Patent Application US 2006/060464 23rd March 2006 Inventor: Chak Chang

A METHOD AND APPARATUS FOR GENERATING PLASMA IN A FLUID

This patent application is for a most unusual system which produces a plasma discharge at room temperature and ambient pressure, using voltages as low as 350 volts and currents as low as 50 milliamps and among other things, it is capable of promoting the production of pharmaceuticals, production of nano-particles, the extraction of metals from liquids, low temperature sterilisation of liquid food, use in paper industries to decontaminate the effluent discharge, fragmentation or de-lignifications of cellulose; the removal of odour from discharging liquid in the food industries, and the treatment of fluid effluent. It is also a method of producing hydrogen gas at low cost.

ABSTRACT

A method and apparatus for generating plasma in a fluid. The fluid **3** is placed in a bath **2** having a pair of spaced electrodes **4, 6** forming a cathode and an anode. A stream of bubbles is introduced or generated within the fluid adjacent to the cathode. A potential difference is applied across the cathode and anode such that a glow discharge is formed in the bubble region and a plasma of ionised gas molecules is formed within the bubbles. The plasma may then be used in electrolysis, gas production, effluent treatment or sterilisation, mineral extraction, production of nanoparticles or material enhancement. The method can be carried out at atmospheric pressure and room temperature. The electrodes may carry means to trap the bubbles in close proximity. Partitions may be present between the electrodes.

DESCRIPTION

The invention relates to the provision and utilisation of a plasma formed in a fluid, and in particular to the provision and utility of a plasma formed within bubbles contained in an aqueous medium.

BACKGROUND

Plasma is an electrically conductive gas containing highly reactive particles such as radicals, atoms, plasma electrons, ions and the like. For example plasma may be formed when atoms of a gas are excited to high energy levels whereby the gas atoms lose hold of some of their electrons and become ionised to produce plasma.

Thermal plasma, including plasma arc is known. However plasma arc is associated with high power consumption, the rapid erosion of electrodes when used in electrolysis, the need for catalysts and high-energy loss due to the associated high temperatures.

Clearly therefore, it would be advantageous if a non-thermal plasma could be devised. This would enable the plasma to be used for a number of applications for which plasma is useful without the disadvantages associated with using a high temperature plasma arc.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention, there is provided a method for generating plasma in a fluid, comprising the steps of providing a fluid, introducing and/or generating one or more gas chambers or bubbles within the fluid, whereby the chambers or bubbles are contained by the fluid, and treating the fluid such that a plasma is generated within the chambers or bubbles.

The fluid may be a liquid that is contained within liquid containment means.

The applicant has discovered that a plasma can be generated relatively easily within bubbles within an aqueous medium. This plasma causes dissociation of molecules and/or atoms which can then be treated and/or reacted to obtain beneficial reaction products and/or molecules and/or atoms.

The liquid container may be open to the atmosphere and the process may therefore be carried out at substantially atmospheric pressure. Alternatively the container may be placed inside a sealed reaction chamber, e.g. under partial vacuum. This reduction in pressure can reduce the energy required to achieve a glow discharge within the bubbles passing over a cathode.

Importantly the process is not required to be carried out in a vacuum.

The plasma may be formed, for example, by applying a potential difference across electrodes which are immersed in the liquid.

Upon passing electricity of sufficient potential between two electrodes, the dielectric barrier associated with the bubble/chamber surface breaks down, with the accompanying formation of a glow discharge and plasma inside the gas bubbles or chambers. This enables plasma formation to be effected at very low voltages, current, temperature and pressure, as compared with known methods of plasma formation.

For example, typical voltages and currents associated with plasma arc are in the region of 5 KV and 200 A respectively, whilst in the present invention, a plasma may be provided with a voltage as low as 350 V and a current as low as 50 mA.

The formation of a glow discharge region adjacent said one electrode is caused by a dielectric breakdown in the bubbles surrounding the electrode. The bubbles have a low electrical conductivity and as a result there is a large voltage drop between the electrodes across this bubble region. This voltage drop accounts for a large portion of the overall voltage drop across the electrodes. The plasma is generated within the bubbles contained within the electrolyte. The liquid electrolyte acts as containment for the plasma within the bubbles.

When plasma discharge occurs, any water vapour inside the bubbles will experience plasma dissociation whereby H+, OH^-, O^-, H, H_3, and other oxidative, reductive and radicals species are formed. The formation of charged plasma species will of course also depend on the chemical composition of the electrolyte.

In the present invention, the voltage needed for plasma generation is much lower than plasma glow discharge generated under gas only conditions. For example experiments have demonstrated that plasma begins to occur at voltages as low as 350 V and the maximum voltage required should not exceed 3,000 V. This requirement is based on a current density of 1 to 3 Amp/cm^2 which can be achieved at the point of discharge whereby the current input ranges from 50 mA to about 900 mA.

Plasma can be created, according to the present invention, in a steady manner with a low voltage and current supply, which leads to an economy in power consumption.

The bubbles may contain precursor materials originating in the fluid, which is preferably a liquid, more preferably being an aqueous electrolyte. This material may have been transferred from the liquid to the bubbles by diffusion or evaporation.

Alternatively the precursor may be introduced directly into the bubbles from outside the system.

The step of generating bubbles within the aqueous medium may be accomplished by one or more of the following: electrolysis, ebullition, ultrasonic cavitations, entrainment, scattering, chemical reaction, dissociation by electrons and ion collisions or local heating or ebullition, hydraulic impingement, ultrasonic waves, laser heating, or electrochemical reaction, electrode heating, releasing of trapped gases in the liquid, and externally introduced gases or a combination of them.

Electrolysis bubbles may be generated by the electrode as a result of the potential differences applied across them, e.g. hydrogen bubbles liberated by the cathode or oxygen bubbles liberated by the anode. Ebullition bubbles may be generated by electrical heating in the region of the electrodes. The bubbles may be generated by direct electrical heating or by heating in proximity to the electrode by a moving wire or grid. Microwave heating and heating using lasers may also be used to generate ebullition bubbles.

Cavitation bubbles may be generated by using an ultrasonic bubble generator or a jet of fluid or a jet of a mixture of gas and liquid injected into the electrolyte in proximity to the electrode. Cavitation bubbles may also be generated by hydrodynamic flow of the electrolyte in proximity to the electrode. Scattering of gas in proximity to the electrode may also be used to generate bubbles.

Bubbles may also be generated by a chemical reaction which evolves gas as a reaction product. Typically such reactions involve thermal decomposition of compounds in the electrolyte or acid based reactions in the electrolyte. Bubbles may also be formed in the electrolyte by adding a frother to it.

Typically the generation of bubbles forms a bubble sheath around one electrode. The bubble sheath may have a thickness of anything from a few nanometres to say, 50 millimetres. Typically the bubble sheath may have a thickness of 1 mm to 5 mm. Further, it should be understood that the bubbles may not be homogeneous throughout the sheath.

Gas or vapour formed external to the container may be pumped or blown into the aqueous medium near the cathode.

Thus the composition of the plasma that is generated within the bubbles may be tailored to suit the application to which the plasma is being put and the bubbles may either be generated within the liquid from components within the liquid or introduced into the liquid from outside the containment means.

The bubbles can assume various sizes and shapes including a sheet form air gap or air pocket covering shrouding the electrodes or spread across the liquid medium in micro bubbles.

Liquid foam may also be considered to be bubbles or gas chambers for the purposes of the present invention. This is a highly concentrated dispersion of gas within a continuous interconnecting thin film of liquid. The gas volume can reach up to 80% of a contained area. Gas generated within or introduced to the reactor externally can also be encapsulated within a foaming agent to enable it to undergo plasma discharge treatment.

Gases trapped inside a thick liquid mist in a confined space are also considered to be gas containing bubbles, which contain the gases, and liquid vapours that provide the condition for generation of non-thermal plasma. The liquid may contribute one or more source materials for dissociation during the plasma discharge.

In practise, gas bubbles evolving near and shrouding an electrode in an electrolysis process create a dielectric barrier which prevents and slows down the flow of current. At the same time the dissolved gas or micro bubbles spread and diffuse in the liquid volume thereby creating a high percentage of void fractions (micro gas bubbles) which in turn increase the electric resistance whereby the voltage across the liquid medium is raised. When the voltage has increased sufficiently, gas trapped inside the bubbles undergoes non-equilibrium plasma transformation. At this point, di-electric breakdown occurs enabling resumption of current flow through the bubbles sheath or air pocket layer.

Any water molecules and atoms lining the gas and liquid interface of a bubble shell will also be subjected to the influence of the plasma to produce H^+ and OH^- and other radical species. Some of these neutralised atoms and molecules will transpose into the gas bubbles as additional gas that increases the size of the bubble. As such the bubbles pick up more liquid vapours before a next succession of plasma discharge. Such a cycle of such repetitive discharge can take place in a fraction of a second to several seconds depending on the make up of the electrode and reactor.

The step of generating bubbles within the aqueous medium may include adding a foaming agent to the aqueous medium such that bubbles are formed within foam. The foam bubbles are confined by an aqueous medium that is electrically conductive. The foam bubbles can vary widely in size down to a fraction of a millimetre.

The step of generating bubbles may include forming an aerosol mist. The gas within the aerosol mist broadly defines bubbles in the sense that there are volumes of gas between liquid droplets. These bubbles in the form of spaces between liquid drops function in a similar way to conventional bubbles within a liquid and a plasma is formed in this gas in the same way as described above.

An advantage of foam and aerosol mist is that it provides for good mixing of gaseous components within the mist and foam. The plasma is generated in the bubbles of the foam and aerosol mist in the same way that they are formed in an aqueous liquid, e.g. by passing electrical current between spaced electrodes within the foam or mist.

The step of forming a glow discharge in the bubble region may be achieved by increasing the potential difference across the electrodes above a certain threshold point.

The formation of a glow discharge and generation of plasma within the bubbles may be assisted by a pulsed or steady power supply, a magnetron field, ultrasonic radiation, a hot filament capable of electron emission, laser radiation, radio radiation or microwave radiation. The energy requirements may also be assisted by a combination of any two or more of the above features. These factors may have the effect of lowering the energy input required to reach the threshold potential difference at which glow discharge is formed.

In conventional electrochemical processes bubbles are regarded as undesirable. As a result concerted efforts are made to avoid the generation of bubbles during the operation of electrochemical cells. By contrast the process of the current invention deliberately fosters the formation of bubbles and utilises bubbles in proximity to the electrode as an essential feature of the invention. The bubble sheath surrounding the electrode is essential to establishing a plasma region which then gives rise to the plasma deposition on the article.

Thus the plasma is formed within bubbles and the molecules and/or atoms that are ionised are surrounded by liquid which effectively provides a containment structure within which the plasma is contained. The liquid in turn generally opens to the atmosphere.

Plasma glow discharge can be fairly easily accomplished within the cell because the sheath of bubbles has the effect of causing a substantial proportion of the voltage drop to occur across the bubble sheath. It is concentrated in this area rather than a linear drop across the electrode space. This provides the driving force to generate plasma glow discharge and from there deposition of the ionic species.

The electrical charge is preferably applied in pulses, since this enables plasma production at lower voltages.

The fluid is preferably a liquid electrolyte, for example an aqueous medium, whereby in one preferred embodiment, the medium is water.

The electrolyte may comprise a carrier liquid and /or a source or precursor of the material to be ionised by the plasma.

When the liquid is water, charged plasma particles include species such as OH radicals, O^- and H^+, -OH, O_2 and O_3, which will react with the surrounding liquid.

Distilled water is known to be dielectric and non-conductive. It is however when water contains impurities such as dissolved minerals, salts and colloids of particles, whereby water becomes conductive, that ionisation and electrolysis can occur.

The method may further include adding an additive, such as an acidic or alkaline conductivity enhancing agent, to the aqueous medium to enhance this electrical conductivity such as organic salts or inorganic salts, e.g. KCl, $MgCl_2$, NaOH, Na_2CO_3, K_2CO_3, H_2SO_4, HCl.

The method may include adding a surfactant to the aqueous medium for lowering the surface tension of the medium and enhancing the formation of bubbles, e.g. to stabilise bubble formation.

The electrolyte may further include additives in the form of catalysts for increasing the reaction of molecules and/or atoms produced in the plasma, additives for assisting the formation of bubbles, and additives for buffering the pH.

The method may further include cooling the electrolyte to remove excess heat generated by the plasma reaction and regulating the concentration of one or more components within the electrolyte.

The cooling may comprise drawing electrolyte from the bath pumping it through a heat exchanger, and then returning it to the bath.

Plasma creation, according to the present invention can be effected in the absence of extreme conditions, for example plasma according to the present invention may be provide under atmospheric pressure and at room temperature.

During plasma production according to the present invention, a shroud of bubbles preferably builds up and smothers around at least one of the electrodes, whereby electrical charge builds up in the bubble shroud thereby creating a dielectric barrier which impedes current flow, whereby electrical resistance in the fluid medium builds up so that voltage through the medium is raised to a degree such that gas within the bubbles is excited to an energy level at which a plasma is produced.

The method according to the present invention preferably comprises the further step of exposing the plasma to a material, which on contact with the plasma undergoes a chemical and/or physical change.

For example the plasma can be used to cause dissociation of toxic compounds and then break down the compounds and/or cause them to undergo reactions leading to innocuous reaction products.

The plasma produced according to the present invention, which will be referred to as 'under-liquid' plasma has the same physical and chemical properties as plasma produced according to known methods and accordingly also has the utility of such plasma.

The under-liquid plasma according to the present invention can create an active catalytic condition which facilitates gas and liquid interaction. As such, the plasma according to the present invention, may promote any reaction which takes place in a liquid medium, for example chemical reactions, the production of pharmaceuticals, production of nano-particles, the extraction of metals from liquid, low temperature sterilisation of liquid food, use in paper industries to decontaminate the effluent discharge, fragmentation or de-lignifications of cellulose; the removal of odour from discharging liquid in the food industries, and the treatment of fluid effluent. Material may be chemically modified by means comprising one or more of the following: ionisation, reduction, oxidation, association, dissociation, free radical addition/removal, whereby, optionally, following chemical modification, the material is removed.

The invention may be used to tackle existing problems. For example, water that has been used in industrial processes or used in some other way has to be treated to remove harmful components before it is returned to ground water. This is typically achieved by reacting the harmful components with other chemical components introduced to the water to form relatively harmless products. Many undesirable components are treated fairly effectively in this way.

However some harmful components within water are not capable of being treated in this fashion. This poses a problem as these harmful components, e.g. contaminants, need to be removed from the water before it is returned to ground water. One known way of treating some of these components is to use an electric arc process to break down these toxic chemicals. However an electric arc process requires a substantial amount of energy to arc between electrodes within the liquid and is therefore costly. In addition the number of chemicals that are able to be treated in this way is limited. A further limitation of these processes is that they often cause rapid consumption and degradation of electrode material. Applicant believes that this water could be better treated by the method of this invention.

Moreover, the electric arc method of providing plasma, applies a high voltage across closely spaced electrodes causing the break down and ionisation of molecules, and then a surge of electrical current between the electrodes.

Further, many metals or mineral occur naturally in the ground in the form of ores as mineral oxides. The minerals need to be reduced to useful minerals. Typically the reduction is carried out using pyrometallurgical techniques, e.g. such as are used in electric arc furnaces. These treatments are very aggressive and utilise enormous amounts of electrical energy. Clearly it would be advantageous if a simpler more streamlined and more energy efficient method of reducing a mineral oxide to a mineral could be devised. Applicant believes that this could be done by the method of this invention.

Yet further, the generation of electrical energy with fuel cells is seen as an exciting new area of technology. Such fuel cells utilise hydrogen as a fuel. Accordingly a relatively inexpensive source of this hydrogen as a fuel is required. Currently hydrogen is produced by solar cells. However the present invention could be used to provide such a source of hydrogen.

In one form of the current invention, the undesirable compounds may be deposited on an electrode, e.g. the cathode, as a layer or coating. The compound can then be removed from the liquid by simply removing it from the aqueous medium.

In another form, the undesirable component can be reacted with a chemical compound, e.g. within the plasma, to form a solid compound, e.g. a salt in the form of a precipitate, that settles out of the aqueous medium and can then be removed from the aqueous medium.

Typically the undesirable component will be toxic to animals or harmful to the environment. However components that are undesirable in other ways are also included within the scope of the invention.

Applicant envisages that this will be particularly useful for the removal of harmful heavy metals from waste water. It will probably also be useful for the treatment of contaminated gases. Such gases will be introduced to the aqueous medium in such a way that they form part of the bubbles passing over the cathode and then be treated as described above.

Another example is the extraction of a mineral, e.g. a metal, from its metal oxide, the method including: dissolving the mineral oxide in an aqueous medium and then subjecting it to the method described above according to the first aspect of the invention whereby a plasma is generated within bubbles passing over the cathode, and the plasma reduces the mineral oxide to the mineral per se.

The ozone which is formed in the plasma can then be reacted with hydrogen to form an innocuous compound such as water. The reduced mineral which is formed in the plasma, e.g. a metal, may be deposited on the cathode or else may be precipitated out as a solid in the container.

In the case of water, hydrogen and oxygen produced, travel to the anode and cathode and are preferably then removed. As such, the process according to the present invention is an economical, simple and effective way of producing hydrogen.

The hydrogen produced in this fashion may be used as fuel, e.g. in fuel cells for the generation of electricity. Applicant believes that hydrogen can be produced relatively inexpensively in this fashion. Fuel cell technology is currently receiving an increased level of acceptance looking for a cheap source of the supply of hydrogen.

According to another aspect of the present invention, there is provided the use of this 'under-liquid' plasma in one or more of the following: chemical and/or physical treatments of matter, electrolysis, gas production, in particular hydrogen gas production; water, fluid and/or effluent treatment; mineral extraction; sterilisation of drinking water and/or liquid food, production of nano-particles, the enhancement of material chemical and physical properties.

According to a further related aspect of the present invention there is provided an apparatus for providing a plasma comprising; a container in which a plasma is provideable, bubble trapping means, arranged within the container, for trapping gas bubbles at a predetermined location in the container and, plasma creation means, in association with the container, for creating a plasma from the gas within the bubbles.

The plasma creation means preferably comprise electrical discharge means which most preferably comprise a cathode and/or an anode.

The apparatus, in one preferred embodiment being an electrolysis cell, further preferably comprises bubble introduction and/or generating means, for introducing and/or generating bubbles in the container.

Furthermore, the apparatus preferably comprises one or more of the following: enhancing means for enhancing plasma formation and one or more non-conductive partitions arranged between the electrodes, whereby the enhancing means preferably comprise bubble trapping means most preferably associated with the electrodes and wherein the enhancing means may also comprise current concentrating means for concentrating the electrical current at a predetermined position in the container which can take the form of one or more channels arranged through one or more of the electrodes.

The electrodes may take any suitable form, for example the electrodes may be so profiled as to entrap/attract bubbles, in order to help gas bubbles being created or introduced to the discharging electrode to form a dielectric barrier by which the voltage can be raised whereby a suitable current density is provided directly by high input of current or passively created by a current concentrating arrangement, for example, by conducting the current through small holes on the electrodes or by reducing the discharge surface area of the electrodes whereby in the latter case, the electrodes may take the form of pins, wires, rods and the like.

For example, the cathode may be formed by a hollow tube with perforated holes therein, e.g. small perforated holes. The holes allow bubbles introduced into the tube to pass out of the tube into the aqueous medium. Alternatively a cathode may be made of wire mesh or have a roughened surface, e.g. to encourage the attachment of bubbles thereto to slow down the movement of the bubbles.

In one embodiment there are a plurality of cathodes spaced apart from each other and in parallel with each other, and a single rod-like anode, e.g. centrally positioned relative to the cathode.

The other electrode (non discharging) preferably has a larger surface area such than the discharging electrode.

The discharging electrode can either be cathode or anode depending on the application necessity.

In an experimental reactor the separating membrane, non-conductive partition, was nylon cleaning cloth having a tight matrix 0.5 mm thick. This semi-permeable membrane is capable of resisting the passage of oxygen and hydrogen ions through it in the aqueous medium, intermediate the anodes and cathodes thereby to maintain separation of oxygen and hydrogen produced in the plasma.

Most preferably, the apparatus according to the present invention is an electrolytic cell.

A known problem with carrying out electrolysis is that any gas/bubble build up in the electrolytic cell creates a barrier to the flow of current through the electrolyte, thereby impeding electrolysis, which increase in resistance in turn forces the required voltage up. As such, electrolytic cells require a great deal of energy and are often very large in order to effect dispersion of such gas/bubbles. However the present invention actively promotes such bubble build up, in order to effect plasma creation which the inventors have shown is effective in carrying out electrolysis.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

A plasma formed in a fluid in accordance with this invention may manifest itself in a variety of forms. It will be convenient to provide a detailed description of embodiments of the invention with reference to the accompanying drawings. The purpose of providing this detailed description is to instruct persons having an interest in the subject matter of the invention how to put the invention into practice. It is to be clearly understood however that the specific nature of this detailed description does not supersede the generality of the preceding statements. In the drawings:

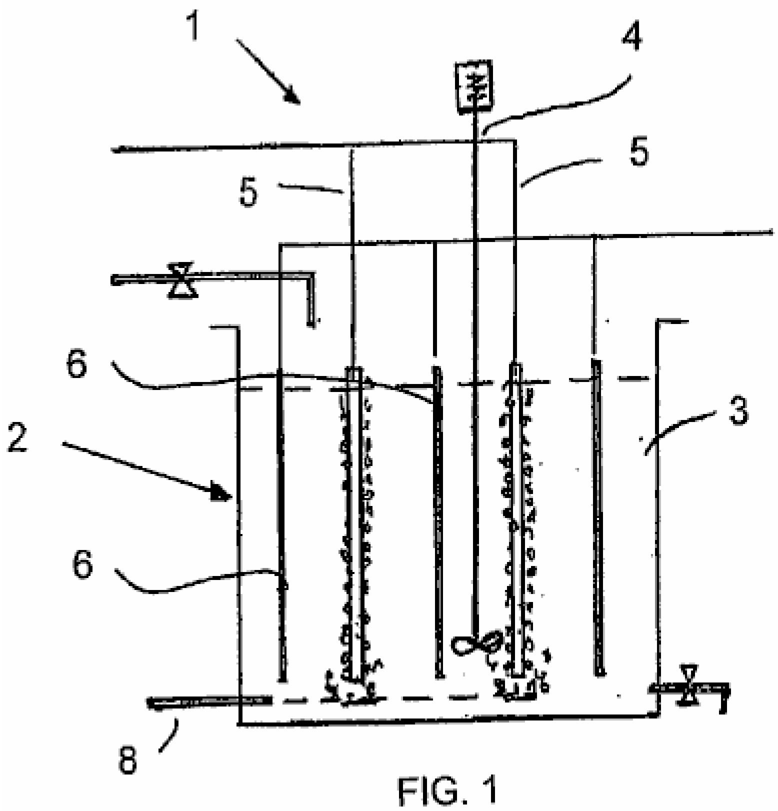


FIG. 1

Fig.1 is a schematic sectional front view of apparatus for carrying out a method in accordance with the invention.

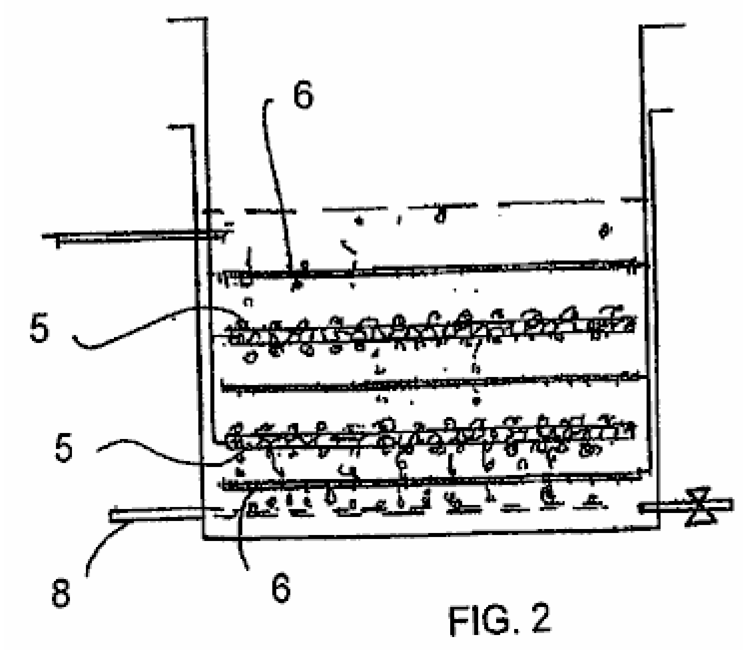


FIG. 2

Fig.2 is a schematic sectional front view of a variation on the apparatus of Fig.1.

