained at about 4 to 5 millimeters of mercury while continuously feeding oxygen and chlorine in the stated proportions, passing the gases between the edges of the electrodes wherein the glow discharge is being sustained and subsequently withdrawing the gases from the reactor.

The gases withdrawn from the reactor are condensed in a cold trap maintained at the temperature of liquid nitrogen. Yellow and red solids collect in the trap during the glow discharge. These solids are determined to contain chlorine and chlorine oxides.

While the invention has been described more specifically with respect to a spherical configuration, it is readily apparent to those skilled in the art that other configurations, such as ellipsoidal or cylindrical can be utilized with correspondingly good results.

While there have been described various embodiments of the present invention, the apparatus and methods described are not intended to be understood as limiting the scope of the invention as it is realized that changes therein are possible. It is further intended that each element recited in any of the following claims is to be understood as referring to all equivalent elements for accomplishing substantially the same results in substantially the same or equivalent manner. It is intended to cover the invention broadly in whatever form its principles may be utilized.

What is claimed is:

1. A method of subjecting gases to an electrical glow discharge comprising the steps of feeding at least one gaseous reactant to a reaction chamber, wherein said reaction chamber is comprised of a reactant inlet means and a reactant outlet mens separated by electrode means, said electrode means comprising a pair of substantially flat conductive sheets lying in the same plane with an edge of each sheet in a spaced relationship with respect to an edge of the other, said edges comprising major straight line edges of said electrodes and being positioned substantially parallel and equidistant from each other over substantially the entire opposing length thereof, said electrode means substantially dividing said reactor into two parts, producing a glow discharge between said electrode means and a field gradient of about 100 to 10,000 volts per centimeter, passing said gaseous reactant through said glow discharge, and subsequently exhausting said gases from said reaction chamber.

2. The method of claim 1 wherein the distance between

said electrode means is about 0.1 millimeter to about 5 centimeters.

3. The method of claim 2 wherein the length of the electrode edges is greater than the distance between said electrodes.

4. The method of claim 2 wherein the length of the electrode edges is about 2 to 100 times the distance between said electrodes.

5. The method of claim 1 wherein the electrode means conform substantially to the internal shape of said reaction chamber.

6. The method of claim 1 wherein the reaction chamber is substantially spherical.

7. The method of claim 1 wherein the reactor is constructed of glass.

8. The method of claim 1 wherein the electrodes are of

a metal selected from the group consisting of platinum, titanium, tantalum, gold, silver, steel, chromium, nickel, copper and alloys thereof.

9. The method of claim 8 wherein chlorine and oxygen are fed into said reaction chamber.

References Cited

UNITED STATES PATENTS

2,468,175 4/1949 Cotton ---------- 204—312

R. K. MIHALEK, *Primary Examiner.*

U.S. Cl. X.R.

204—312