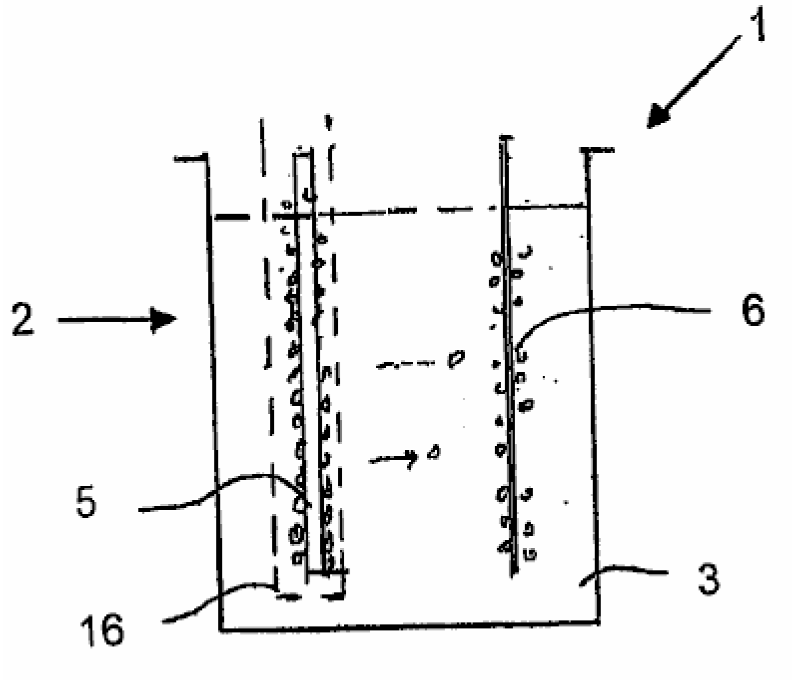


FIG. 3

Fig.3 is a schematic sectional front view of an apparatus in accordance with the invention suitable for producing hydrogen gas.

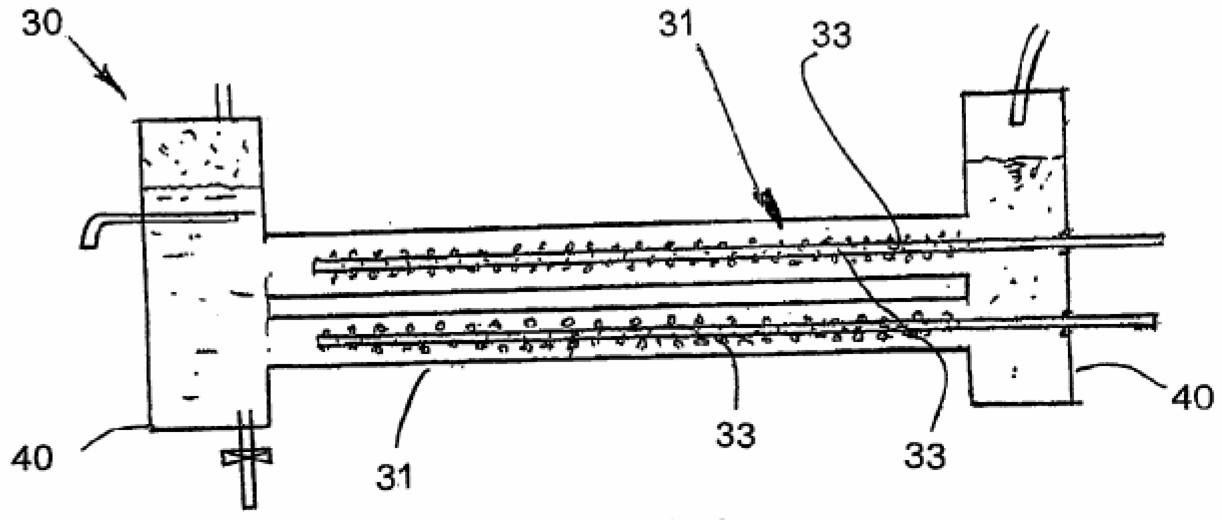


FIG. 4

Fig.4 is a schematic sectional front view of a tubular reactor carrying out a method in accordance with another embodiment of the invention.

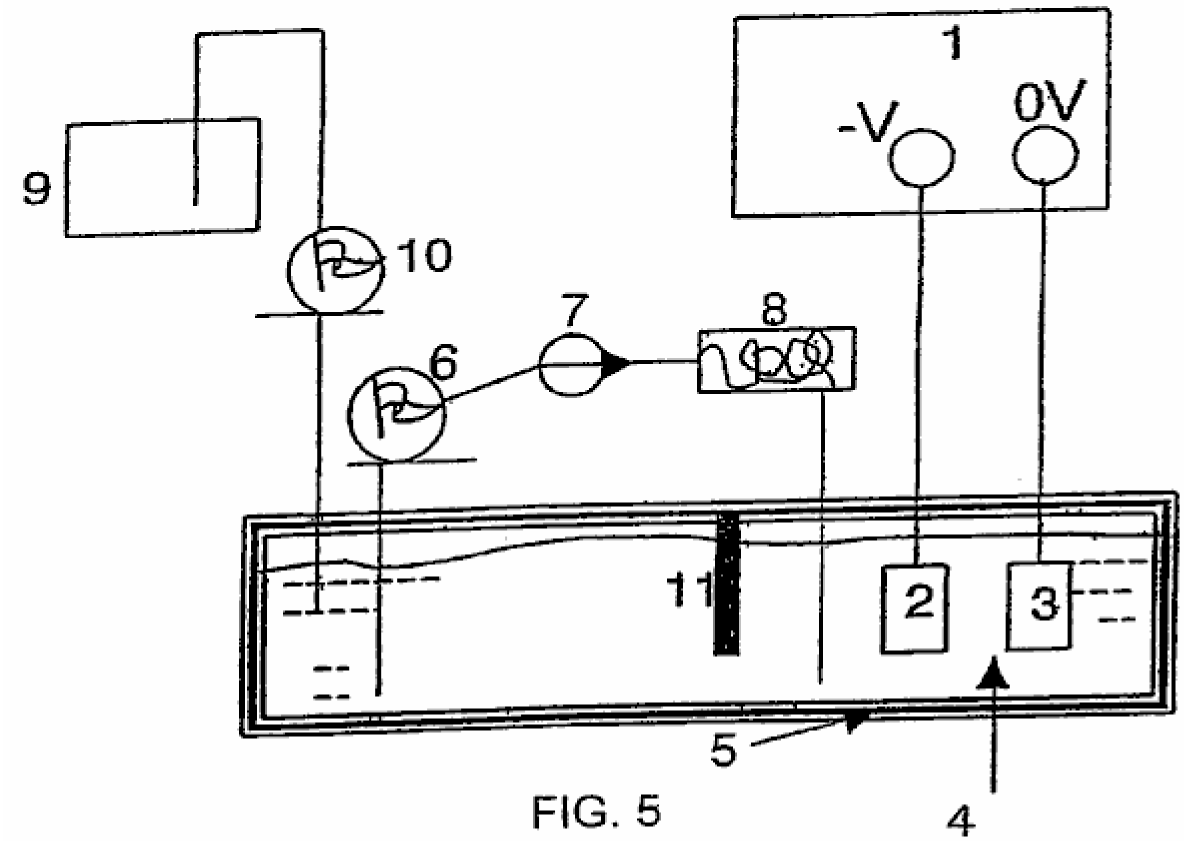


FIG. 5

Fig.5 is a schematic flow sheet of apparatus in the form of a cell for carrying out the invention.

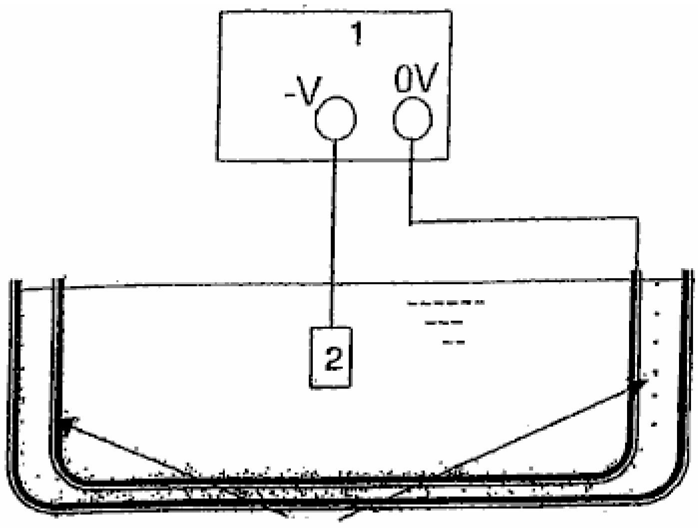


FIG. 6

Fig.6 is a schematic view of a bath for the cell of Fig.5 having an ultrasonic generator for generating bubbles.

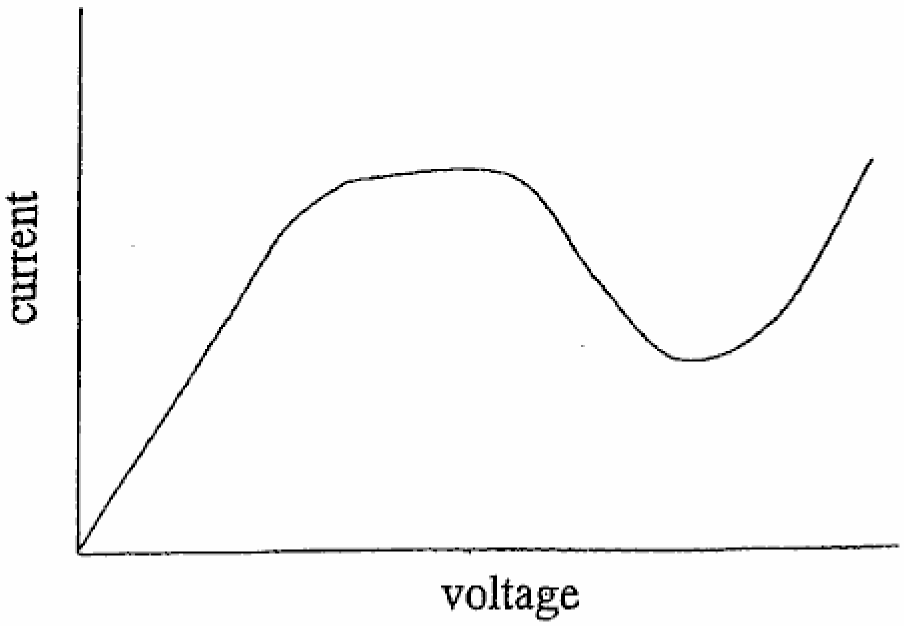


FIG. 7

Fig.7 is a schematic graph of current against voltage in an electrolytic cell.

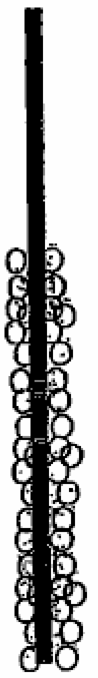


FIG. 8

Fig.8 shows the initial formation of a bubble sheath around the cathode due to the application of voltage across the electrodes.

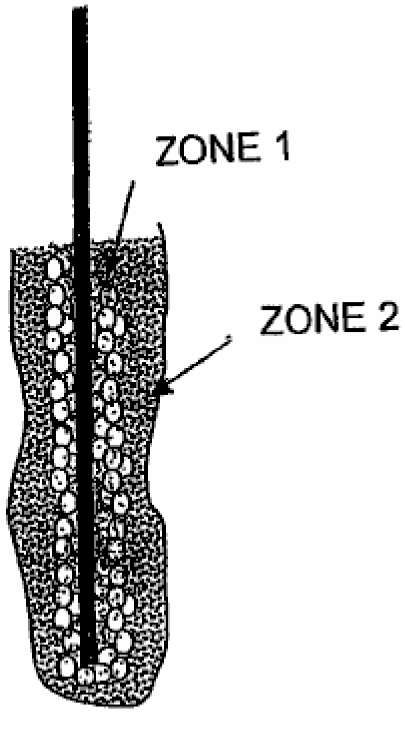


FIG. 9

Fig.9 shows the bubble sheath around the cathode during stable glow discharge within the cell, and

Figs.10-53 refer to further embodiments and experimental results in respect of the present invention.

The present invention relates to the production of non-thermal plasma contained in a liquid by generating corona discharge and or glow plasma discharge inside the bubbles or air pockets present in the liquid.

Upon passing electricity of sufficient potential through the liquid, electric breakdown of the dielectric bubble barrier results in the formation of plasma discharge inside the gas bubbles or pockets present in the liquid. In most cases glow discharge occurs near the electrodes but occasionally glow discharge is also observed away from the electrode.

The bubbles can be produced either by electrolysis, electrochemical reaction, heating of electrodes, releasing of trapped gases in the liquid, ultrasonic cavitations, laser heating, and externally introduced gases.

Bubbles produced by electrolysis of water contain hydrogen gas at the cathode and oxygen gas at the anode. Such bubbles can also contain other chemical vapours originating from the electrolyte or additives.

The liquid serves as an electrolyte which provides conductivity of electricity, the source material from which gases and vapour are produced for plasma dissociation to form, for example, reduction and oxidation, radicals and neutral species. The liquid also provides an active catalytic chemical environment for forming new compounds. It also serves as containment of gases in the form of bubbles or air pockets in which the non-thermal plasma discharge takes place.

In practise, gas bubbles evolving and shrouding the electrodes during electrolysis create a dielectric barrier which inhibits the flow of current.

At the same time the dissolved gas or micro bubbles spread and diffuse in the liquid volume create a high percentage of void fractions (micro gas bubbles) which also increase the electric resistance and so raise the voltage across the liquid medium.

When the voltage between two electrodes reaches a critical level, the gas trapped inside the bubbles undergoes non-equilibrium plasma transformation. This is also known as electric breakdown which enables the resumption of current flow through the bubble sheath or air pocket layer. In the case of water electrolysis, the production of hydrogen will then resume.

During plasma discharge, light emission may be observed in the bubbles in a sporadic or steady manner in short and continuous flashes near the surface of the electrodes and in the liquid medium.

Continuous light spots may also be observed in areas distanced from the electrodes where suspected small air bubbles are trapped and yet remain under the influence of strong electrical field.

The temperature in the electrolyte near the electrodes has been measured to be in the region of $50^{O}C$ to about $90^{O}C$ with an experiment running in water for 30 minutes, which indicates that the plasma is non-thermal plasma.

The temperature variation may be influenced by electrode geometry, electrolyte concentration, level of inception voltage and current density for the glow discharge. The temperature measured directly over the discharging electrode can reach over $200^{O}C$ during reformation of methanol for example.

Configurations of electrodes, size, spacing, dielectric barrier coating, electrolyte temperature, current density, voltage and reactor geometry are factors influencing plasma formation.

A special structure and arrangement to retain gas or gas bubbles close to the electrodes provide favourable circumstances for the ready formation of a steady and cyclical plasma glow discharge with lower voltage and current input.

Electrode configurations can be in following forms: plate to plate, plate to pinned plate, dielectric coated plate to plate or pinned plate or both, wire mesh to plate, wire mesh to wire mesh or to perforated plate, wire or groups of wires in perforated cylinder tube, and tube in tube.

The electrode material may be sponge porous metal electrode, electrode covered with honeycomb non-conductive materials and porous ceramic filter to entrench gas or using non-conductive plate with drilled holes and gas traps that retain gas bubbles and concentrate the current density next to the electrode surface.

In general keeping the bubbles close to the surface of the electrodes can also be achieved by attaching a porous non-conductive nylon foam mattress and/or a honeycomb or porous ceramics slab of suitable thickness, so that the mobility of the bubbles is slowed down and at the same time the conduit for current flow is narrowed by a shading effect of the dielectric materials which in turn raises the current density locally.

For the same reason glass beads, plastic beads and beads of catalytic material i.e. TiO_2, graphite of suitable size can be placed between the electrodes in order to slow down the flow of bubbles.

A non-conductive, heat and corrosion electrode covering material, structured to retain and trap gas bubbles which also concentrates current density through small openings arranged through it whilst providing an adequate exposed electrode surface for electro-chemical and electrolysis reactions, improves the generation of steady and short cyclical reactions under-liquid plasma discharge.

Multiple layers of very fine stainless mesh, sandwiched between two plastic cover plates with small perforated holes, have produced a steady glow plasma. The void space created by the layered wire mesh provides a trap for air bubbles as well as enlarging the contact surface for electrochemical and electrolysis reaction.

In an experiment both vertical or horizontal electrodes were covered and bonded with non-conductive materials (plastic) with patterned perforations to trap gas bubbles while at the same time allowing for electrical contact of the electrodes through the perforations.

The electrode contact surface was enlarged underneath the shielding to increase gas production during electrolysis or heating. Current flow was concentrated through small holes of 1 to 3 mm leading to the trapped gas and bubbles, which underwent plasma transformation. Cyclical and steady plasma was observed with an input DC voltage ranging from 350V to 1900V and current ranging from 50 mA to 800 mA.

A non-conductive diaphragm, which does not restrict the free flow of ions and electrolyte, is placed between two opposite electrodes to prevent crossing of bubbles between two half electrolytic cells avoids re-mixing of the gases which have been separated by electrolysis.

A reactor may be so structured that the electrolyte is able to enter into the reactor through the separating membrane or opening form in the reactor to replenish the loss of electrolyte within the enclosed reactor.

There are other techniques which can be incorporated into the proposed invention for the enhancement of plasma generation such as pulsed power supply, RF power, microwaves, ultrasonic waves, magnetron field, and laser. Some of the above techniques may also be applied in pulsed form.

Ultrasonic cavitations in liquid (sonic-technology) will enhance the plasma formation and the catalytic reactions that benefit a number of under-liquid plasma applications.

The under-liquid plasma requires an input of DC or AC voltage in the range from 350V up to 3000V and current density ranging from 1 Amp to 3 Amp per cm^2 in dealing with a large range of liquid media. The specific voltage and current requirement for a given application depends very much on the chemical and physical properties of electrolytic liquid as well as those factors mentioned above.

The under-liquid plasma method according to the current invention, can operate at atmospheric pressure and ambient temperature. However, an external pressure less than one atmosphere or over one atmosphere with higher temperatures does not deter the generation of plasma in the bubbles. A higher temperature in the liquid also means more active gas molecules within the bubbles, which can benefit plasma formation.

Non-thermal plasma generated in a liquid according to the present invention, has advantages over known types of plasma discharge, for example in gas, under water plasma arc and pulse power electric discharge, these being:

> It requires only simple electrolytic cells to be the reactor to perform such discharge. There is little erosion to the electrodes and wider range of electrode materials can be chosen such as stainless steel, graphite, aluminium and good conductive materials which are resistance to chemical erosion. The polarity of the electrode can be reverted if necessary to compensate the lost of electrode materials if so desired.
>
> It works under one atmospheric pressure and ambient temperature. The liquid electrolyte will be primary source of materials for the chemical and physical reaction take part in the process. There are number of

ways that bubbles can be produced within the electrolytic cell. Gas can also be introduced to the reactor where plasma catalytic and dissociation is taking place.

It is a low-temperature system as the plasma discharge is non-thermal. Any excessive or undesirable high temperature can be lowered by increasing the circulation rate of the liquid which can lose its temperature through heat exchange. Heat generated can be recovered as secondary energy.

The electrolyte (liquid) will serve as extension of the conducting electrodes in contact with the gases or vapour trapped inside the bubbles. The air gap between two electrodes is reduced to the thickness of the gas bubbles or air pocket which thus enables plasma discharge at a much lower voltage and current compared with other plasma discharge systems. Plasma glow discharge, according to the present invention, can be initiated under conditions of a voltage as low as 350V and the current ranging from 50 mA to 800 mA. Extra energy is not required in splitting the water molecules to transient bubbles as in the other underwater electrical discharge system which requires voltage not less than 5 to 6 KV, and very high current over 200 A in pulsed supply. Plasma discharge will also take place in gas pockets or bubbles away from the electrode as long as the electric field strength is sufficient to cause such discharge.

The electrolyte also serves as a confinement of gas generated within the system, or purposely introduced gas of known properties, instead of ordinary air which may lead to production of unwanted NOx for example. Noble gas such as argon is not necessary to enhance the initiation of glow discharge sometime required in the air discharge system.

The electrolyte also serves as a conductor and passage for the transportation of ionised species and transmission of electrons. The ionised atoms and molecules deriving from the electrolyte will be collected in their respective electrodes in the form of gas or material deposit. These ionised species are either serving as a reduction or oxidation agent in their respective half-cell. Since the gas ions produced during the discharge migrate to their respective poles to be collected individually, hydrogen gas and oxygen gas can be collected separately.

The gas and vapour molecules and atoms inside the bubble which undergo plasma glow discharge are ionised, excited or dissociated to produce the very active species for reduction, oxidation, and the forming of neutral or radical species which in turn react with the chemical elements present in the gas and liquid interface aligning bubbles wall. The large number of bubbles generated near the electrodes and in the nearby liquid, come into contact with a much larger volume of liquid nad so provides effective treatment, breakdown, transformation of chemicals, organic matter or elements which have been targeted.

Liquid is a good medium for transmitting ultrasonic waves. Sonic-excitation is beneficial for the dissociation of materials and extermination of microbes and it aids the breakdown and local melting of colloidal solids during impact which also enhances the plasma oxide reduction process. The generated ultrasonic cavitations may be fully utilised to work in conjunction with the under-liquid plasma discharge. An ultrasonic cavity is micro in size and uniformly distributed in the entire liquid volume. The cavities are a high vacuum which contain liquid vapour and gas, and these favour plasma discharge. The high temperature and pressure reaching 10,000^{O}K and a thousand times atmospheric pressure, produced on the collapsing phase of these cavities work is complementary to that of the electro discharge plasma. This enables under-liquid plasma discharge to spread further from the electrodes and be well distributed in the liquid volume which increases its overall effectiveness.

The electrolyte may also be in the form of a mixture, an emulsified liquid, a colloid, or foams encapsulating gas emissions either coming from the liquid or introduced externally. The emulsified liquid of an oil/water mixture and encapsulating gas of hydrocarbon fuel with the ultrasonic irradiation, will facilitate their reformation for hydrogen production.

Fine granular insoluble particles of mineral oxide such as aluminium, titanium, iron, silica etc. can be suspended in the form of colloid with the liquid which is than subjected to reduction with active ionic hydrogen atoms in a highly reactive plasma catalytic environment to become deoxidised and refined. This will be more so, with the assistance of sonic impedance. The Plasma glow discharge has also demonstrated the ability to dissociate soluble ionic metal compounds, whereby subsequently the positively charged metal ions will be segregated near the cathode electrode in the form of precipitation and plasma electroplating deposition.

The electrolyte may be a source of materials for thin-film deposition with the assistance of plasma glow discharge. In addition, nano size particles of certain compounds and elements i.e. metal hydride, oxide, pure metals, semi metals, organic, ceramic etc. can also be produced with the assistance of the under-liquid plasma discharge in conjunction with the ultrasonic cavitations mechanism, to cause breakdown and reformation of certain compounds. The highly catalytic, reactive and dissociation capacity of the glow discharge plasma, reforms and reconstitutes chemical elements and compounds from basic atoms or molecules to form nano particles. These include organic, inorganic, metallic and non-metallic materials such as silica, titanium carbon etc. This is also a very effective way to extract or remove heavy metals from a liquid by oxidising such as Hg to HgO; Cu, Zn, Cr etc. to form hydroxide precipitation and ionic metal solute to be deposited by the plasma electroplating process.

The under-liquid plasma creates a highly catalytic and reactive environment for chemical reactions which would not take place under normal circumstances. The reductive species i.e. H+ and oxidative radicals i.e. O-, O_3, H_2O_2, OH- and other radical species produced in the electrolysis and plasma dissociation derived from the liquid itself. The sonic excitation action which enhances the effectiveness of plasma discharge can only be conducted spontaneously under and within liquid.

The under-liquid plasma technique, coupled with the sonic-excitation and electro-chemical action, creates an environment of localised high temperature up to $10{,}000^{O}K$ and pressure up to thousands of atmospheres which favour the generation of cold-fusion phenomena.

It is a low-energy system. Generally high voltage from 0.35 KV up to 3 KV with low current density rarely required more than 3 Amp/cm^2 will be needed to deal with a vast number of different types of the under-liquid plasma process. If other enhancement method is applied, the high voltage and current requirement will be further reduced.

It is a method for producing hydrogen, oxygen with water or other gases and material deposition with liquid containing chemical solute, other than the conventional exchange of ions. The molecules and atoms are being ionised, excited and subjected to dissociation to form ionised, radicals and neutral species by the influence of plasma discharge. The dissociated species can be produced near either anode or cathode electrodes. The ionised species are then attracted to their respective polarity to be neutralised to produce gas or deposition of materials. The dissociation of atoms or molecules are the result of electron collisions and a wide variety of dissociated species is produced which creates the reactive elements for reduction, oxidation, and highly catalytic environments that facilitate chemical reaction of those relatively stable compounds and elements.

No chemicals are needed as an additive in a decontamination process, of which chemicals, i.e. chlorine and ozone, could become a secondary source of pollution.

EXPERIMENTAL OBSERVATIONS

When sufficient micro bubbles originating from the electrode surface block the current flow, the voltage rises steadily until a point of voltage inception is reached whereby some micro bubbles begin experiencing glow discharge. This precedes an avalanche effect which spreads through other micro bubbles close by.

A massive light is then emitted in a flash with a sound of bursting bubbles. The light is yellow to orange in colour indicating plasma discharge in hydrogen gas at the cathode electrode. Soon after switching on the reactor, temperature in the electrode rises which contributes to the formation of vapour bubbles which in turn creates a large bubble environment full of water vapour whereby the next succession of plasma discharge takes place within a fraction of a second.

The features which enable the trapping of gas, the concentration of current density within a small region, and the continued replenishment of gas, are steady and a self-regulating voltage and current power supply, electrode spacing, electrode configuration and electrolyte concentration, all of which have a bearing on generating desirable steady, and short cycle plasma glow discharges.

The invention has a number of applications including:

Plasma assisted electrolysis for hydrogen generation.
Non-thermal plasma reformation of hydrocarbon and hydrogen rich compounds for the production of hydrogen.
Treatment of polluted and contaminated liquid waste containing chemical and heavy metal pollutants.
Treatment of polluted gas emission and removal of odours.
Sterilisation of drinking water and liquid foods.
Extraction and refinement of mineral from its oxide or oxide ores.
Production of nano particles.

Enhancement of a material's chemical and physical properties by plasma discharge irradiation in under-liquid conditions. This also favours the need of any plasma reaction and treatment under-liquid.

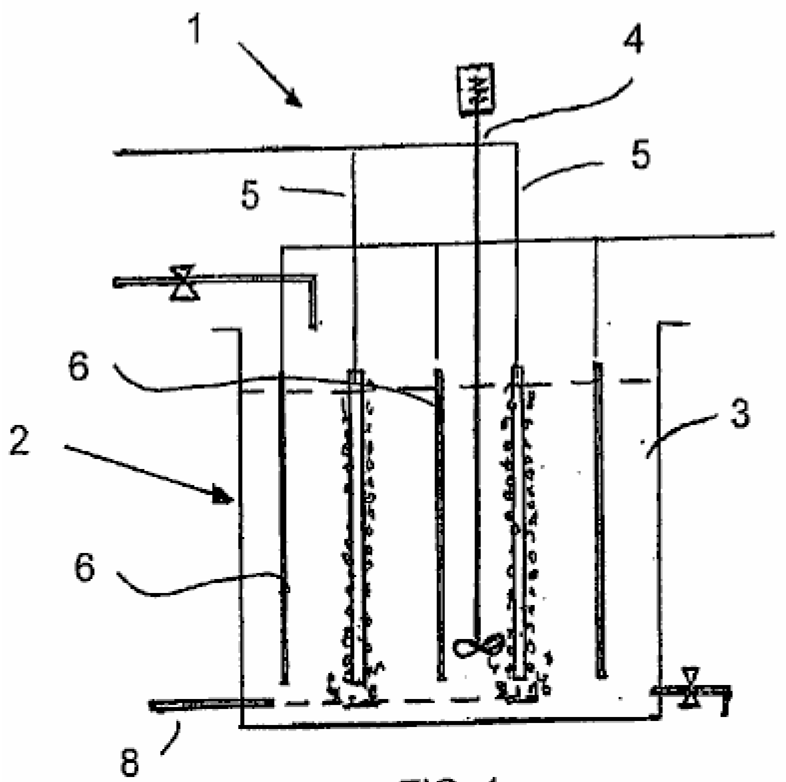


FIG. 1

Fig.1 illustrates a basic apparatus **1** for carrying out the method of the invention, namely, generating a plasma within bubbles formed adjacent to a cathode within an aqueous medium. The apparatus **1** comprises a liquid containment means in the form of an open rectangular tank **2** opening to the atmosphere and containing an aqueous liquid **3**. A stirrer **4** for agitating the aqueous liquids in the tank **2**.

Two spaced cathodes **5** are positioned in the tank **2** alternating with three anodes **6** projecting into the tank **2** and extending generally parallel to the cathodes **5**. A bubble pipe **8** is positioned at the bottom of the tank **2** for introducing bubbles into the aqueous medium in proximity to each of the cathodes **5**.

The application of a suitable potential difference across the anodes and cathodes leads to a glow discharge being formed and a plasma within the bubbles adjacent the cathode. This ionises the atoms and/or molecules within the bubbles and can be used to achieve a number of industrially and commercially useful objectives. For example, it can be used to generate hydrogen gas, one of its uses includes placement in a fuel cell to generate electricity. It can also be used to neutralise harmful compounds within the aqueous medium, e.g. originating in a liquid source or a contaminated gas and treating these harmful compounds. Finally, it can also be used to coat the surface of an article with a particular material.

Each of the cathodes is in the form of a perforated tube. At least one end of the tube is open and typically gas is introduced through such an open end. The side wall of the tube is perforated such that gas issues from the tube into the aqueous medium around the cathode. Alternatively, each of the anodes may be rod-like.

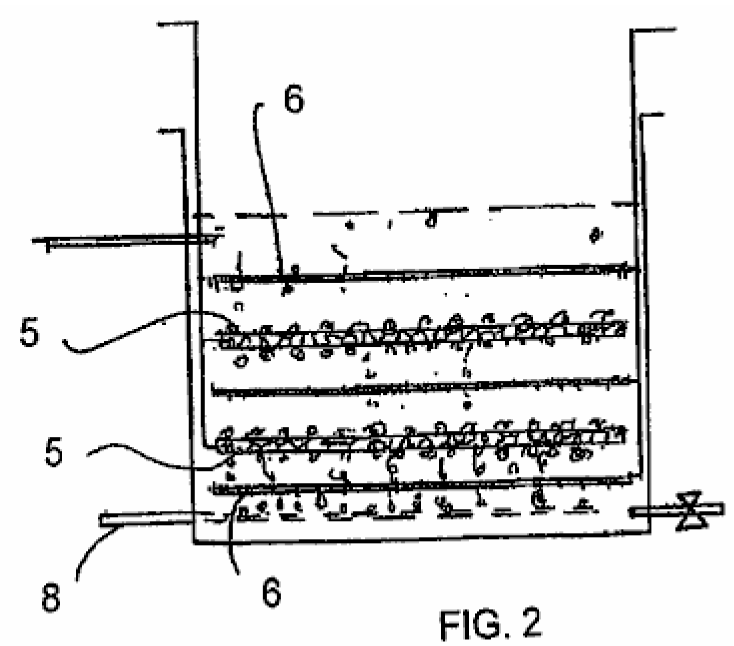


FIG. 2

Fig.2 illustrates a variation on the apparatus of **Fig.1**. This description will be confined to the difference between the **Fig,1** and **Fig.2** apparatuses. In **Fig.2** the electrodes extend horizontally with each cathode positioned between two vertically spaced anodes.

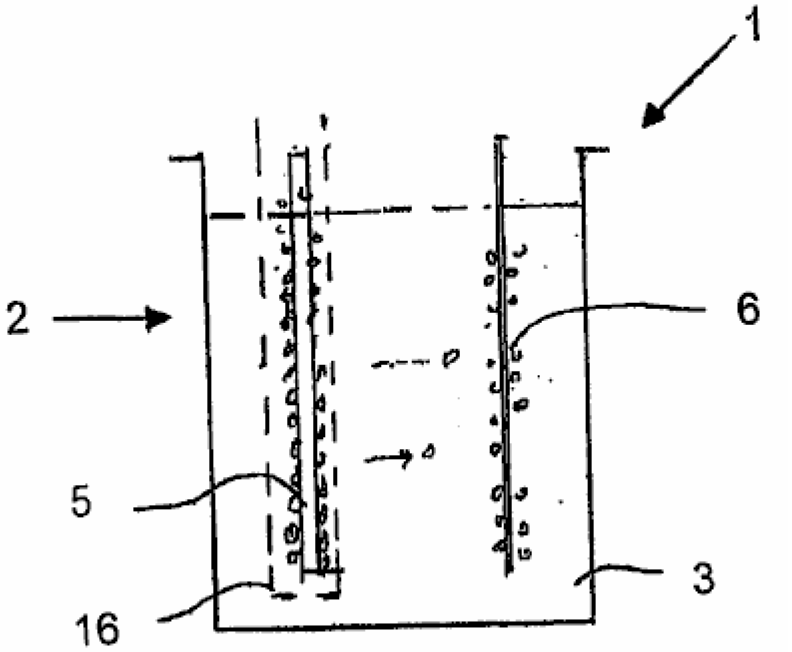


FIG. 3

Fig.3 illustrates an apparatus suitable for the generation of hydrogen. The tank contains an anode and a cathode spaced apart from each other. The electrodes are generally the same as those described above with reference to **Fig.1**. The cathode is surrounded by a semi-permeable membrane. Specifically the membrane is designed to resist the passage of hydrogen and oxygen bubbles through it. Hydrogen gas is formed from the combining the two neutralised hydrogen ions adjacent to the cathode and then is drawn off from the aqueous medium above the cathode and collected for use.

Similarly, oxygen gas is formed adjacent to the anode and this is also drawn off separately and collected for use. An advantage of this method for the formation of hydrogen fuel is that it consumes essentially less energy than other known methods, and as a result, will be a very attractive source of hydrogen for use in fuel cells.

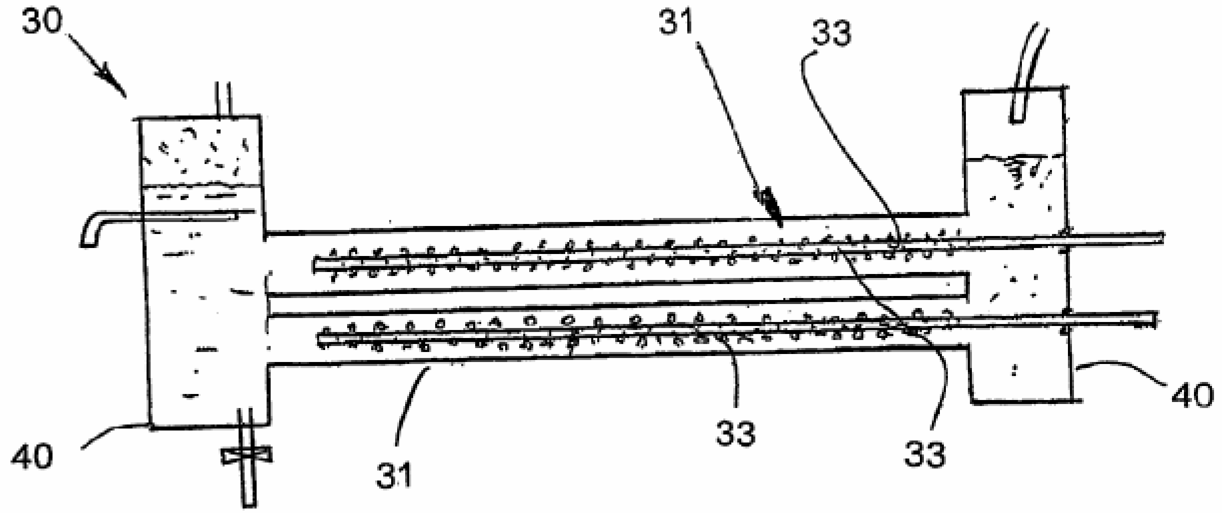


FIG. 4

Fig.4 illustrates a tubular reactor which is quite different to the tank **2** shown in the previous embodiment. The reactor **30** comprises a circular cylindrical body **31** with its longitudinal axis extending horizontally. A pair of electrodes **32**, **33** extend longitudinally through the body, spaced in from the wall of the body **31**. Each cathode **33** is formed by a perforated tube. By contrast, the anode is formed by the body **31**. Thus the single anode **31** extends concentrically around the cathodes **33**, positioned radially inwards from them. A gas, which ultimately forms the bubbles, is pumped into the cathodes, e.g. through their open ends, and then issues through the openings along the length of the cathodes **33**.

Settling tanks are located at each end of the body **31**. The settling tanks **40** permit gas to be separated from the liquid. The gas rises to the top of the tanks **40** from where it can be drawn off. The aqueous liquid can be drawn off through a drain point positioned below this level of aqueous medium in the tank **40**. An aqueous medium can also be introduced into the apparatus, by passing it through an inlet into one of the tanks **40**. Otherwise, the method of generating plasma in bubbles adjacent to the cathodes is very similar to that described above with reference to **Fig.1** to **Fig.3**.

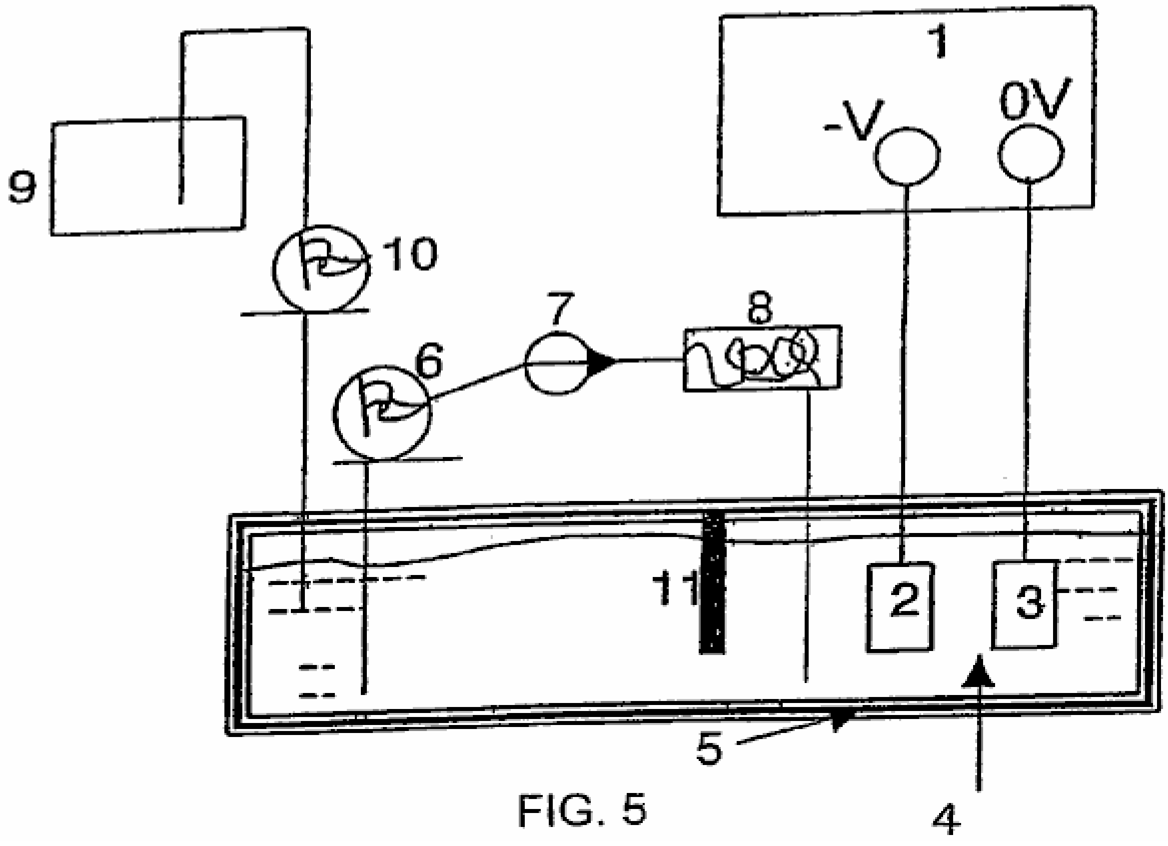


FIG. 5

In **Fig.5**, reference number **1** refers generally to apparatus in the form of a cell and associated components for carrying out a plasma electroplating process (PEP) in accordance with the invention. The cell **1** comprises broadly, a liquid container in the form of a bath which is filled with an electrolyte which also forms part of the apparatus or cell. A pair of spaced electrodes are positioned in the bath, one being a cathode and the other being an anode. An electrical circuit is formed by electrically connecting up the anode and cathode to a power supply, e.g. a mains power supply. When the bath is being used, a potential difference is applied across the electrodes. A partition divides the bath into an electrode compartment and a circulating compartment. Electrolyte is drawn off the circulating compartment and pumped through a heat exchanger to cool it and then return it to the bath. This helps to keep the temperature of the electrolyte within a suitable range during operation. In addition a make-up tank is positioned adjacent the circulating compartment to replenish the level of electrolyte within the bath as and when required.

The apparatus also includes the means for producing a bubble sheath around the cathode. The bubbles can be generated by gas evolved at the cathode as a result of a cathodic electrochemical reaction. This is one of the ways in which the bubbles were generated in the experiments conducted by the applicant. There are however, alternative ways of generating the bubbles for the bubble sheath. One alternative way, is by boiling the solution (ebullition bubbles). Other ways of producing the bubbles are by cavitation generated by ultrasonic waves or by hydrodynamic flow. Entrainment bubbles can also be produced by a mixture of gas and liquids.

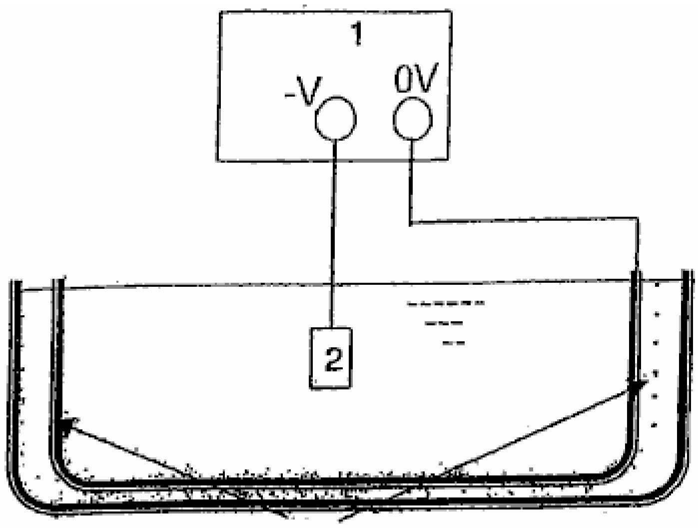


FIG. 6

Fig.6 illustrates an ultrasonic generator surrounding a bath similar to that in **Fig.5**. The generator generates ultrasonic waves which are transmitted into the electrolyte liquid and act to generate bubbles in the electrolyte which then surround the cathode. The cathode, which typically provides the surface for deposition, can be formed of a conductive material, a semi-conductive material or a non-conductive material, coated with a conductive coating. Cathodic materials that have been successfully used in this method are nickel, mild steel, stainless steel, tungsten and aluminium. The cathode can be in the form of either a plate, a mesh, a rod or wire. There may be any number of cathodes and the cathodes can be any shape or size. Any conductive material can be used for the anodes. Graphite, aluminium and stainless steel have all been successfully used to practise this method by the applicant. Generally, aluminium is preferred for the anodes. There may be any number of anodes and the anodes can be any shape.

In use, the bath is filled with an appropriate electrolyte. Broadly speaking, the electrolyte contains a solvent or carrier which provides a liquid environment, within which, electrolysis can occur and which also provides a support for plasma generation in the sense that it provides containment for the plasma generation. The electrolyte also contains a source of the material to be deposited in the form of a precursor. The electrolyte may also include additives for example for enhancing the electrical conductivity of the electrolyte and for assisting in bubble formation and a buffer to maintain a suitable pH in the cell.

In use, the article to be coated is placed in the bath where it typically forms the cathode. In some instances however, it may also form the anode. A voltage or potential difference is then applied across the electrodes and this voltage is set at a level that is higher than the firing point at which the system or cell achieves a stable glow discharge in which glow clusters envelope the cathode surface.

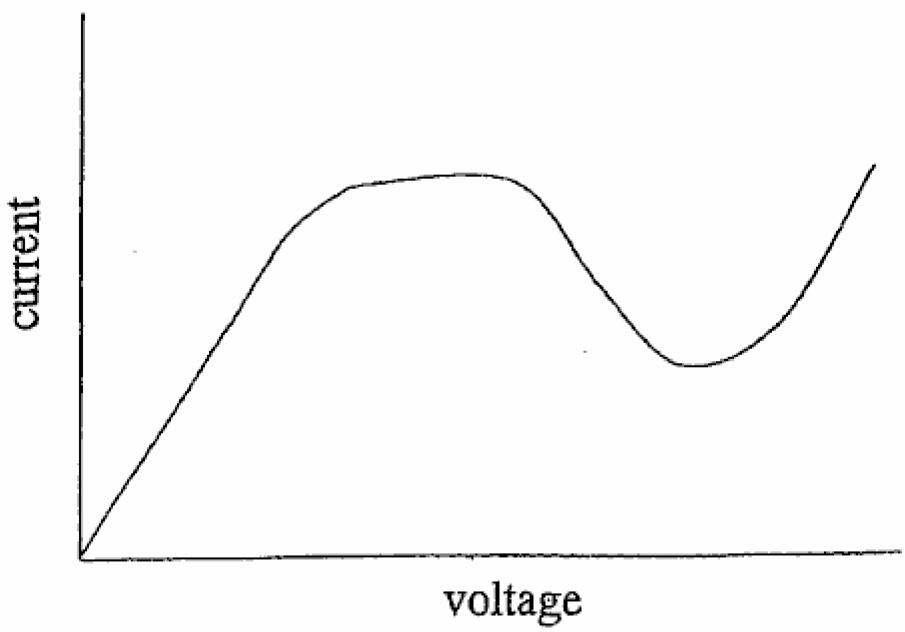


FIG. 7

Fig.7 illustrates a typical current against voltage profile for such a cell as the voltage is progressively increased. Initially there is an ohmic zone where the current increases proportionally with the voltage. After that the curve enters an oscillation zone where the current starts to oscillate. Applicant believes that this condition may be due to the fact that bubbles are evolving out of the solution and partly obscuring the electrodes. The bubbles form plasma, grow and then burst forming a shield shrouding the electrode. These bubbles block the conducting part of the cathode and this might lead to a decrease in apparent current density.

At the cathode, the evolved bubbles include hydrogen generated by the electrolysis of water in the electrolyte and by evaporation of liquid within the electrolyte. The bubbles may also be generated by other means as described above, for example ultrasonic generation. After some time, the number and density of bubbles increases until the entire cathode surface is sheathed in bubbles. At a critical voltage that is constant for a given system, known as the fire point, a glow discharge is formed. Experimental observation shows that this occurs when there is a near continuous bubble sheath around the cathode.

With a wire cathode, a tiny fireball or cluster of fireballs usually appears at the tip of the wire at the fire point. With further increases in voltage a glow discharge is established across the entire cathode. The glow discharge is dynamic and usually shows evidence of glow clusters and/or flashing through the bubble region. The glow discharge is caused by a dielectric breakdown in the bubbles. This is caused mainly by a high electrical field strength. Due to the presence of the bubbles the majority of the voltage drop from the anode to the cathode occurs in the near cathode region occupied by the bubbles. The electric field strength in this region may be of the order of 10,000 to 100,000 V/m. The voltage is set at a setting of 50 to 100 volts higher than the ignition point. This may typically mean a setting of 250 to 1500 volts. A preferred voltage setting would be at the low point of the graph in **Fig.4** within the glow discharge region.

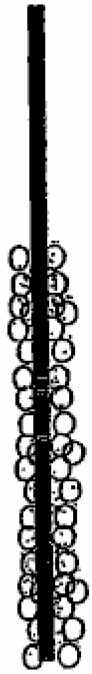


FIG. 8

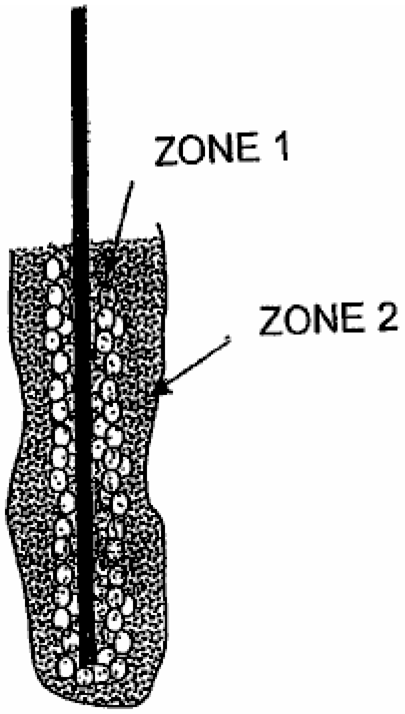


FIG. 9

The glow discharge causes the generation of a plasma in the bubble. **Fig.8** shows the formation of a bubble sheath around the cathode. **Fig.9** shows the cathode during stable glow discharge. As shown in the drawings, applicant has observed the formation of two distinct zones during stable glow discharge. In zone 1 where the glow discharge clusters are present, there is a plasma envelope that directly shrouds the cathode surface. This envelope is where plasma deposition takes place. The plasma interacts with the cathode surface in a process similar to ion plating and deposition occurs. A film is progressively formed through nucleation and growth on the cathode surface. Zone 2 is a plasma-chemical reaction zone, which forms the interface between the electrolyte and zone 1. This zone envelopes the plasma deposition zone and is often clearly visible as a separate region with a milky appearance.

Dissociation, and possibly also ionisation of the electrolyte components, including the precursor, occur in the outer zone, zone 2. This gives rise to the species that are deposited on the cathode. The species is transferred from the outer zone 2 to the inner zone 1 by the electric field strength, diffusion, and convection. Deposition on the cathode then occurs for as long as these conditions are maintained and the precursor material is available in the electrolyte. After the glow discharge commences the temperature of the electrodes increases in a short space of time. The temperature of the electrolyte must be maintained within acceptable limits for certain type of application. To do this, electrolyte is drawn off from the bath and pumped through a cooling system as shown in **Fig.5**. The cooled electrolyte is then re-introduced into the bath. This cooling is required for both stability and safety reasons. Some of the electrolyte components are flammable. In addition electrolyte is consumed during the deposition reaction. Accordingly, it is necessary to top up the bath with additional electrolyte from time to time. A replenishment tank containing electrolytes is provided to perform this purpose.

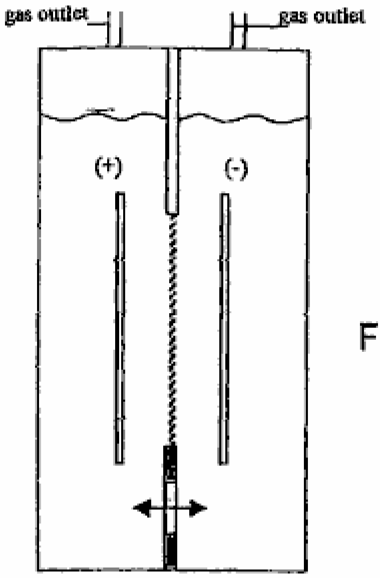


FIG. 10

BASIC TWO ELECTRODE REACTOR
WITH GAS SEPARATOR DIAPHRAGM

As shown in **Fig.10**, the reactor may include a pair of metal electrodes spaced apart and separated by an ion-conducting diaphragm. The electrodes can also be positioned horizontally or vertically.

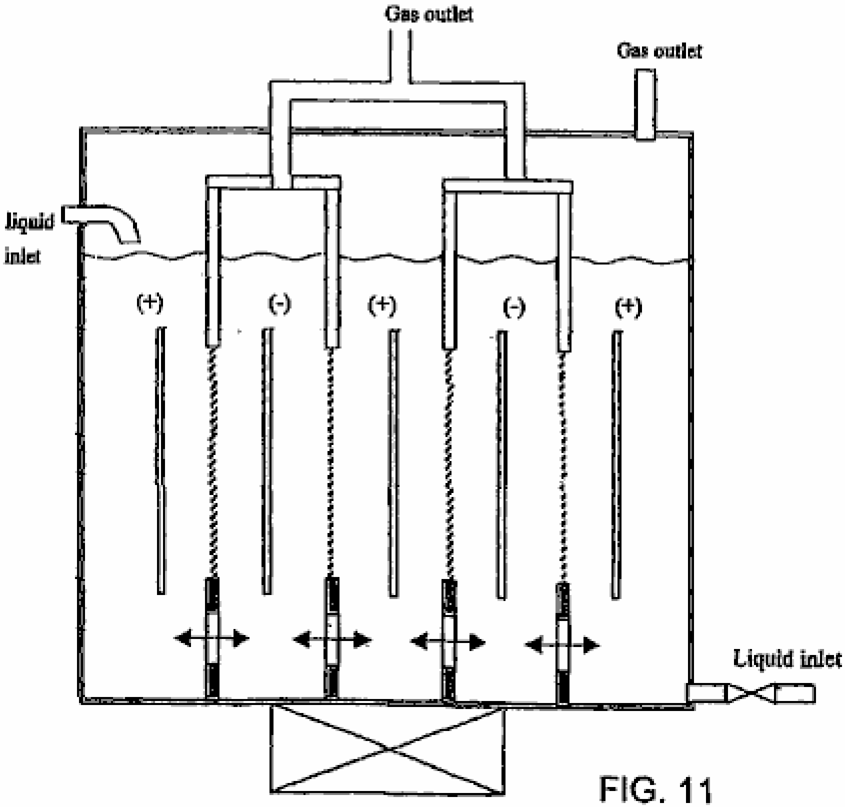


FIG. 11

Multiple Cell Reactors with common bath

As shown in **Fig.11**, the reactor may also include multiple pairs of alternating anodes and cathodes with a diaphragm. The diaphragm can be removed for decontamination and partial oxidation reformation process (**Fig.12**). In the case of reduction process, the hydrogen atoms produced on the side of cathode electrode are kept well separated from mixing back with oxygen by a diaphragm (**Fig.13**). It is possible to increase the throughput capacity of the reactor in treating contaminants with transverse flow through multitudes of alternating electrodes of anode and cathode (**Fig.14**). Wires or rods in tube reactors are suitable to adopt for hydrogen production and reduction process with the metal oxide confined within the narrow space within the cathode half cell and subjecting it to ultrasonic irradiation (**Fig.15** and **Fig.16**).

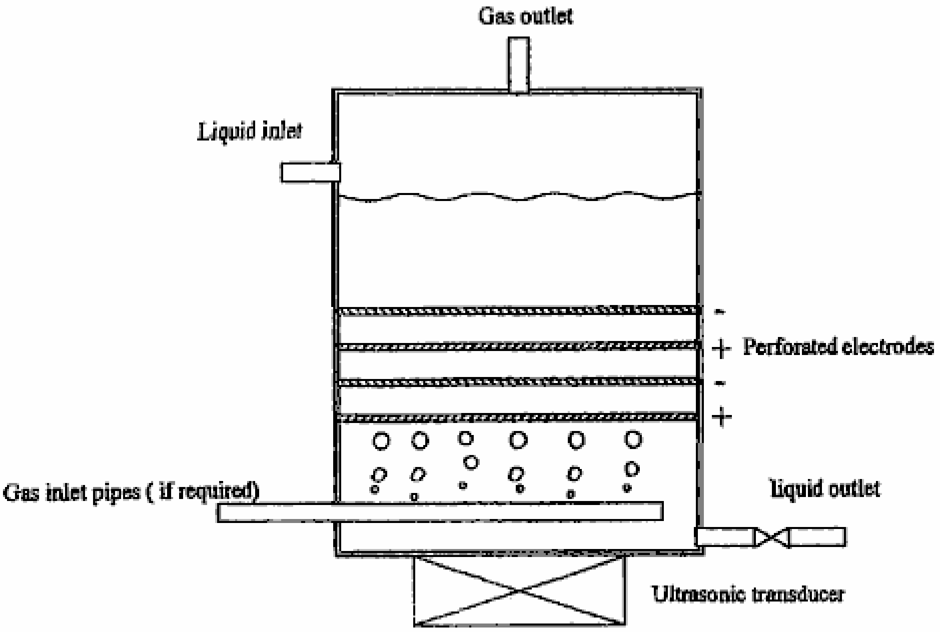


FIG. 12

Tower Reactor with Perforated Electrodes

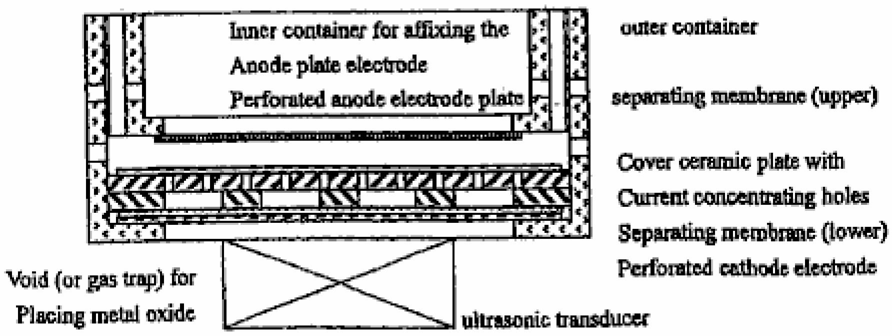
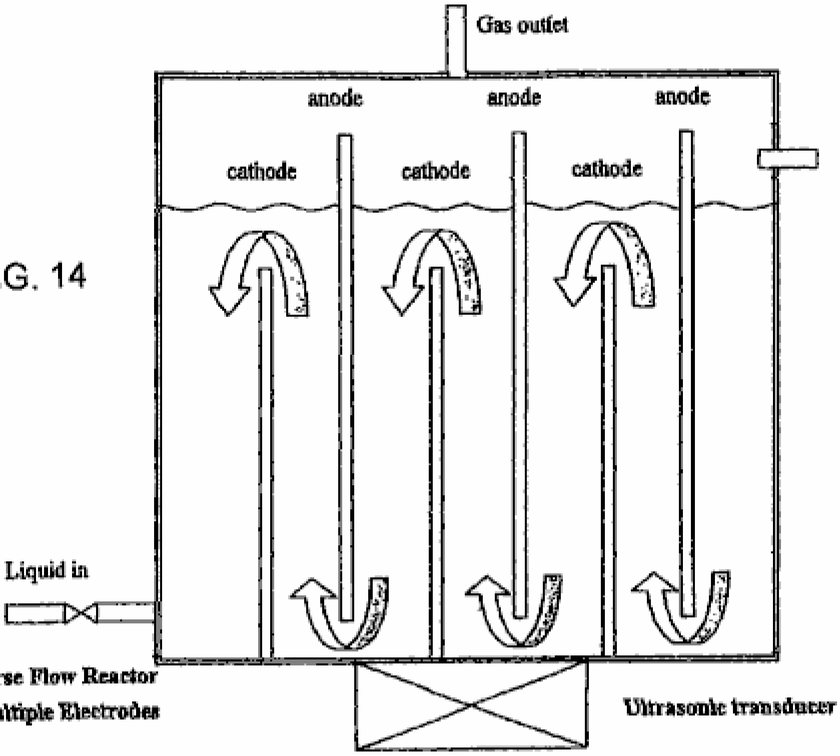


FIG. 13

Reactor for Metal Oxide Reducing Process
(which is to be placed inside an electrolytic bath)

FIG. 14



Transverse Flow Reactor
With Multiple Electrodes

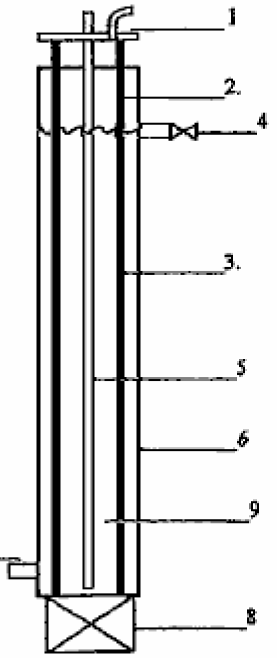


FIG. 15

WIRES OR RODE IN TUBE REACTOR
THE OUTER ELECTRODE SERVING AS BATH

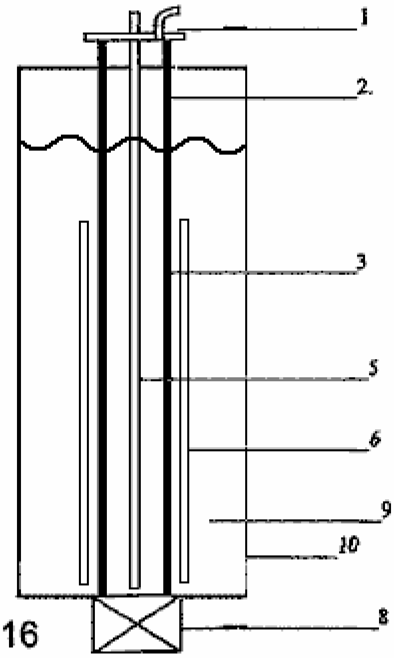


FIG. 16

WIRES OR RODE IN TUBE REACTOR

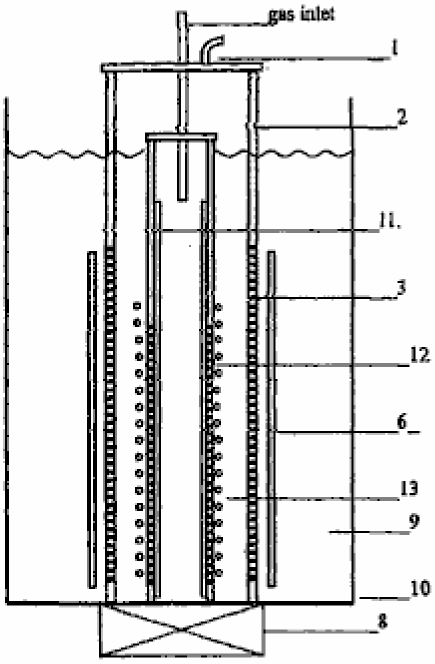


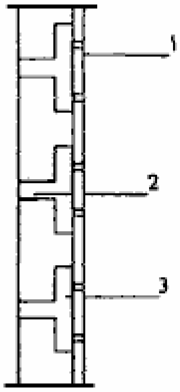
FIG. 17

TUBE IN TUBE REACTOR WITH PERFORATED INNER TUBE COVERED WITH GAS-TRAPPING COVER LAYER

Tube in tube reactor (**Fig.17**) has a tube electrode within the outer tube electrode instead of wire or rod. The inner tube is covered with non-conductive materials of suitable thickness with small diameter holes and gas trap forming in between the inner metal tube which also have small holes formed correspondingly. The gap between the outer electrode and inner electrode is kept close but giving a minimum 3 mm to 5 mm space between the separation diaphragm and the dielectric cover of the inner electrode, to allow free flow of electrolyte and gas. Bubbles of gas will be discharged into the plasma discharging zone with hydrocarbon rich gas i.e. methane, natural gas, H_2S to undergo reformation for the production of hydrogen gas. It can also be adopted for decontamination of polluted gas laden with NOx, SOx and particulates; and reduction process where the metal oxide will flow through the space between the electrodes with the ultrasonic irradiation keeping the fine powder in colloidal and at the same time hydrogen gas or methane gas may also bubble in to provide the extra H_2, H+ and CO to enhance the reduction process.

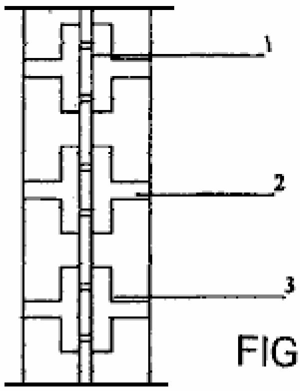
Configuration of Electrode with Gas Trapping and Current Concentrating Cover Arrangements

FIG. 18A



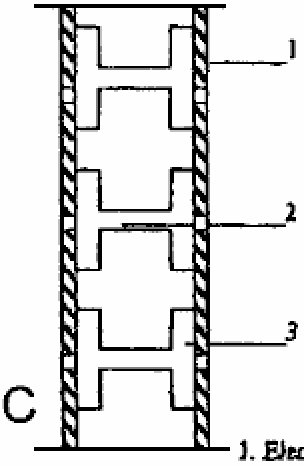
Type 1

FIG. 18B



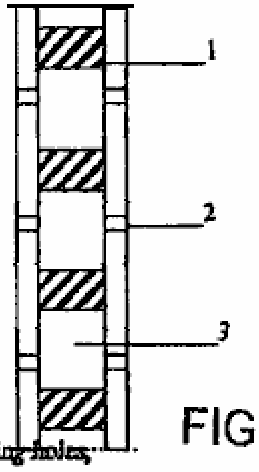
Type 2

FIG. 18C



Type 3

FIG. 18D

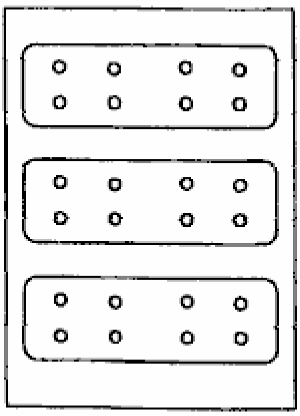


Type 4

1. Electrode, 2. Current concentrating holes, 3. Gas traps

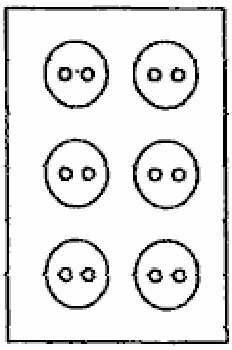
Cross Section of Electrodes showing the Gas Trap and Current Concentrating holes

FIG. 18E



Type 5

FIG. 18F



Type 6

Plan or Elevation of Gas Trap Cover Plate (with perforated current concentrating holes)

A number of gas trap and bubble retaining arrangements are shown in **Fig.18A** to **Fig.18F**.

The under-liquid plasma discharge, in order to produce various reductive, oxidative, radicals and neutrals species through excitation, ionisation and dissociation of the liquid molecules and atoms, requires high voltage input DC or AC, normally within 3 KV and current density under 3 Amp/cm^2. The electrodes cathode and anode have to be kept as close as possible but not close enough to cause arcing. The electrode surface is preferably flat, even and smooth with no pronounced irregularities. Because of the need of placing diaphragm and complementary gas trapping and retaining construction on the discharging electrode, a minimum distance of 6 mm to 15 mm has been experimented with and shown to produce steady glow plasma under-liquid. With better material choice and engineering capability, there is no reason why the electrode space distant cannot be further reduced. The size, shape and arrangement of the electrodes is not restricted, but the electrodes will usually be somewhat smaller than those required for conventional electrolysis, for the same gas production volume. Both the electrodes, anode and cathode, can be at work at the same time as the plasma discharging electrodes especially if a gas-trapping dielectric cover construction is provided.

Experiments have been conducted to establish the basic criteria to generate steady and rapid cyclical non-thermal plasma glow discharge under-liquid with basic DC high voltage and low current input at atmospheric pressure and ambient temperature leading to the proposal of a phenomenal model of reactor structure and electrode configuration which demonstrate the usefulness of bubbles or gas pocket that creates the under-liquid environment for plasma discharge and it also provides the back ground of further improvement and construction of reactor unite which verify the inventive idea of under-liquid plasma and it subsequent practical applications.

A reactor according to the present invention can basically follow that of a simple water electrolysis cell with one anode electrode separated from the cathode electrode with an ion conducting membrane and yet has the capability to prevent re-mixing of the produced gas on each half-cell. The electrolyte allows moving across the membrane or replenish through the opening in the reactor. In order to increase the proficiency of the reactor the cathode electrode is placed inbetween two anode electrodes and separated from them by a membrane. The hydrogen gas produced is isolated and collected independently. The polarity of the electrode can be reversed with the anode electrode in the middle when oxidative species are needed for the decontamination process. Most importantly, the simple electrode and reactor unit will form the basic module, placed inside a common bath and linked together to form a lage production unit, and these modules can be replaced individually.

Despite the apparent success of the simple perforated plate-to-plate electrode arrangement, it does not preclude other electrode configurations and arrangements such as tube in tube, wire in tube and other flat surface electrodes having different surface structure e.g. wire mesh, expanded metals, pinned plate, sponge porous metal, corrugated plate etc. as long as it is a good electric conductor, corrosion resistant, heat-tolerant material, i.e. stainless steel, aluminium, graphite, platinum etc. The shape and size of the electrode piece is not restricted and sometime it may form the object article which is to undergo plasma surface enhancement treatment.

In practice, a reactor with vertical electrodes, suits plasma-assisted water electrolysis, reformation of hydrocarbon liquid fuel, production of nano materials and decontamination process, while the reactor with horizontal electrodes suits reformation of hydrocarbon gas such as natural gas, methane, hydrogen sulphurs and the like.

This ability to generate steady plasma discharge, can well be adopted for other useful purposes such as thin and thick-film deposition and additional method in the creating of cold fusion.

There have been a series of experiments conducted to generate non-thermal plasma under-liquid by utilising the gas bubbles self generated during electrolysis, electrochemical reaction, heating and releasing of dissolved air or gases in the liquid. Bubbles can also be produce with the influence such as transient bubbles created by shock waves resulted from pulsed power input, ultrasonic cavitations, laser heating and hydraulic impingement. External introduced gas (e.g. air & fuel gas) is found to work well in providing bubbles environment for ready plasma discharge in a steady manner. A number of experiments have also been conducted to test the applicability of under-liquid plasma in the field of hydrogen generation, hydrocarbon fuel reformation, sterilisation and decontamination and reduction of metal oxide. Because of the restriction of the power converter that some result is less than ideal but it all indicate the potential of the under-liquid plasma which is in the first place having the same physical/chemical capability as its counter part operating in gases environment in exciting, ionisation and dissociation, but with some distinctive advantage which has well been described in the foregoing text.

Generation of steady plasma discharge under-liquid has been one of the primary objectives in the research. In general the generation of steady plasma glow discharge are influenced by a number of factors, such as physical and chemical properties of the liquid, its conductivity, temperature, electrode type, electrode spacing, gas retaining or trapping arrangement, current density, voltage input, reactor construction, liquid circulation, influence of ultrasonic irradiation, pulsed power input etc.

There are of course a number of electrode shapes, size and configuration one could choose. In order to find out the how important is the supply of bubbles or gas pocket affects the generation of plasma, a gas retaining or trapping covering with current concentrating conducting holes over perforated plate electrode is formulated, which has proved effective producing steady glow plasma discharge within the range of 350 V to 2 KV (2,000 V) and current up to 850 mA, but most the time around 100 to 300 mA range. This is considered low in compare with other under-liquid plasma system (i.e. Plasma arc, pulsed high voltage and current electric discharge). Throughout the experiments, a horizontal reactor was used. However an alternative reactor is a vertical reactor.

INTRODUCTION TO THE EXPERIMENTS

Several groups of experiments have been conducted:

1. Preliminary trial experiments
2. Plasma assisted water electrolysis
3. Reformation of methanol
4. Reformation of emulsified diesel
5. Reformation of LPG as hydrocarbon gas (methane is not available in the market)
6. Decontamination or sterilisation of food drink
7. Reduction experiment of TiO_2.

In the preliminary trial experiments a number of electrode types have been adopted and have eventually select the wire to plate configuration and perforated plate to perforated plate or wire mesh as the most suitable under the limiting power supply condition where max. voltage available is 2,000 V and the maximum current is 1,200 mA. In reality, the current input is voluntarily restricted to work below 900 mA for durations not exceeding 30 minutes, to avoid damage to the converter which has happen in a number of occasion which caused stoppage of the experiments for weeks.

To overcome the power supply limitation, and to achieve steady plasma glow discharge, a gas-retaining or trapping cover or layer with current concentration holes has been devised to cover the discharging electrode surface (perforated electrode plate) which is the basic features adopted in the construction of reactor.

In the trial experiments, it has been demonstrated that infrequent visual plasma discharge begins with a voltage of 350 V and steady plasma can be achieved in around 550 V. The initial current input reaches 850 mA and begins to fluctuating in the range of 150 to 650 mA. On many occasions the current fluctuated at 100 mA to 350 mA.

Through these experiments, the mechanism of generating bubbles or gas pocket dielectric barrier which impedes the current flow, leading to an increase of voltage until a threshold voltage is reached which causes the electric breakdown and the formation of plasma inside the bubble, at which point the current immediately returns to its normal level and then another cycle of discharge is established. When the discharge is infrequent it resembles a corona streamer discharge but as the voltage increases, the glow discharge becomes a continuous glow over an extend electrode surface resembling a glow plasma discharge. The colour of the discharge appears as an orange-yellow or red colour in the electrolysis of water and the temperature of the discharging electrode ranges from $50^{O}C$ to about $90^{O}C$ and the temperature of the bath liquid ranges from $40^{O}C$ to $70^{O}C$. No sign of any damage to the electrode or its covering plastic gas trapping plate was observed even after prolong experimentation. When the voltage is allowed to increase beyond the glow plasma region, a plasma arc begin to occurs and becomes an intensive bright blue discharge when voltage is further increased and this causes damage to the metal electrode and plastic covering plate which is easily seen.

On two occasions, hydrogen production was recorded which produced a gas volume with an equivalent energy conversion efficiency up to 56%. Due to damage to the reactor by the plasma arc, that particular experiment cannot be repeated as new model of reactor is designed to achieve low current input and early high voltage response. However with the apparent success of the trial experiment, it shows that a more suitable reactor can be designed specifically for the purpose of hydrogen production by plasma assisted water electrolysis and a higher energy efficiency figure can be achieved with a small reactor.

PLASMA ASSISTED WATER ELECTROLYSIS

Experiments to check the behaviour of plasma discharge at different voltage input levels were carried out. Despite the apparently large volume of bubbles boiling inside the reactor, the total volume of gas produced was unexpectedly low. This may have been caused by the horizontal reactor design adopted throughout the experiments. This may have allowed the hydrogen gas recombine with the hydroxyl ions and convert back into water again. A vertical reactor would be more suited for the plasma assisted water electrolysis where the produced hydrogen gas will rise quickly to the top of the reactor and can be channeled away from the area filled with OH ions.

In this experiments plasma discharge begin to occur at 1,350 V with current fluctuating around 100 mA to 200 mA. At about 1,550 V the reactor produced highest volume of gas. Plasma arc discharge occurs at 1,900 V and is becoming vigorous when the voltage is increased further. KOH of 0.02% concentration has been used as electrolyte additive throughout the experiment.

The production of gas appears to have a linear relation with time but various substantially with different voltage input. The rate of energy consumption is increasing slowly with time in a constant rate which various with the voltage input and its corresponding energy consumption per unit gas volume produced is having a peak at the first 10 minutes of the experiments and level off with time. The temperature in the electrode rise sharply to from 50^{O}C to 90^{O}C and is maintained more or less at that level throughout the test. The temperature in the bath liquid within the reactor rises slowly from its ambient temperature to around 50^{O}C to 55^{O}C.

EXPERIMENTS WITH METHANOL

Several sets of tests have been conducted with the aim of finding out how different hydrocarbon fuels will be affected by the non-thermal plasma under-liquid system. A methanol / water mixture with methanol concentrations of 5%, 10%, 15%, 20%, 25%, 30% and 40% were tested using the same method and equipment set-up already used for the plasma-assisted water electrolysis. There are three independent tests for each methanol concentration. It has been observed that the gas production is peaked at 25% methanol concentration and the energy consumption per unit gas volume produced is also lower than the others and is nearly at constant rate around 0.0225 Kw.h/L. The voltage input for each test is kept at 1,850 V and the current fluctuating in the range of 100 mA to 200 mA. The temperature measured at the cathode electrode started at 80^{O}C and rose quickly to reach over 200^{O}C at the end of a 30 minute experiment. The temperature recorded in other tests stayed within the range of 60^{O}C to 80^{O}C. The temperature of bath liquid at 25% concentration stayed in the range of 50^{O}C to 60^{O}C, which is typical for each of these tests.

The greatest surprise coming out of the experiments is that the produced gas is composed of two gases. One is hydrogen gas and the other is oxygen gas and no trace of carbon dioxide is found. Repeated examination of the gases produced shows the same result and the hydrogen is having an average value of 51.3% and oxygen 48.7%. This is later found out that the presence of oxygen in the gas is the result of the removal of the separating diaphragm. An acidic electrolyte is preferable in order to increase the hydrogen gas percentage in the output gas mix. This is shown in the latest experiments using sulphuric acid of 0.02% concentration.

A set of experiments with the use of 40 KHz ultrasonic bath having methanol concentration of 10%, 15%, 20% and 25% with the same reactor and equipment arrangement have been conducted to find out the influence of ultrasonic radiation. It has been observed that gas production at 25% is substantially higher than the others and yet the energy consumption per unit gas volume produced is around 0.015 Kw.h/L throughout the 30 minute experiment, which is lower than that without ultrasonic radiation.

The chromatographic analysis of the output gas having an average value of 97.56% hydrogen and 2.4039% of carbon monoxide. Chromatographic analysis of gas produced by reformation of methanol with ultrasonic radiation. Methanol concentration at 25%, and conductive reagent 0.02% sulphuric acid.

TABLE 1

Test	Resident time minutes	Composition V/V %	Gas type
First Test	0.364	98.9937	H_2
	1.047	1.0063	CO
Second Test	0.364	96.7418	H_2
	1.047	3.2582	CO
Third Test	0.354	96.9719	H_2
	1.048	3.0281	CO
Average		97.5691	H_2
		2.4309	CO

EXPERIMENTS WITH LPG

Decomposition of LPG by under-liquid plasma has been conducted (methane or natural gas is preferred but none is available in the market). The LPG is allowed to pass through the horizontal reactor through the perforated anode plate and enter the reactor and trapped at the cathode plate where plasma is taking place at voltage 1980V and current at 100 to 130 mA input. C_3H_8 and C_4H_{10} are the two main components of LPG, it is expected that the volume output having been subjected to plasma dissociation should be larger than the original input volume. This is found to be so that the output gas volume increases by about 50%. The experiment is conducted together with ultrasonic radiation. It is regrettable that the chromatogram is incapable of undertaking analysis of the output gas composition. The next set of experiments should be conducted with methane or natural gas so that more definitive result could be obtained. Rudimentary analysis of the produced gas has shown the presence of H_2, CO_2 and C_3H_6 etc.

REFORMATION OF EMULSIFIED DIESEL AND WATER WITH ULTRASONIC IRRADIATION

Decomposition of emulsified diesel with distilled water has also been carried out. Diesel oil in 25% and 50% by volume has been emulsified by adding 1.25% emulsified agent inside the ultrasonic bath. Since the diesel oil is dielectric, a KOH additive is needed. The emulsified liquid is subjected to plasma discharge at a voltage of 1,850 V and a current fluctuating from 100 mA to 200 mA for a period of 30 minutes. The temperature of the cathode electrode increased from $70^{O}C$ to about $94^{O}C$ during the experiment. The gas volume produced was 160 ml with 25% diesel and 1,740 ml with 50% diesel, which is substantially higher and its energy consumption is 0.1213 KWh/L. It is clearly indicated, that gas production is proportional to the diesel contend in the emulsion. Because of the limited power supply capability, the voltage of 1,850 V is merely adequate to produce some plasma discharge but it is far from establishing extensive vigorous plasma with higher current and voltage input, which would produce more gas.

STERILISATION (DECONTAMINATION) OF MULBERRY FRUIT DRINK

The ability of non-thermal plasma to decontaminate noxious chemicals and gases has already established. This experiment is conducted to find out how well the under-liquid plasma may apply in the field of beverage sterilisation with low levels of plasma radiation and keeping the treated liquid within an acceptable temperature.

Two litters of 15% concentrated fruit drink is placed in the bath where a horizontal reactor is submerged. The bacteria count and mold colony count is obtained before the forty minute test. A sample of the fruit drink is extracted at 20 minutes and 40 minutes. The mulberry drink has good natural conductivity so no additive is required. The applied voltage is kept at 1,200 V and the current fluctuates around 200 mA. The temperature at the electrode is maintained at around $62^{O}C$ and the bath liquid (fruit drink) is kept at around $50^{O}C$.

TABLE 2 - The micro-organism count

Time (minutes)	Bacteria count/ml	Mold colony count/ml
0	3,400	37,000
20	1,300	17,000
40	90	10

The favour and colour of the fruit drink had not changed after the test. The bacteria sterilisation is 97.5% and that of mold colony has been sterilised more than 99%. This has given proof that the under-liquid plasma has the same capability as those operated in a gaseous environment.

The time for the treatment could be reduced by providing forced circulation of the liquid and increasing the electrode size. Sterilisation of drinking water imposes no limit on the temperature. Higher voltage input for better plasma glow discharge spreading over larger and multiple electrodes should be able to remove all harmful chemical substance, bacteria, biological matter and microbial matter, thus meeting the municipal requirement for drinking water.

REDUCTION OF METAL OXIDE

One trial experiment to reduce TiO_2 back to Titanium metal has been attempted with little success. It was found that in the X-ray diffraction test, minor traces of titanium nitride and titanium monoxide (TiO) were found. In the experiment, only a minor electrolyte of 0.05% KOH with 25% methanol added to the distilled water was used to increase the production of hydrogen. The applied voltage was fixed at 1,850 V and the current fluctuated in the range of 200 mA to 500 mA. Ultrasonic radiation up to 40 KHz was also provided through an ultrasonic bath. The temperature recorded in the bath liquid rose from $46^{O}C$ to $75^{O}C$ at the end of the 60 minute test. The fine TiO_2 with was suspended with ultrasonic radiation, in the bath liquid in colloidal form, showing as a milky white colour, which gradually became a milky yellow colour towards the end of the experiment. The bath liquid also became viscous.

The X-ray refractive “d” value of TiO_2 were:

Before the experiment: 3.512, 1.892, 2.376 but after the experiment there were two new groups of “d” measurements not seen before the experiment:
a: 2.089, 1.480, 2.400
b: 2.400, 2.329, 2.213
This indicates a new material, positioned between TiO and n-Ti_3N_2-x.

This experiment indicates that a change did happen to the TiO_2, possibly because of the limited voltage and current available as input, which could not provide the intensity of plasma discharge needed to effect the reduction process properly. Higher concentration of either HCl or H_2SO_4 should be use as reagent demonstrated in the following chemical reaction and in the same time serving as electrolyte. The horizontal reactor is not a suitable piece of equipment to undertake such experiment; it is adopted merely for convenience. A wire-in-tube and tube-in-tube reactor would be a suitable candidate, which would keep the metal oxide exposed to plasma discharge throughout the whole of the duration of the experiment. Further, more hydrogen or CO gases produced during the process may be passed back to the reactor to enhance the reaction. (Methane is a suitable gas for this type of reduction process, as both hydrogen and CO gas will be produced to enhance the reaction). The following are the chemical formula, which suggested by transforming TiO_2 to either $TiCl_4$ or $TiOSO_4$ as a soluble ionic compound, will facilitate its reduction with prolong exposure to active atomic hydrogen under the influence of a plasma catalytic environment.

$TiO_2 + 4HCl \rightarrow TiCl_4 + 2H_2O$,
$TiCl_4 + 4H \rightarrow Ti + 4HCl$.
$TiO_2 + H_2SO_4 \rightarrow TiO(SO_4) + H_2O$,
$TiO(SO_4) + 4H \rightarrow Ti + H_2SO_4 + H_2O$
Where $TiCl_4$ is readily produced by an established process from ilmenite.

Similarly, aluminium oxide Al_2O_3 can first be transformed to $AlCl_3$, which is soluble ionic compound, ready to be extracted by electro-deposition enhanced with plasma-reduction and plasma-electroplating process:

$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$,

$2AlCl_3 + 6H \rightarrow 2Al + 6HCl$.

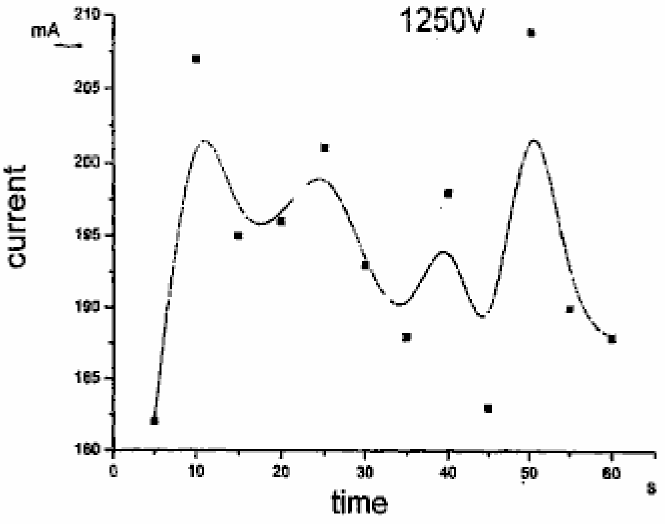
In the case of electrode positive oxide such as Fe_2O_3, it can be reduced in the presence of ionised atomic hydrogen and the presence of carbon monoxide with catalytic reactive plasma irradiation.

Fine metal oxide powder irradiated with ultrasonic waves will maintain in colloidal form allowing it to be exposed to the reduction agent atomic hydrogen and/or carbon monoxide. The process of ultrasonic cavitations and collapse is also known to create extreme localised high temperature up to $10,000^{O}K$ and thousands of atmospheres of pressure together with the high temperature at the impact point of the fine powder particles which is beneficial to the entire reduction process.

DETAILS OF THE EXPERIMENTS CARRIED OUT

Establishing Generation of Under-Liquid Plasma:

Distilled water is used in the experiments with 0.05% KOH as a conducting reagent. The voltage is controlled at 1,250 V & 1,850 V. The current is raised in steps of 100 mA until it reaches 850 mA. In the beginning the voltage remains low and gradually builds up as more gas bubbles are generated. Once it reaches a certain high level the current drops immediately. The self-regulating current and voltage input of the power unit automatically switches from current input control to voltage input control. At 45 seconds after switching the experiment on, the voltage rose to 470 V and the current dropped below 500 mA. From 3 min. 10 sec to 5 min 20 sec, the voltage rose to a relatively high level while the current kept on fluctuating. After a period of unstable voltage and current movement they become stabilised at 20 min with the characteristic high voltage and low current. At this instant prominent glow is observed at the perforated cover plate (current concentrating holes). The temperature of the cathode electrode has risen and stays steady at around $70^{O}C$.



Glow discharge at stable 1250V input

FIG. 25

Fig.25 shows the current fluctuating with stable 1,250 V voltage input and a steady plasma glow discharge. The temperature of the cathode increases rapidly in the early stages and then becomes steady at the 5 min mark, and then rising slowly to it's highest temperature of about $96^{O}C$.

OBSERVATION

Generating Under-Liquid Plasma:

In accordance with the experimental results, it is possible to generate non-thermal plasma under-liquid providing that certain conditions are met: a suitable power supply, electrolytic liquid, reactor and other supplementary equipment.

The design of the reactor, with relatively low voltage and limited power rating (restricted current input) requires special construction to trap or retain gas and at the same time to raise the current density at the discharge area. The gas trap or chamber should be of a suitable size. If the gas trap or chamber is too big, then the trapped gas is too thick which requires a much higher voltage for discharge breakdown and prolongs the time of each cycle of discharge. It becomes difficult to maintain rapid cyclical steady glow discharge. The perforated covering plate, is also an important part of the electrode structure, concentrating the current density. The thickness of the perforated plate and the size of the gas trapping chamber should be carefully controlled so that the electrode spacing gap is not unduly wide as that also influences the voltage requirement. The size and disposition of perforated holes can be determined by trial and error. Wide electrode spacing increase the voltage input requirement and unsuitably close electrode spacing will cause early occurrence of plasma arcing with high current surge and generation of temperatures which will damage the electrodes and their attachments.

The power unit should be of adequate power rating. The electric breakdown is highly dependent on the high voltage supply. If the rating of the power supply unit is inadequate, it could easily be damaged during sudden the high current surge caused at cyclical electric breakdown. There will be no plasma discharge if the power input is inadequate.

The electrolytic liquid should have suitable conductivity, not too low nor too high. Voltage cannot be easily raised between two electrodes the liquid has high conductivity and no plasma discharge will be generated unless there is a high voltage input. The discharging electrode may be fully encapsulated inside a bubble barrier, but high conductivity liquid allows the current to pass through the bubble-liquid interface which in turn, also prevents the voltage rising high enough. If the conductivity of the liquid is too low, then the bubble barrier forms a complete dielectric barrier which requires a much higher inception voltage to cause electric breakdown or discharge and at the same time, the passage of current becomes too low which results in a low current density which also influences the occurrence of discharge. A much higher breakdown voltage (discharging voltage) creates electric arcing in gaseous condition which is no longer considered non-thermal under-liquid plasma discharge.

CONCLUSIONS

1. Gas layer or bubbles form the dielectric barrier that provide the environment for building up the discharge voltage and gaseous space for plasma discharge to take place. High voltage and relatively low current input is characteristic of under-liquid plasma.

2. With the characteristic high voltage and low current requirement, the under-liquid plasma can be generated over a wide range of liquids. The electrolyte liquid can be acidic, alkaline or a solution of salts. Liquids containing conducting impurities or a mixture of organic compounds may also serve as electrolyte such as the case of tape water and fruit drinks.

3. There are a number of factors which would affect the generating of under-liquid plasma such as voltage, current density, configuration of electrodes, area of electrode surface, electrode gap spacing, electrolytic physical and chemical properties, gas retaining and trapping arrangement, provision of plasma enhancement, ultrasonic cavitations, pulsed power supply, ambient temperature and reactor construction. This appears complicated, but the experiments undertaken have demonstrated that all the mentioned factors can be manipulated to achieve generation of stable non-thermal plasma at one atmosphere of pressure.

4. Plasma is the fourth state of matter. It has been widely employed in the field of chemical, electronic, materials and energy industries. Plasma generated under-liquid plasma has its own intrinsic characteristics and advantages, which have already proved to be a useful tool for plasma electroplating or deposition of both metallic and non-metallic materials. It will find its application in the plasma-assisted water electrolysis for hydrogen production; reformation of hydrogen rich compounds or hydrocarbon fuel (gas and liquid); decontamination of both liquid and gas pollution discharges containing persistent harmful chemicals, dissolved heavy metals and organic and biological contaminants; sterilisation of fruit drinks, potable water supply; and reduction of material oxide such as oxide ores, metal oxide as an alternative method metal refinement. It is probable that the proposed under-liquid plasma generation, and this established basic scientific information, would form the basis for further refinements leading to the practical new applications put forward in this patent application.

PLASMA ASSISTED ELECTROLYTES FOR HYDROGEN PRODUCTION

Water electrolysis is still used for the production of pure hydrogen. This hydrogen production is restricted because of it's relatively low energy conversion efficiency. In order to achieve higher energy efficiency, the electric voltage must be kept low to avoid energy loss through heat conversion. There are also claims that the energy efficiency can be improved by better electrode configuration, an increase in the reactive surface area, reduction of the electrode gap and increasing the operatingpressure. The PEM solid electrode system is in its early development and its efficiency remains similar to that of water electrolysis system. In any case the basic principle of water electrolysis has not changed since it was first put to use. Electrolysis as a whole, is considered to be non-competitive with the competing production process of reforming hydrocarbon fuel, but electrolysis has the advantage of being a clean process producing high gas purity and CO_2 is not produced.

The hydrogen bubbles evolving from the electrode surface slow down with time when tiny bubbles gradually built up and smother the electrode surface. These are not easily dislodged and the rate of hydrogen production is reduced further as those tiny bubbles become a barrier to current flow between the two electrodes.

The proposed invention is closely related to the water electrolysis process but the mechanism of separating hydrogen from water molecules is different. Generating non-equilibrium plasma within the bubbles that smother the electrodes will break down the dielectric barrier bubble layer and cause the normal flow of current to be resumed. At the same time, water molecules contained in the bubbles coming into contact with the plasma discharge, will be dissociated to produce extra hydrogen. In addition, the vigorous plasma discharge near the electrode surface will also create an hydrodynamic condition, which will wash away the fine bubbles which block the current flow. The mechanism of producing hydrogen by plasma discharge is different from the conventional electrolysis which splits the ionic water molecules by electro-polarity attraction, while in the plasma discharge the water molecule is broken down as the result of electron collisions. The water molecules under the plasma discharge irradiation would lose one electron due to electron collision to yield $H_2O + e \rightarrow OH + H^+ + e$

The hydrogen produced is of high purity. Ordinary potable water or rainwater with a very low concentration of electrolyte can be used as the main source of material, instead of distilled water, as they contain sufficient impurity to be slightly electro-conductive.

The experiment has demonstrated that hydrogen gas can be produced with plasma glow discharge as a supplementary process to the conventional method. The energy required to produce 1 cubic meter of hydrogen with plasma glow discharge with a very rudimentary reactor has achieved an efficiency of 56% which can be further improved with better engineering, by closing the electrode gap distance, selecting the right concentration of electrolyte, reactor construction and better means of trapping and retaining gas near the discharge electrode.

High temperatures of up to $90^{O}C$ is recorded in the electrolyte, which increases within very short time of the reaction. This may in part due exothermic reaction of recombining H and OH to water. The excessive heat can well be utilised as secondary source of energy. The gas or vapour bubbles by heating assuming greater importance as source materials for plasma dissociation leading to the production of Hydrogen. The high purity oxygen co-produce is also a valuable by-product with many applications.

Since high voltage with moderate current is needed in the plasma process, the production rate per unite area of electrode surface is high, and so only a small reactor is needed for the production of hydrogen, especially when other plasma enhancement methods are employed, such as ultrasonic cavitations, pulsed powers and RF input.

The electrodes could be of any conductive materials such as aluminium, stainless steel, graphite, tungsten, platinum, palladium etc. The size of the electrode for the plasma discharge is much smaller than that required by the conventional electrolysis to produce the same quantity of gas. As a result of this, a smaller reactor is possible.

Sponge porous electrodes will increase the reactive surface area available to produce electrolysis gases. In the experiment, several layers of fine wire mesh were packed tightly together to mimic a sponge porous electrode plate.

Some of the basic electrode configuration is: plate to plate; perforated plate to perforated plate; plate or perforated plate to wire mesh; wire mesh to wire mesh; plate to pinned plate; dielectric coating on one or both electrodes plate or mesh or pinned plate, tube in tube and wire in tube arrangement. It is noted that electrode configuration including any lining or covering materials that help to concentrate the current density and having the ability in retaining gas around the electrode would be adopted which will help to lower the voltage and current requirement to generate steady plasma discharge.

In order to create an environment for steady and short cyclical plasma glow discharge as already mention in the previous text, the electrode configuration should be so structured to retain the bubbles and concentrate the current density and yet keeping the true electrode gap distance to a minimum. This creates a suitable voided space either in the metal electrode or in the covering materials, capable of retaining gas while at the same time having the mechanism to concentrate the current density to a localised discharge point. This leads to a wide variety of designs and choice of materials to satisfy plasma discharge requirement.

In order to avoid recombination of H^+ and H_2 with OH ions and reverting back to water, the hydrogen atoms after regaining their lost electrons through contacting the cathode should be allowed to escape quickly from the area which abounds with other oxidation species and radicals. This has greatly influenced the productivity of hydrogen gas. If H^+ and OH is allowed to recombined, despite of the apparent bubble boiling in the reactor very little gas can be collected and the temperature in the reactor rises quickly which could well be the exothermic effect of recombination of H^+ and OH.

The hydrogen produced is collected separately from the oxygen. Since the produced hydrogen gas contains a fair amount of water vapour, the hydrogen gas is collected by passing it through a water chiller or other known method, so that the measured gas volume is at room temperature with minimum water vapour content.

The basic plasma assisted electrolysis cell or reactor can be produced in modular form which can be mounted side by side and placed inside a single electrolytic tank with their respective power and output gas collected to form a major production unit. Several reactor types can be employed for the production of hydrogen. Rod or wire in tube reactor, tube in tube reactor, single or multiple cell reactors are also suitable for the plasma assisted water electrolysis. The gas retaining and current concentrating cover will be affixed on the cathode electrode facing the anode electrode. A horizontal reactor whose cathode has a gas-retaining cover can be placed on top of an anode which is separated by a diaphragm and the hydrogen gas will then collect in isolation.

The introduction of ultrasonic cavitations into the electrolytic liquid is easy since the electrolysis bath is also the ultrasonic bath and ultrasonic transducers can be attached to the bath externally. A mixture of sonic frequency should be used to avoid any occurrence of a dead sonic zone. The introduction of sonic excitation through cavitations enhances the production performance of plasma-assisted electrolysis.

Pulsed high-voltage DC supply with single polarity square wave from 5 KHz up to 100 KHz has been found to be beneficial for generating plasma at a much reduced voltage.

The distinct advantage of the under-liquid plasma enables ionised species migrate to the respective half cell and electrodes which will avoid and minimise re-mixing of the produced hydrogen and oxygen causing a reversion to water again and creating a hazardous, explosive condition. The oxygen is considered as a by-product which can be collected for use or it can be channelled to the combustion chamber if hydrogen is used as direct fuel for a combustion engine.

Water is the primary source material for hydrogen production, being economically available and of unlimited supply. It is a completely clean source material that produces no unwanted by-products.

The anode may be gradually losing its materials due to electro transportation, but if so, it will be a very slow process. In practice the polarity of electrodes can be reversed which reverses the materials transportation and deposition. Conductor materials which are inert to electro-chemical corrosion are a good choice to serve as electrodes.

A chemically conductive reagent may be added to water to increase its conductivity and a foaming agent added to enhance generation of bubbles. The electrolyte can be of acidic or alkaline base. The concentration of the electrolyte should be maintained at a steady level for best results. High electrolyte concentration increases liquid conductivity as well as productivity of gas bubbles but it might prevent the rising voltage required for discharge as the current flow between electrode will not be inhibited by the presence of bubbles. However, a very low concentration of electrolyte will favour dielectric breakdown of bubbles, as a lesser current will be carried by the liquid medium inbetween the bubbles. It has been found that either acidic or alkaline electrolyte with 0.02% concentration work extremely well in maintaining steady glow discharge with DC voltage ranging from 350 V to 1,800 V and a current from 100 mA to 800 mA.

Tap water has been used without adding any conducting reagent and it often works unexpected well, most likely due to present of impurity and high pH, in the plasma-assisted electrolysis where steady glow discharge occurs at around 450 V to 900 V and current around 200 mA to 350 mA. The power input requirement varies in accordance to electrode spacing, electrode and reactor configuration, electrolyte concentration and the structure of gas retaining arrangement. Again other plasma assisted method such as pulsed power input and ultrasonic cavitations etc. also help to lower the power input requirement.

The process is in general, conducted at one atmosphere pressure. An increase of pressure will slow down upward movement of the bubbles and raise the temperature of the electrolyte. Some increase in temperature in the electrolyte is not detrimental to the generation of plasma. Water vapour bubbles provide the source materials and active environment for plasma discharge. In general, electrolyte temperature is well below boiling point as non-thermal plasma produces little heat. The temperature sometime rises quickly in the electrolyte due to occurrence of infrequent plasma arc and exothermic in the recombination of H+ and OH- in quantity.

During the steady glow discharge, vigorous bubbles with yellow/orange/red colour light spots appear all over the plastic perforation. The light spots also appear widely on the electrode surface when the voltage is increased. On examination of the electrode and plastic cover sheet, no burn marks were observed. This proves that the plasma glow is non-thermal after an hour of glow discharge. The temperature in the electrode plate recorded with a thermal couple was around 50^{O}C to about 90^{O}C. The gas produced is composed mainly of hydrogen with some water vapour, which condenses quickly on cooling. The rate of hydrogen production is variable and energy conversion rate also fluctuated throughout the test. This is suspected to cause by the recombination of H and OH, which is affected by the electrode and reactor structure and configuration.

Hydrogen can now be produced with high voltage and low current, which is contrary to the conventional electrolysis system where a small reactor with a high rate of production is becoming possible. This has clearly demonstrated that the mechanism of producing hydrogen with plasma discharge is different from conventional water electrolysis in a number of ways. Steam and gas vapour produced due to heating of the electrodes (cathode) in short space of time are becoming an importance source of materials for plasma dissociation that also influence the productivity of hydrogen.

1.3 Experimental Procedure

1.3.1 A flow diagram for carrying out experiments in relation to this invention is shown in **Fig.28**.

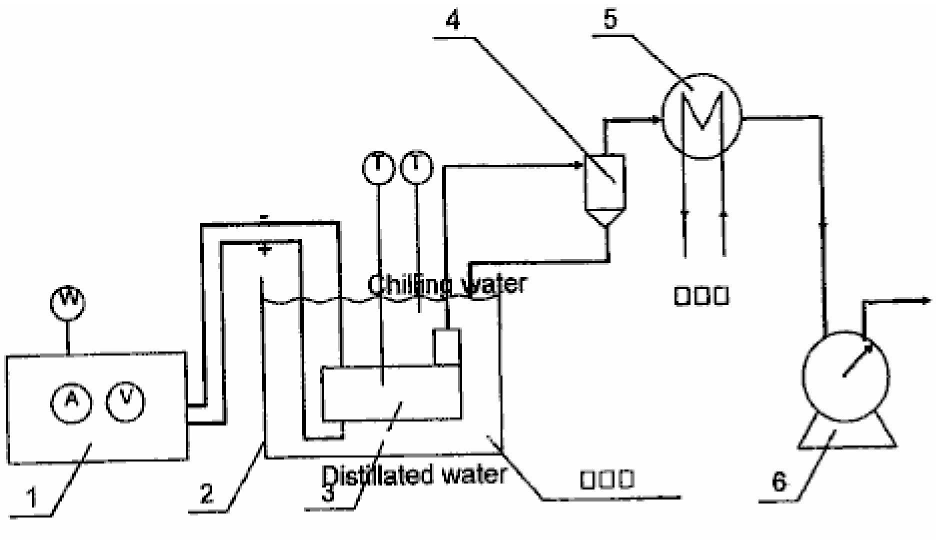


FIG. 28

The apparatus comprises broadly, a DC power source **1**, liquid bath **2**, reactor **3**, gas and liquid separator **4**, water chiller **5**, and gas-volume measuring meter **6**. Gas was produced by electrolysis which was catalysed by the plasma. Hydrogen gas was produced at the cathode and oxygen gas at the anode.

1.3.2 Equipment Function:

DC power source: provides high voltage DC.
Horizontal reactor: generation of non-thermal under-liquid plasma.
Gas and liquid separator: to separate liquid from gas and return as chilled liquid.
Chiller: to condense any liquid vapour admixed in the gas and return to reactor.
Gas-volume measuring meter: to measure the volume of gas flow.

1.4 Method and Operation of the Experiments

(1) The experiment is conducted in according to the occurrence of plasma discharge. Six different levels of voltage are selected to produce under-liquid plasma with same reactor for the generation of hydrogen. They are: 1350 V, 1450 V, 1550 V, 1650 V, 1750 V, and 1850 V. Each experiment lasts 30 minutes and the experiment is repeated three times under the same set of conditions. The data obtained are than averaged out.

1.5 Experimental Observations

Plasma discharge at 1,350 V is observed to have few and limited lighting illumination on the electrode in comparing with those vigorous, steady discharging over a much larger electrode surface at voltage 1,850 V. The corresponding current input is also very much reduced. It has been recorded that the temperature at the cathode electrode rises with time until it reaches about 90^{O}C and gradually becomes steady. The colour of the plasma discharge appears to be orange and red and it's colour is greatly different from that of electric arc (plasma arc discharge) which appears to be sharp bright blue in colour.

Applicant also conducted experiments with the same equipment utilising the under-liquid plasma to transform methanol for use in hydrogen production. Applicant found that the plasma was efficacious in producing hydrogen gas from the methanol. CO and CO_2 gases were completely absent from the gas produced. This was unexpected. Without being bound thereby, Applicant believes that CO and CO_2 may have been absorbed by KOH which was added as a conductive agent to the electrolyte. Some oxygen gases were recorded before methanol was added to the electrolyte.

Applicant also conducted experiments with the same equipment utilising the under-liquid plasma to reform hydrocarbons for hydrogen production. Applicant found that the plasma was efficacious in reforming the hydrocarbons and producing amongst other things hydrogen gas.

Applicant also conducted experiments with the same equipment utilising the under-liquid plasma to treat diesel oil. The diesel oil was emulsified in water to disperse it through the body of liquid. After being subjected to plasma conditions near the cathode, a gas was produced that was smoky and resembled an exhaust gas emission that did not easily burn. Applicant established by means of these experiments that diesel oil could be reformed and also dissociated by the in liquid plasma with this equipment.

Reformation of hydrocarbon liquid and gas fuel, and hydrogen rich compounds for hydrogen production:

Water is one of the primary source materials, which serves as carrier, conductor and confinement to the bubbles space where plasma corona and glow discharge would take place when adequate electro-potentials apply across single, or multiple electrodes pairs. The hydrocarbon fuel methane (gas), methanol, diesel, gasoline, kerosene (paraffin), ethane, natural gas, LPG gas, bio-diesel etc. and hydrogen sulphur (H_2S) are also good source material for hydrogen production.

The majority world-wide of hydrogen production conventionally is by high-pressure steam reformation of methane. This requires high pressure and high temperature. The production plant is large and costly to set up. Storage and delivery in association with the production are an added cost for the supply of hydrogen gas. The importance of hydrogen as an alternative environmentally clean fuel is well understood. The upcoming fuel cell technology demands an economic and ready supply of pure hydrogen gas. To produce hydrogen with a small processor to enrich fuels for combustion engines and gas turbines will not only be reducing fuel consumption but it also reduces polluting emissions.

The proposed plasma reformation process can deal with both gaseous fuel and liquid fuel. The gas fuel will be bubbled into the reactor along with an inhibitor to slow down the upward flow of the fuel gas. Since the dissociation of the hydrocarbon fuel will be mainly achieved by plasma dissociation which is similar to the plasma-assisted electrolysis process, but with electrolytic liquid containing hydrogen rich compounds. In the case of liquid fuel, it can either form a mixture with water or be emulsified with water. The percentage of fuel in the mix depends on the type of fuel, its conductivity, boiling point, flammability and electrochemical reaction. The reformation is mainly due to partial oxidation either with the active OH^-, O^-, O_2, O_3 created by the plasma dissociation. At the same time, the hydrogen-rich compound such as CH_4 or CH_3OH will be dissociated directly with electron collisions. Since carbon dioxide is a major by-product together with some other minor gases coming out from the impurity of the fuel, they will be separated by the conventional absorption method or the membrane separation method.

Transformation of hydrocarbon fuel by corona and glow plasma has been attempted by passing the hydrocarbon gas such as methane, natural gas, LPG and vaporised liquid fuel sometime mixed with water vapours through the plasma reactor. They have all been successful in producing hydrogen-rich gas through corona discharge at atmospheric pressure by subjecting methane, vaporised methanol, diesel fuel mixed with water vapour, by passing it through a plasma gild arc reactor, wire in tube reactor and reactor proposed by MIT plasmatron or other gas phase corona streamer reactor.

The proposed under-liquid plasma reactor has many advantage over the gas-phase plasma reactor as it is able to generate a steady plasma-glow discharge at a very much lower voltage, i.e. from 350 V to (rarely) 1,800 V with current in the range of 100 mA to 800 mA in water. The liquid medium will also permit the application of ultrasonic waves producing an effect which will enhance the generation of glow plasma and thereby increase the overall transformation process. Again, no external air or gas is need be introduced for the reaction. However, the hydrocarbon gas such as methane, natural, LPG or hydrogen sulphurs gas can be introduced to work in conjunction, and complementing the liquid fuel in the reformation process. The fuel gases will enhance plasma-discharge reformation and allow it to take place without having to rely on gas produced by electrolysis.

Those hydrocarbon fuel molecules which come in contact with the plasma-discharge, will be subjected to dissociation and partial oxidation depicted in the following:

$H_2O + e \rightarrow +OH + H^+ + e$ dissociation
$CH_4 + e \rightarrow CH_3 + H^+ + e$ direct plasma dissociation
$CH_4 + H \rightarrow CH_3 + H_2$ reacting with H radicals
$CH_4 + H_2O \rightarrow CO + 3H_2$ partial oxidation
$CO + H_2O \rightarrow CO_2 + H_2$ water shifting
$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$ electrolysis and partial oxidation
$H_2S \rightarrow S + 2H$ without experiencing oxidation
$H_2S + 2H_2O \rightarrow SO_2 + 3H_2$ partial oxidation
$SO_2 + 2H_2O \rightarrow H_2SO_4 + H_2$

Endothermic catalytic conversion of light hydro-carbon (methane to gasoline):

$CnHm + nH_2O \rightarrow nCO + (n + m/2)H_2$

With heavy hydro-carbon:

$CH1,4 + 0,3H_2O + 0,4O_2 \rightarrow 0,9CO + 0,1CO_2 + H_2$
$C_8H_{18} + H_2O + 9/2O_2 \rightarrow 6CO + 2CO_2 + 10H_2$

The hydrogen gas and carbon dioxide are collected. The CO_2 is separated by establish absorption or the membrane separation method.

The OH radical produced by the plasma dissociation will play an important role in oxidising the CH_4 to produce CO which would further be oxidised to become CO_2. The same applied to methanol CH_3OH and H_2S. The S is being oxidised to form SO_2 and further oxidising to become SO_3 and subsequently reacting with H_2O to produce H_2SO_4. This type of chemical reaction will be possible only with the encouragement of the highly chemical reactive and plasma catalytic environment. Not every CO will become CO_2 and sulphur particles may be observed in the precipitation.

REACTOR

There are number of reactors which can be used for the reformation of hydrogen-rich compounds. Reactors such as the wire in tube, tube in tube; single cell and multiple cell reactors; and the multi-electrodes without diaphragm separation. The tube in tube reactor and tower reactor with horizontal electrodes are suitable for treating both liquid and gas hydrocarbons and both at the same time. The anode and cathode are closely spaced with a gap distance ranging from 6 mm to 12 mm and are covered with dielectric gas-retaining and current-concentrating construction on one side or both sides of the electrode. One important aspect of the reactor is having the construction, which will accommodate the ultrasonic transducer, which would induce proper sonic cavitations uniformly distributed throughout the reacting volume. The size, shape and arrangement of the electrodes can vary but its size would be restricted by the electric power available. A small reactor electrode plate is quite adequate for good uniform discharge and high productivity. The size of reactor plate use in most of the experiments is in the range of 16 cm^2 to 30 cm^2. It is preferable that the non-discharging electrode has an electrode area larger than the discharging electrode with the dielectric gas-retaining construction. With sufficient power available, both the anode and the cathode electrode can be functioning as plasma discharging electrodes at the same time. This is particularly useful in the partial oxidation process.

In the case of an emulsified oil/water mixture, it is best maintained with ultrasonic excitation which at the same time generates transient micro bubbles which enhance the whole reactive process. Hydrocarbon gas may also introduce to the reactor to form air bubbles or trapped gas pockets for the ready formation of the plasma glow discharge. Since the oily hydrocarbon fuel is highly dielectric this would require a higher concentration of conducting reagent than that required for the plasma-assisted water electrolysis, in order to maintain a suitable level of current density for the discharge to occur.

Reformation of methane gas by the under-liquid non-thermal plasma is by bubbling the gas through the perforated horizontal electrodes of tower a reactor or a tube-in-tube reactor. Since the methane gas is to be oxidised by the plasma dissociated water molecule ($OH- + H+$) to form carbon monoxide and hydrogen gas ($CH_4 + H_2O \rightarrow CO + 3H_2$). The CO will be further oxidised to form CO_2 with oxygen derived from the plasma dissociated water molecule, releasing two more hydrogen atoms (H_2). The resultant gas is either H_2 or CO_2 with perhaps small amount of CO. The hydrogen gas will be collected with reasonable purity after the CO_2 or CO is removed by absorption or membrane separation. Since the methane gas may not thoroughly reform with one past through the reactor, it is important to regulate the gas flow rate to ensure suitable resident time for the reformation or to have the methane gas recovered by the next round of reformation or to have the gas going through a series of reactors to made sure that the methane gas is fully utilised. The later case may not be energy efficient.

Reformation of methanol for hydrogen production can be achieved in the first place, by ordinary electrolysis or by partial oxidation. When CH_3OH is subjected to plasma discharge irradiation, it will react with the oxidising species and radicals dissociated from the water molecules. Conventional electrolysis will also contribute to the overall production of hydrogen gas. Reformation of methanol/water mixture will achieve better efficiency when plasma discharges is used in conjunction with ultrasonic excitation and cavitation. Several types of reactor can be adopted for the methanol reformation such as a tower reactor with horizontal electrodes, a tube-in-tube reactor, a transverse flow reactor, etc. These types of reactor offer very active oxidising species and hydroxyl radicals needed in the reformation.

Reformation of heavy oil such as diesel by under-liquid plasma discharge will be with emulsified liquid. The best way to maintain a thorough emulsification of diesel fuel and water is by ultrasonic excitation. Micro droplets of diesel will be encapsulated in the water. It is again observed that the conductivity of the emulsified liquid is very low as diesel oil is dielectric and current can only be conducted through the water film inbetween. This has rendered the need of more electrolytes added, especially as the diesel content increases. Bubbles are not easily produced by electrolysis due to its low current flow. It is therefore an advantage to either introduce gas to the reactor from outside or to produce ultrasonic cavitations in the liquid at the same time as the emulsification of the water/oil mixture. The tower reactor, tube-in-tube reactor and the transverse-flow reactor are all suitable for heavy hydrocarbon fuel reformation provided that an adequate ultrasonic transducer is properly located to ensure effective excitation and cavitations distributed throughout the liquid volume. A pulsed power supply will enhance the plasma generation and electrode heating will assist the generation of bubbles at the discharging electrode.

REDUCTION OF METAL AND MINERAL OXIDE PROCESS

Mineral refinment is an expensive and polluting process. To remove oxygen from the oxide, is either by reacting with higher electro-positive elements, which is uneconomic, or by exposing the metal oxide to C, CO, and hydrogen inside a high-temperature furnace such as the case in iron production. The electrolysis of a molten melt of Al_2O_3 or TiO_2 to extract pure metals Al or Ti respectively, consumes a large quantity of electricity, and requires the use of expensive refractory and electrode materials along with polluting emissions, render these two useful metals very expensive and inhibit their common application.

An under-liquid plasma reductive process to reduce oxide of ore or metals is proposed. The plasma discharge irradiation of the metal oxides in a highly catalytic environment, will cause interaction with the active hydrogen atoms produced by the plasma dissociation of water or methane or a methanol/water mix and introduced hydrogen gas together with the assistance of ultrasonic excitation would be sufficient in many instances to dislodge the most stubborn oxide.

It is reported that research is underway to extract Al from Al_2O_3 by electrolysis. Aluminium is electrode wired to cathode from porous Alumina anode electrode. The reduction of TiO_2 and Al_2O_3 by hydrogen plasma discharge is also being actively researched elsewhere with the aim of economically refining these two useful metals. A tube-in-tube reactor, or a wire-in-tube reactor can be used for this reduction process. These two reactors can be easily modified for continuous processing of either the granular form of the mineral or the metal oxide. The metal oxide will be exposed to the influence of highly active hydrogen atoms and subsequently the oxygen in the metal will be removed. This would not be a problem for those electro-positive elements but would present some difficulty for oxides such as Al and Ti.

The oxygen is strongly bonded with the parent metals such as Al_2O_3 and TiO_2 which cannot be reduced easily. This rudimentary horizontal reactor serves to demonstrate that metal oxide can be refined by exposing it in granular form to plasma discharge irradiation, ultrasonic excitation and in a highly reactive environment containing active hydrogen atoms. Additional hydrogen can be derived from the plasma dissociation of methane gas introduced to the reaction chamber where CO and atomic H are produced. Similarly by plasma dissociation of the methane water mixture that active hydrogen and CO_2 are also produced to supplement the reductive atomic hydrogen. Hydrogen gas can also bubble into the reactor and any excess will be collected and passed back to the reactor.

Reduction of Al_2O_3, TiO_2, TiF_3, TiO, $AlCl_3$ will be taking place in the following manner, where:

$TiO_2 + 4H(2H_2) \rightarrow Ti + 2H_2O$
$Al_2O3 + 6H(3H_2) \rightarrow Al + 3H_2O$
$TiF_3 + 3H(3/2H_2) \rightarrow Ti + 3HF$

The alternative is to have:

$TiO_2 + H_2SO_4 \rightarrow TiOSO4 + H_2O$
$TiOSO_4 + 2H \rightarrow TiO + H_2SO_4$
or $TiO + 2H \rightarrow Ti + H_2O$
and
$TiO_2 + 4HCL \rightarrow TiCl4 + 2H2O$
$TiCl_4 + 4H \rightarrow Ti + 4HCl$
where $TiCl_4$ is ionic and is soluble in water

The above reaction is under the influence of a non-thermal plasma so that the oxide of ores or metal is subjected to a highly catalytic environment and comes into contact with the reactive atomic hydrogen whereby the oxygen will be taken out. To enhance the matter further, the whole reaction process is also subjected to sonic excitation. The fine particles in the colloidal suspension of the granular oxide will collide with each other and at the point of impact, the temperature will rise over $1,500^{O}C$ to $3,000^{O}C$ and local melting is reported. The high temperature and pressure of a collapsing sonic bubble will work in conjunction with the plasma glow discharge irradiating the oxide particles with atomic hydrogen with localised high temperature due to collision and cavitations implosion which in the end remove the oxygen. The refined metals will be in powder form down to nano size.

The other method of extracting and refining metals from their oxides is to subject the ionic solution of the metal such as $AlCl_3$ to an electrolysis process which is reported to have achieved efficiency of 3 KWh/Kg of Al. The whole process can be further improved with the plasma electroplating technique with the proposed under-liquid glow plasma discharge. The Al will be deposited on the cathode electrode. Part of the chlorine gas will come out from the anode side and will react with the active hydrogen to form Hcl.

The fine granular metal oxide is placed inside a horizontal reactor on top of cathode electrode. A close matrix separator membrane, used to prevent the metal oxide from crossing over, placed above and below the anode electrode is used to separate it from the cathode. The whole reactor is submerged inside an ultrasonic bath. Ultrasonic waves will penetrate the membrane separator to cause the granular metal oxide in colloidal suspension. The oxide will be subjected to the under-liquid plasma glow discharge irradiation and atomic hydrogen reduction. The percentage of metal oxide being reduced after a period of time is evaluated. Metal oxide of TiO_2 will be put to test. A methane/water mixture will be employed as the liquid medium which will produce larger amount of active atomic hydrogen serving as reduction agents.

DECONTAMINATION OF LIQUID

The problem of pollution is a major issue affecting every living being on this planet. A lot of effort has been expended by Governments, universities and private enterprises, seeking a comprehensive process to deal with a vast variety of pollution issues. Polluting gas emissions from industries and motor vehicles produce large quantities of CO_2 causing global warming; NOx, VOC, and particulates causes cancer and smog; SO_2 causes acid rain. Decontamination of the gases discharged from industries is costly to achieve and what is urgently needed is a comprehensive and economical treatment process to reduce the overall trestment cost. Water contamination is another major issue. Contaminated water unfit for human consumption, enters the sea and kills marine life near the shore. Governments worldwide are passing stringent laws setting a pollution standard, which demands the development of efficient and economic ways to control pollutants. The present proposed invention is put forward as a versatile process, which can treat a variety of contaminants either separately or together.

Corona discharge and glow plasma discharge as non-equilibrium plasma has been developed for applications in the decontamination of a wide range of noxious chemical compounds and recalcitrant chlorinated organic compounds such as dichloro-ethane, pentachlorophenol, perchloroethylene, chlorom, carbon tectrachloride, organochlorine presiticides, endocrine disrupter, dioxin etc. It is also capable of sterilising tough microbial, bacteria and biological contaminants present in ground water such as cryptosporidia parvum. Noxious gas emissions such as NOx and SOx can also be neutralised by passing them through the wet reactor, which includes the removal of particulates as well as the pollution emissions. This is mainly due to the ability of plasma to create a very reactive catalytic environment for those normally very stable and inactive compounds to be reduced, oxidised or neutralised by reacting with the OH* radicals, atomic hydrogen H+ and other oxidative species such as O^-, O_2, O_3, H_2O_2 etc. present and is reported to have high efficiency especially in dealing with diluted contaminants.

Microbial bacteria is removed by both oxidations when they come in contact with the oxidative species such as O_3, O_2^-, O^-, H_2O_2, and OH*. At the same time, they are subjected to the electromechanical stretching of the cell wall, which weakens its oxidative resistance, especially when ultrasonic cavitations, implosions and shock waves created by pulse power, are incorporated into the reactive process. Again reports of over 99% sterilisation are not uncommon.

At the present, most of the treatment work is conducted in a gaseous environment, by spraying or vaporising the contaminated liquid over the plasma discharging electrodes, or by producing plasma discharge irradiating over the surface of a liquid which contains the undesirable contaminants, or by passing the polluted gas through a dry reactor sometimes mixed with water vapour or using plasma torch irradiation of the polluted object.

A surface water contact plasma glow discharge system has also been developed as a decontamination process under the name “Plasmate”. Under water plasma by pulsed high voltage electric discharge with high current input to dissociate the water to produce H and OH* radicals to treat bacterial and microbial decontamination has also been reported as being successful.

The proposed under-liquid plasma is a low energy consumption system, which produces steady plasma by utilising the present of bubbles. The voltage required for dealing with a wide range of liquids having variable electrolytic properties, ranges from 350 V to 3,000 V and current intensity ranging from 1 to 2 Amp/cm^2. It produces a highly reactive environment with a supply of oxidative radicals and reductive atomic hydrogen spread over a large volume of liquid, making it highly effective as a decontaminatinf process, and one which is also both economic and easy to operate.

The under-liquid plasma has the advantage of being able to decontaminate several pollutants at the same time and it also has a very active gas and liquid interaction which makes it highly effective as a treatment process. Liquid waste, containing harmful chemical, bacteria, microbial, heavy metals, noxious gas, polluted air and odour can be treated in the same reactor simultaneously.

Recalcitrant organic chlorinated materials in water, which include dichloromethane, pentachlorophenol, chloroform and carbon tetrachloride, will either be oxidised or degraded to CO_2 and chlorine. While the pathogens in drinking water such as cryptosporidia with thick phospholipids wall protecting the trophs is in the first place being stretched and weakened and subsequently broken down by the oxidising species. Some of the oxidative species such as OH radicals, O^-, O_2^-, and O_3 are present in quantity and are more active than chlorine and other mild oxidants. It has the advantage that no chemical is needed as an oxidation agent, which can sometimes result in secondary pollution.

Heavy metals in dilute solution, can be extracted or removed through a simple electrolysis process by turning the metal to hydroxide which could than be removed by filter. Soluble metal ions can also be extracted by deposition on to the cathode electrode, which can be further facilitated by the plasma electroplating process owned by the inventor, and which uses the same under-liquid bubble plasma process.

The treatment of NO, SO_2 and particulates is to pass the polluted gas through the reactor where the particulate will be removed and the NO is either oxidised to become NO_2 or NO_3 by O^-, or O_3. It can also be reduced to N by the active hydrogen. NO_3 will react with water to become nitric acid. NO_2 is not considered to be a noxious gas. SO_2 reacting with O_3 or oxygen radical to form SO_3 can be easily oxidised and then react with water to become H_2SO_4 (sulpheric acid). When the said gas is introduced to the reactor it can be utilised as a gas bubble for plasma discharge especially when this gas bubble is collected or retained near the electrodes.

The effectiveness of non-thermal plasma discharge in treating carcinogenic organic compounds and pollutant gases is well established. Removal or reduction of the amount of heavy metals, arsenic and mercury to an acceptable safe low concentration level from or in water, have been successfully carried out by a simple electrolysis process. The extraction efficiency is further improved by the presence of an under-liquid plasma discharge where some of them will readily react with the OH radicals to become metal hydroxide or to be deposited by the very active plasma electroplating (deposition) method which has been adequately proven as a useful technique.

Further experiments in this area are unnecessary. Adequate information can be drawn upon from much research work which already been carried out. Concentrated effort has already been used to search for a better way of generating steady plasma glow discharge under-liquid by utilising the bubbles which will enable the manufacturing of a simple and economic reactor which requires only low power input and wich will work well in treating a wide scope of contaminants.

Sterilisation of drinking water at municipal scale can be simplified by adopting the under-liquid plasma discharge which will effectively neutralise and degrade carcinogen organic compounds in the water by creating the dissociation and active catalytic environment which encourages the breakdown of the inert chemicals and at the same time subject it to the active reductive and oxidative radicals. The heavy metals dissolved in the water will also be removed or reduced in the same time through the plasma electrolysis and electroplating as described previously. The biological contaminants will be sterilised by the highly oxidative environment existing during the glow discharge. The effectiveness of the combined treatment to produce potable water fit for human consumption is further enhanced by the adoption of ultrasonic cavitation and shock waves with a pulsed power supply.

The entire sterilisation process does not require any added chemicals such as ozone, chlorine or any electrolytic additive. The impurity in the pre-treated liquid will be adequate to serve as conductor for the under-water plasma discharge to take place. Any excessive ozone, which has not been used up in the oxidation process during the plasma discharge, will be easily neutralised by the presence of active hydrogen atoms. Hydroxyl radicals (OH) are one of the most aggressive oxidising agents, which being produced in quantity will do most of the useful work. There will be no chlorine remnant left in the water, as it is unnecessary.

The under-liquid plasma technique will be useful in food industries for low temperature sterilisation and removal of odour. The same method may also find its use in the paper-making industry in fragmentation and de-lignification of the fluidised pulps, treating the highly polluted discharge, and treating fabrics and dyes in the textiles industry.

There are several types of reactors which can be employed in the decontamination process. The separation membrane diaphragm in the wire-in-tube and tube-in-tube reactor is no longer required. Other reactors such as the transverse-flow reactor and the tower reactor can also be adopted.

The reactor can be arrange in such way that the plasma discharge occurs either at the cathode or at the anode provided that a good gas-trapping cover is provided on the electrode. Since much of the decontamination action relies on the presence of strong oxidation agents such as hydroxyl radicals, atomic oxygen, ozone, singlet oxygen and hydroperoxyl radicals, plasma discharge on the side of anode electrode enhanced with the gas retaining cover will cause the formation of said species represented by the following equations:

$H_2O + e \rightarrow +OH + H + e$ dissociation
$H_2O + e \rightarrow + H_2O_+ + 2e$ ionisation
$H_2O_+ + H_2O \rightarrow H_3O_+ + OH$ dissociation
$O_2 + e \rightarrow O_2^* + e$ excitation
$O_2 + e \rightarrow +2O + e$ dissociation
$O_2 + e \rightarrow O- + O$ dissociation
$O_2 + O \rightarrow O_3$ association
$OH + OH \rightarrow H_2 O_2$ association

Some chemical contaminants can only be broken down by reduction with active atomic hydrogen, which would require plasma discharge at the cathode electrode. In the tower reactor (**Fig.7**) and transverse-flow reactor (**Fig.6**) it is possible to have the gas-retaining cover on one side of electrode facing the side of the opposite electrode with the gas-retaining covers, so that an alternating zone of oxidation and reduction is created in the reactors to deal with a variety of contaminants.

Production of hydrogen by plasma dissociation of water molecules is the result of electron collisions, which is different from the conventional electrolysis, which separates the dipole water molecules by electro-induction. They also have different sets of requirements to dissociate water molecules for the production of hydrogen:

Conventional electrolysis	Plasma glow discharge under water, according to the present invention
1. Low voltage and high current density	High voltage and relatively low current density
2. High concentration of electrolyte (up to 25% KOH)	Low concentration electrolyte (0.01% KOH) low electrolytic requirement
3. Avoid bubble attachment to the electrodes	Bubbles smothering the electrodes is welcome to create a dielectric barrier.
4. Electrode space distance is not restricted.	Electrode space distance has to keep close as far as possible.
5. Water molecules is split by induction	Water molecules are dissociated by electron collision.
6. Large production unit is required for efficiency and productivity	Small production unit favours the decentralisation of production.

The reactors and gas-trapping and retaining structures enclosing the electrode is made of perspex plastic. No sign of burning is observed in the plastic covering plate directly over the discharging electrode and the light emission is an orange/red colour (burning of hydrogen) which is distinctively different from the plasma arc which is bright blue colour when the voltage is brought beyond the glow discharge voltage level. A burn mark will be observed after plasma arc discharge. This proves that the plasma glow discharge with it’s orange yellow colour, is non-thermal in nature.

Applicant also conducted experiments with the same equipment utilising the under-liquid plasma to sterilise mulberry juice. Applicant found that the plasma was effective in reducing the bacterial count and the mold colony count in the juice. After 40 minutes the counts of both bacteria and mold had been reduced substantially to less than 100 per ml. This demonstrates that the invention could be used to sterilise potable water, waste water, food, and liquid food and others.

CONCLUSION

A further advantage of the method described above is that plasma can be generated with relative ease within bubbles in the aqueous medium. It does not require excessive amounts of energy and can be done at atmospheric pressure. It certainly does not require a vacuum chamber.

A further advantage of the invention is that it provides a method of treating aqueous waste which contains components that cannot be neutralised or otherwise rendered harmless by the addition of chemicals to the liquid.

It will of course be realised that the above has been given only by way of illustrative example of the invention and that all such modifications and variations thereto as would be apparent to persons skilled in the art are deemed to fall within the broad scope and ambit of the invention as herein set forth.

Figures which are included in the patent application but which are not directly referenced in it:

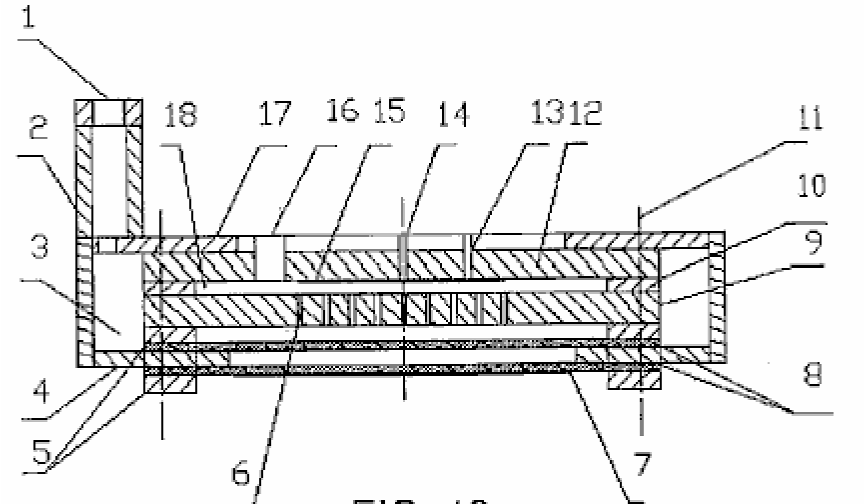


FIG. 19

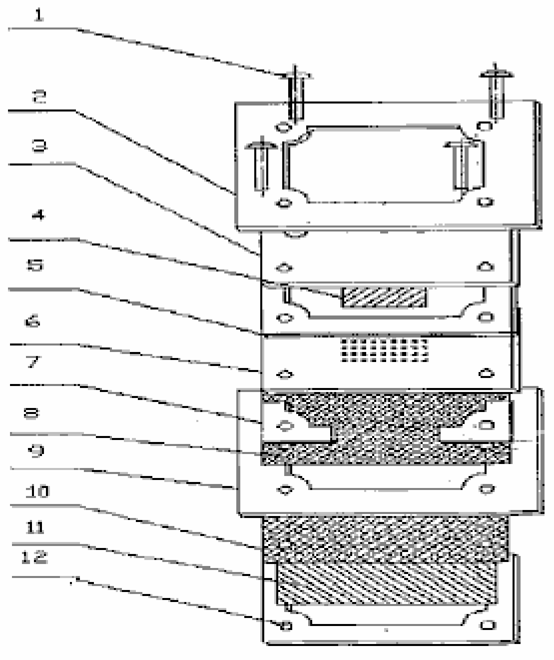


FIG. 20

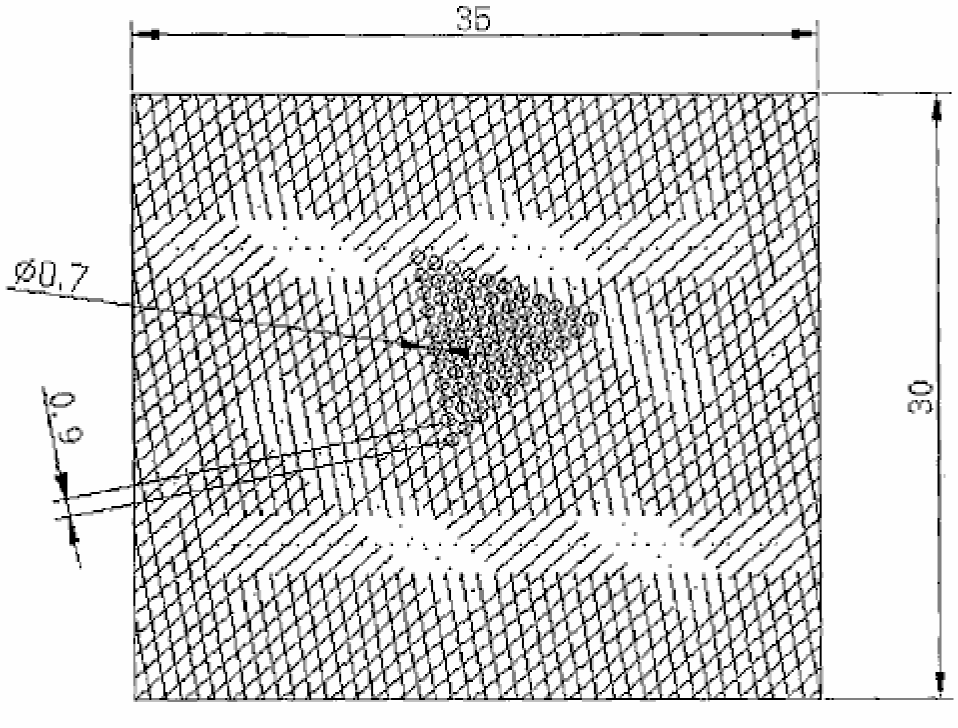


FIG. 21

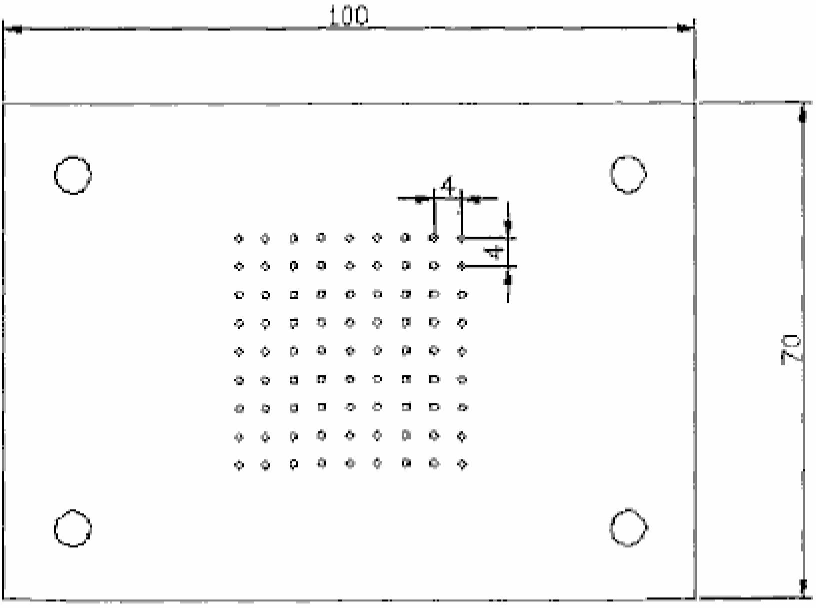


FIG. 22

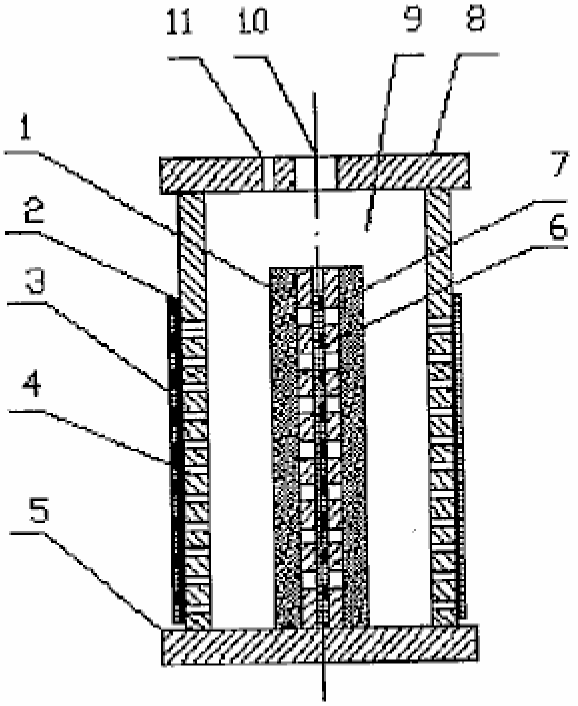


FIG. 23

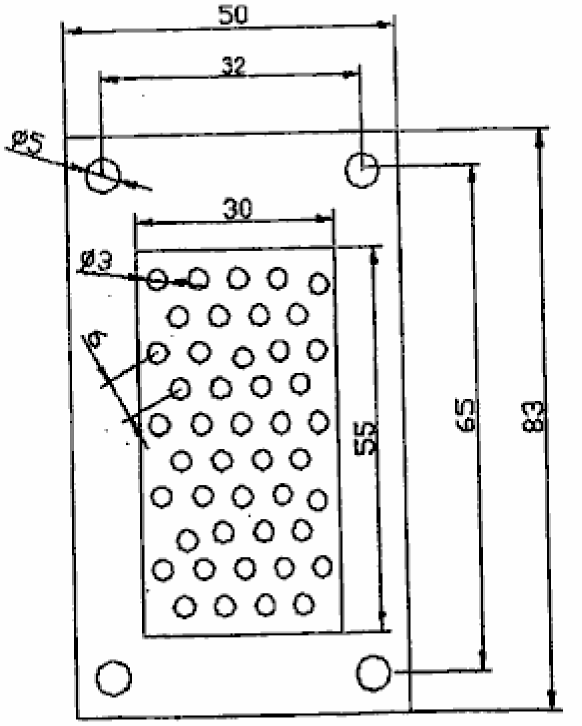
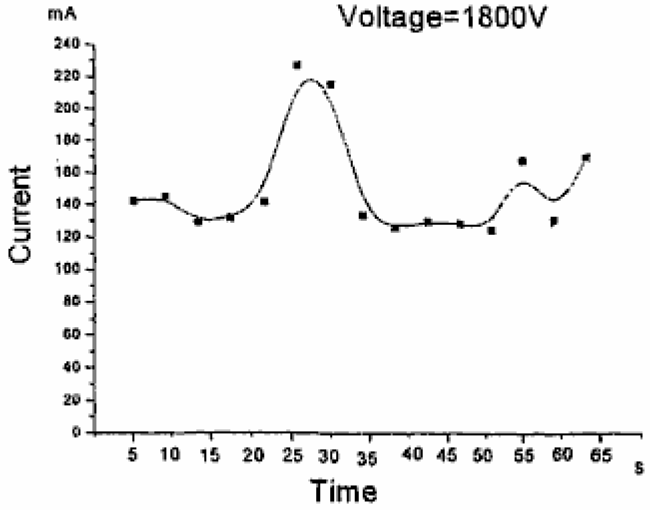
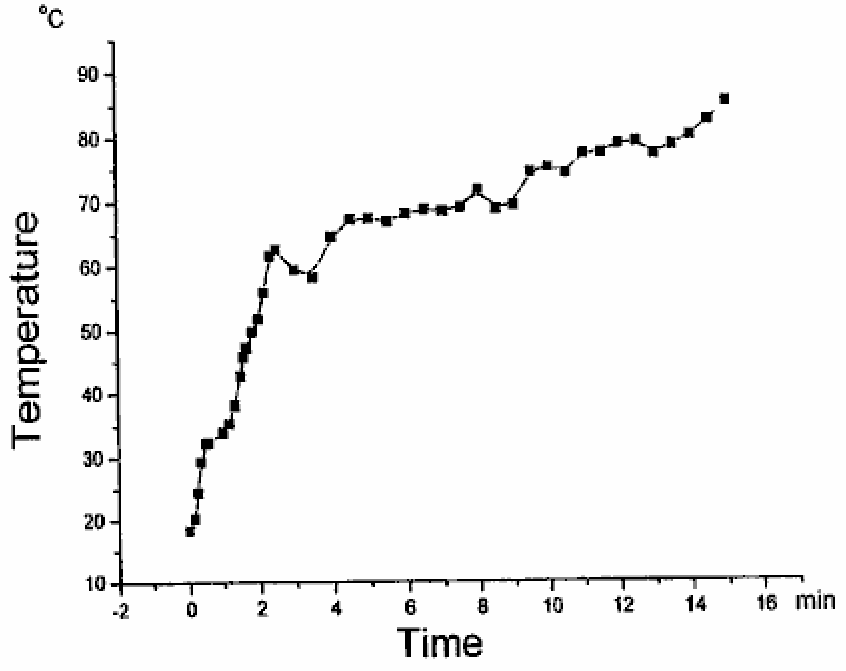


FIG. 24



Glow discharge at stable 1800V voltage input

FIG. 26



Temperature measured in the cathode electrodes

FIG. 27

Time=0~10min

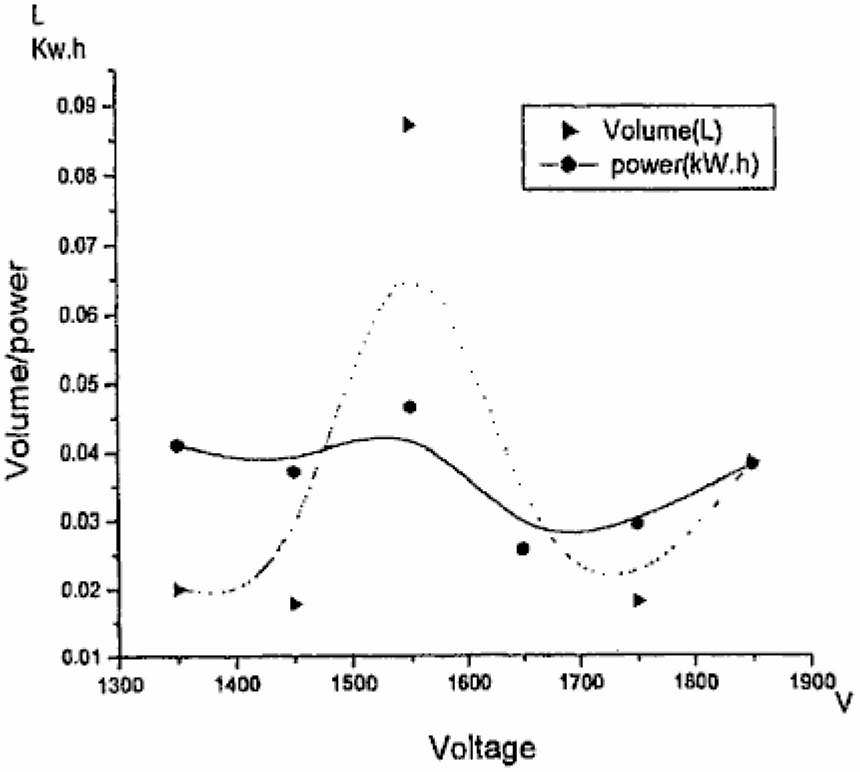


FIG. 29

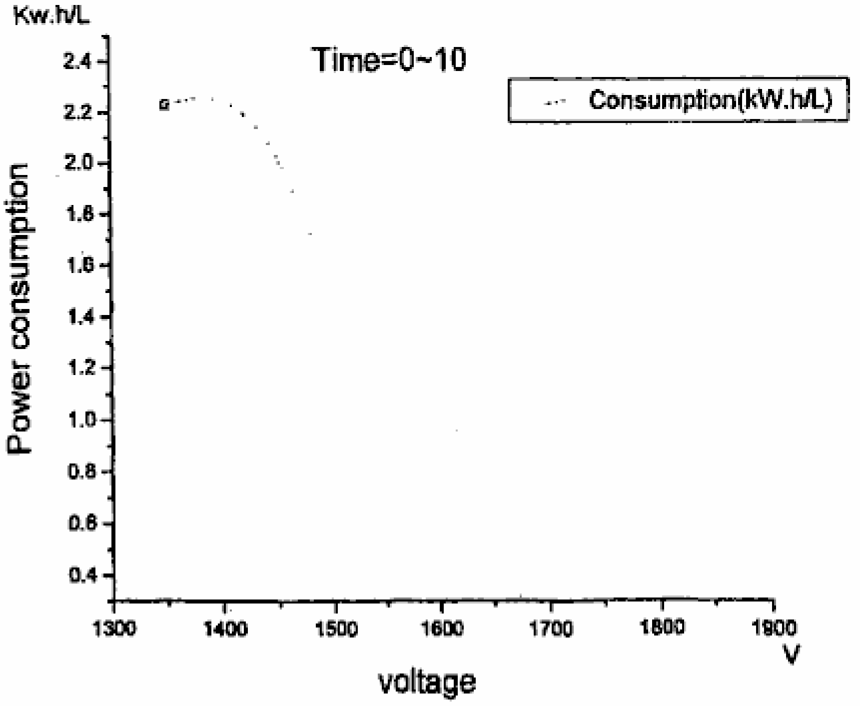

Kw.h/L
Time=0~10
Consumption(kW.h/L)
Power consumption
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
1300
1400
1500
1600
1700
1800
1900
V
voltage

FIG. 30

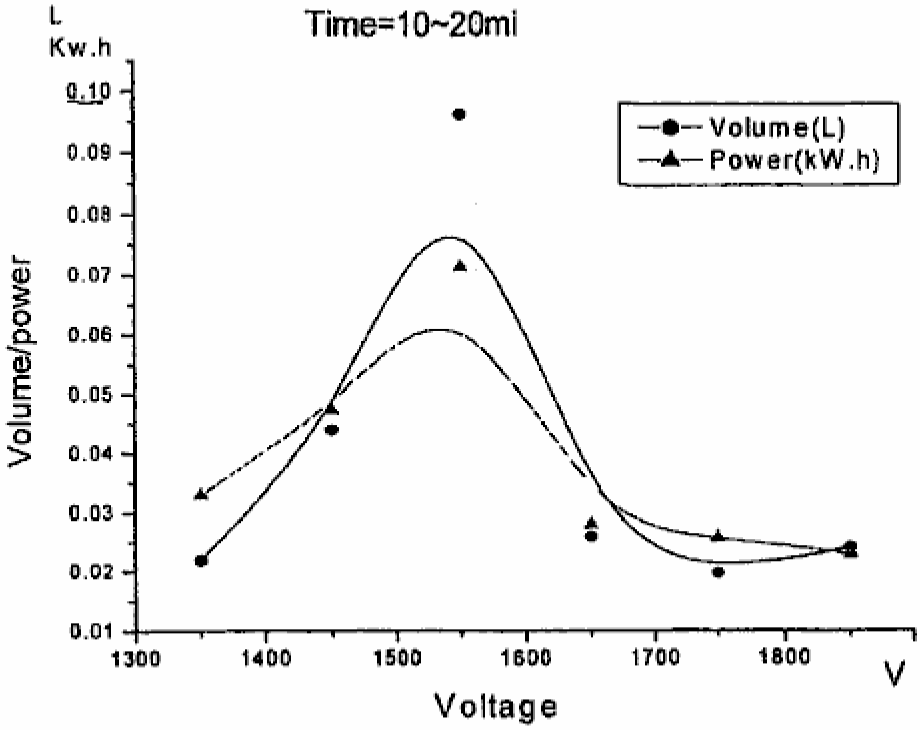

L
Kw.h
Time=10~20mi
Volume(L)
Power(kW.h)
Volume/power
0.10
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
1300
1400
1500
1600
1700
1800
V
Voltage

FIG. 31

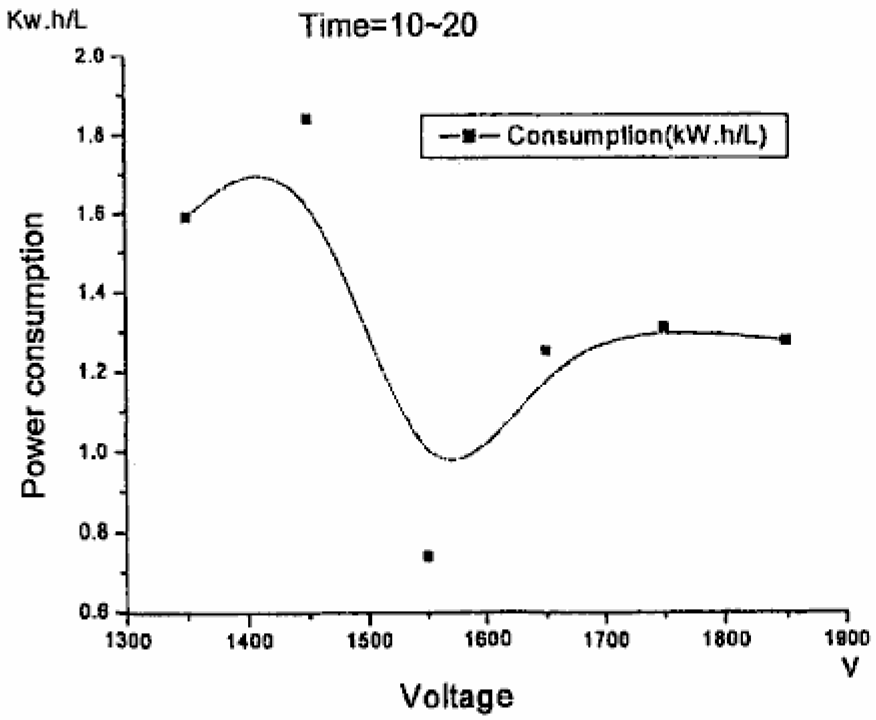

Kw.h/L
Time=10~20
2.0
1.8
1.6
1.4
1.2
1.0
0.8
0.6
Power consumption
Consumption(kW.h/L)
1300
1400
1500
1600
1700
1800
1900
V
Voltage

FIG. 32

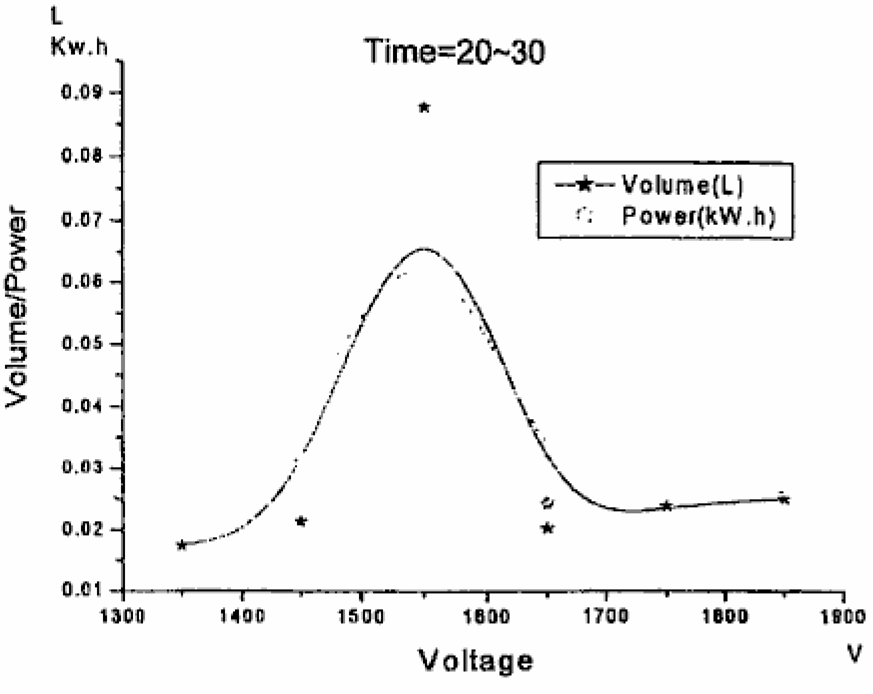

L
Kw.h
Time=20~30
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
Volume/Power
Volume(L)
Power(kW.h)
1300
1400
1500
1600
1700
1800
1900
V
Voltage

FIG. 33

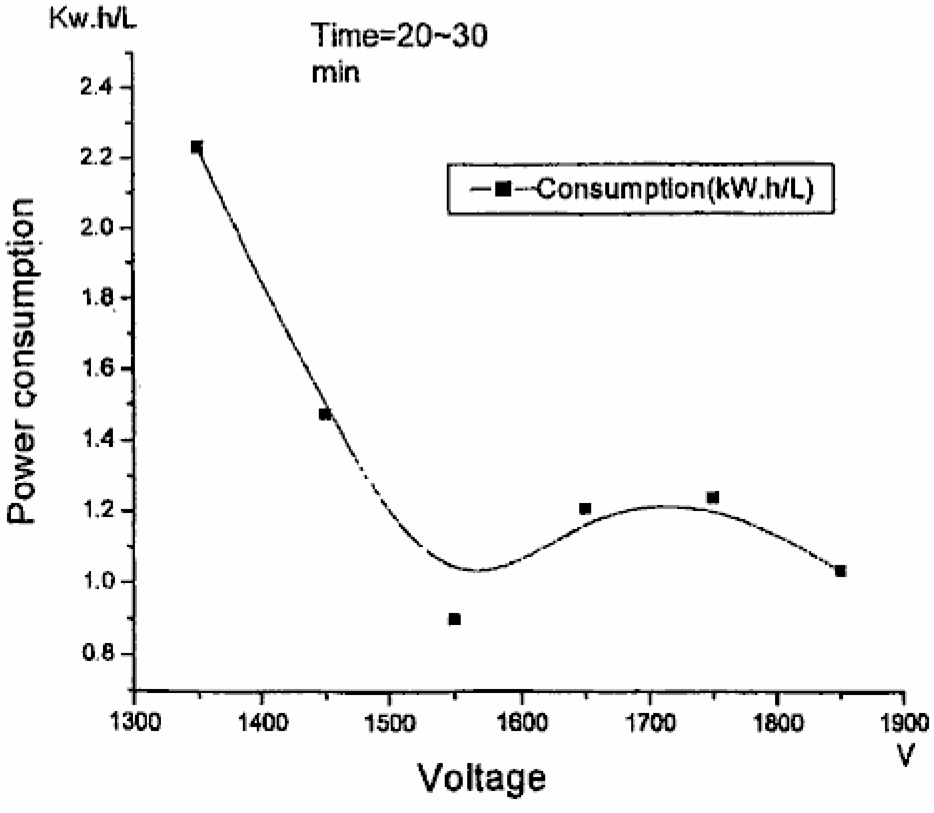

Kw.h/L
Time=20~30 min
2.4
2.2
2.0
1.8
1.6
1.4
1.2
1.0
0.8
Power consumption
—■—Consumption(kW.h/L)
1300
1400
1500
1600
1700
1800
1900
V
Voltage

FIG. 34

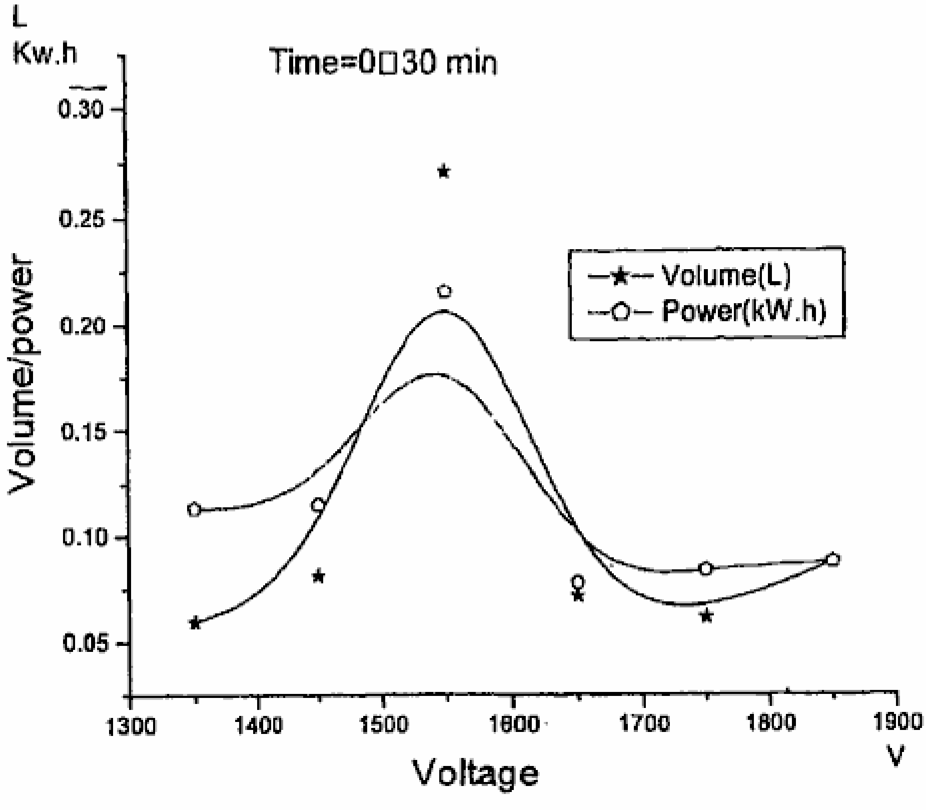

L
Kw.h
Time=0□30 min
0.30
0.25
0.20
0.15
0.10
0.05
Volume/power
—★— Volume(L)
—○— Power(kW.h)
1300
1400
1500
1600
1700
1800
1900
V
Voltage

FIG. 35

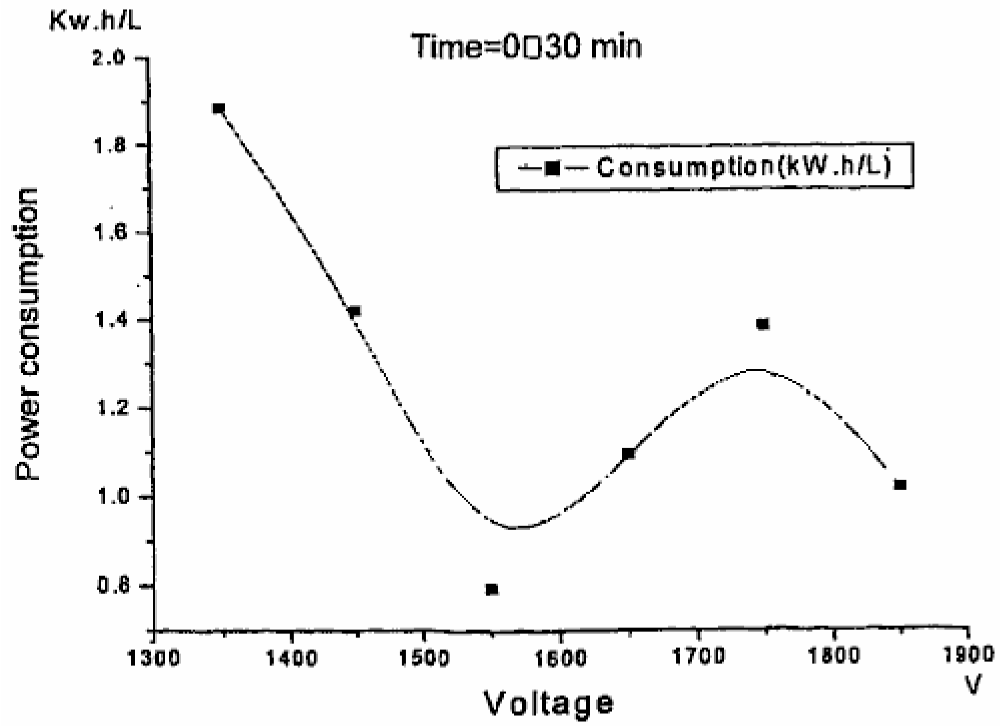

Kw.h/L
Time=0□30 min
Power consumption
2.0
1.8
1.6
1.4
1.2
1.0
0.8
—■— Consumption(kW.h/L)
1300
1400
1500
1600
1700
1800
1900
V
Voltage

FIG. 36

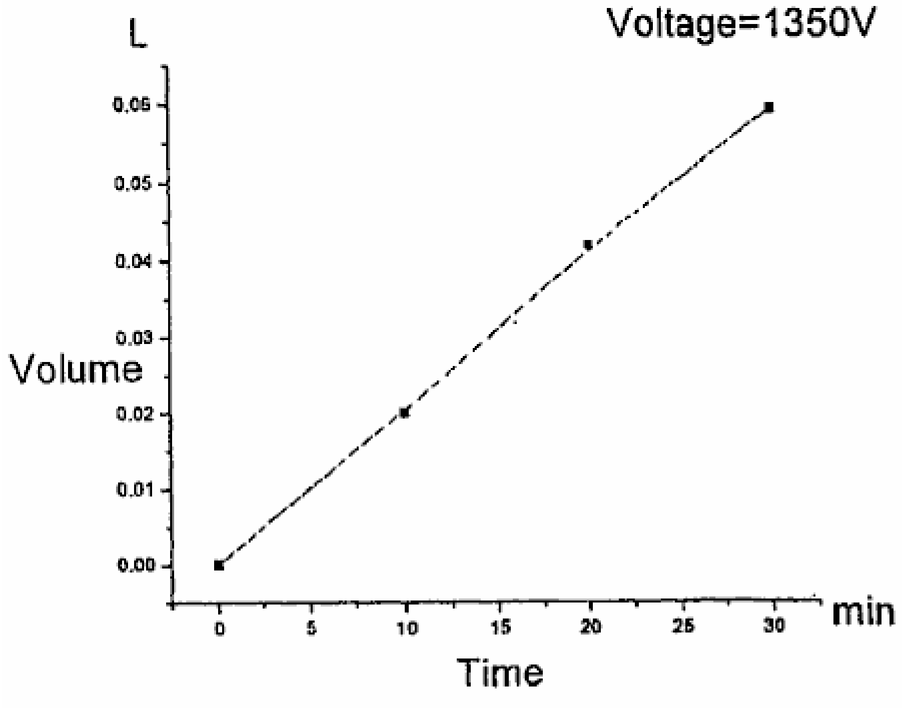

L
Voltage=1350V
Volume
0,06
0,05
0,04
0,03
0,02
0,01
0.00
0
5
10
15
20
25
30
min
Time

FIG. 37

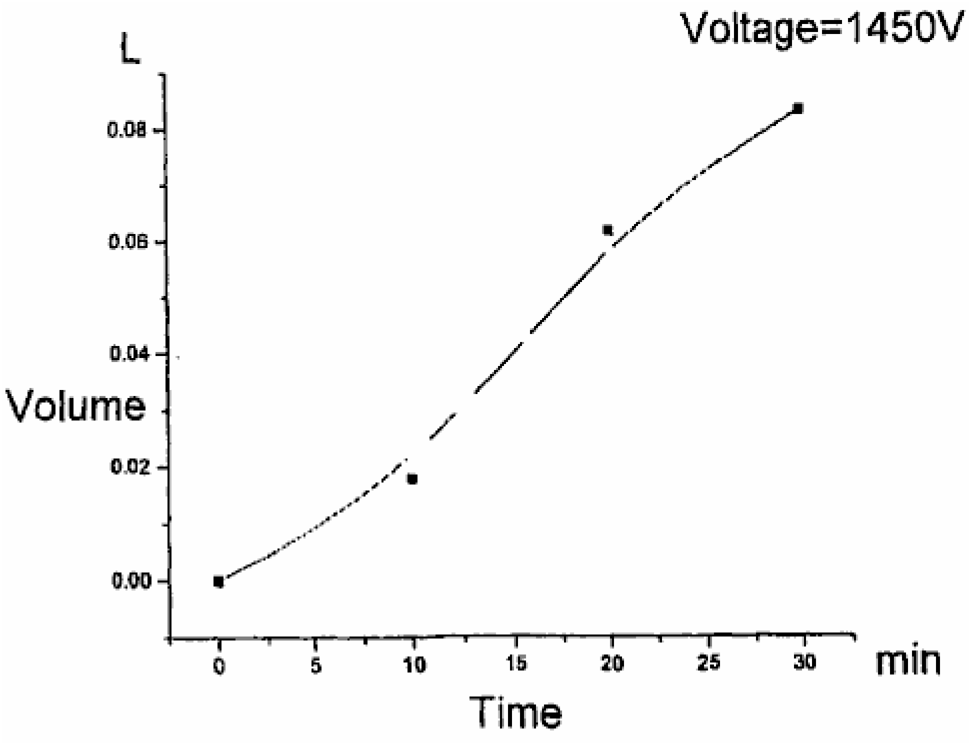

Voltage=1450V
L
0.08
0.06
0.04
Volume
0.02
0.00
0
5
10
15
20
25
30
min
Time

FIG. 38

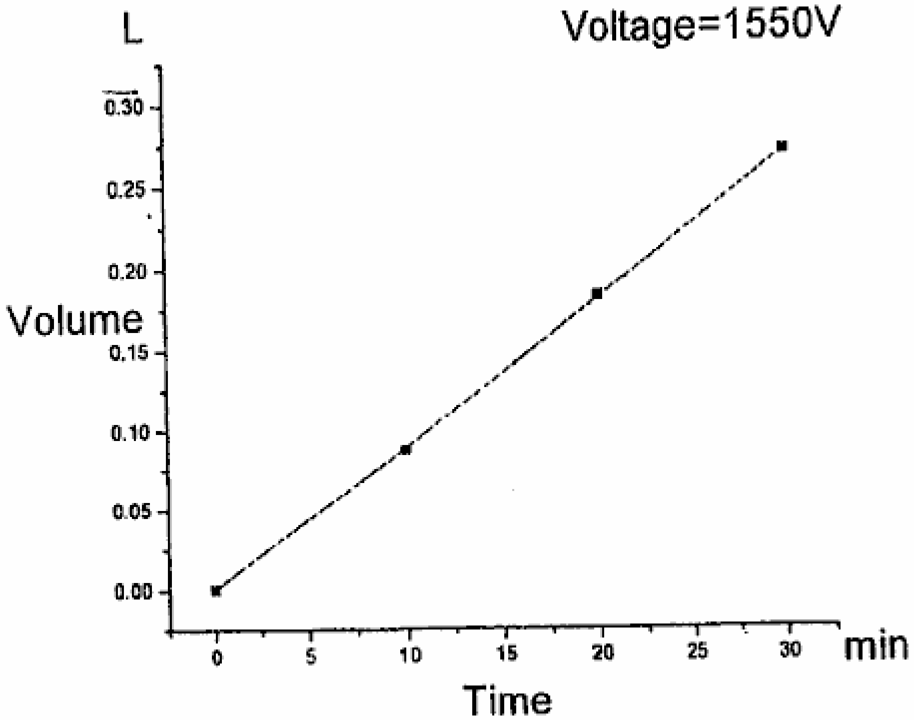

L
Voltage=1550V
0.30
0.25
0.20
Volume
0.15
0.10
0.05
0.00
0
5
10
15
20
25
30
min
Time

FIG. 39

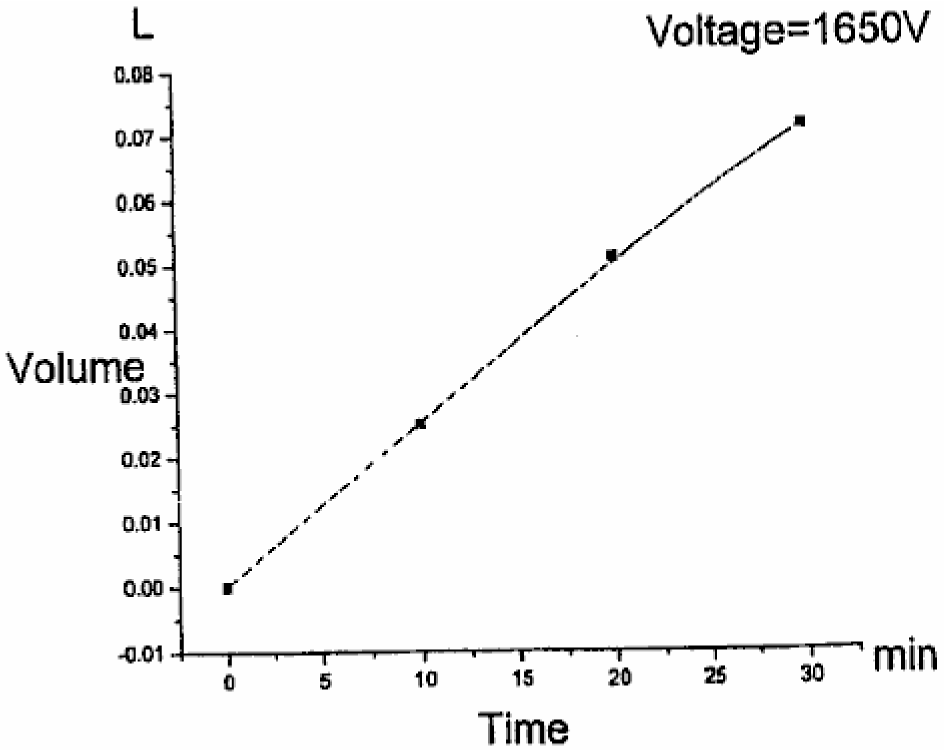

L
Voltage=1650V
0.08
0.07
0.06
0.05
0.04
Volume
0.03
0.02
0.01
0.00
-0.01
0
5
10
15
20
25
30
min
Time

FIG. 40

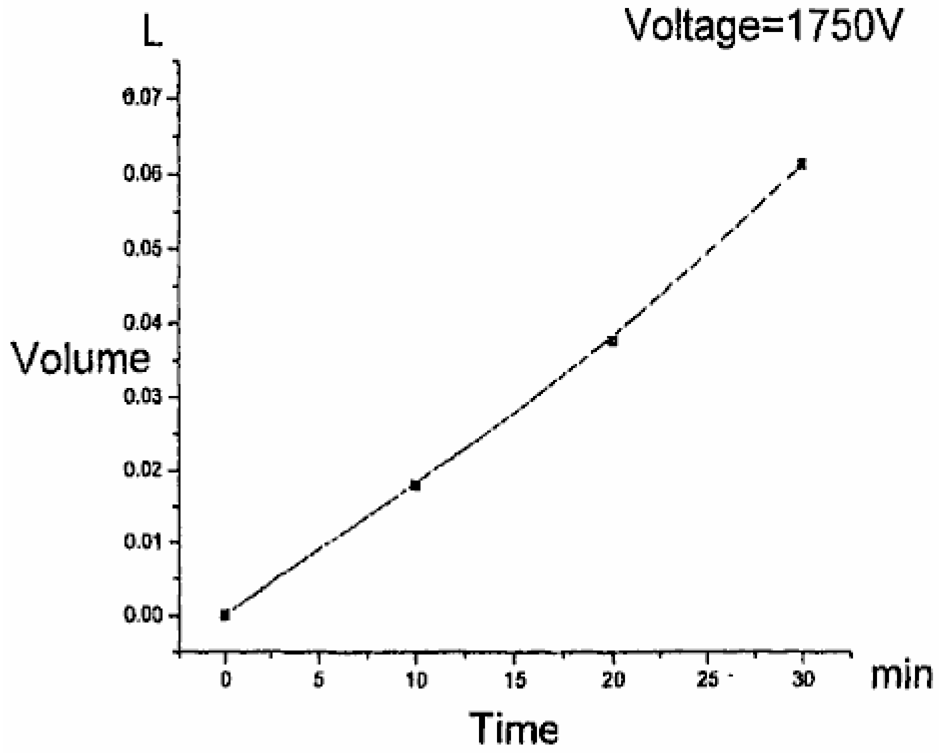

L
Voltage=1750V
0.07
0.06
0.05
0.04
Volume
0.03
0.02
0.01
0.00
0
5
10
15
20
25
30
min
Time

FIG. 41

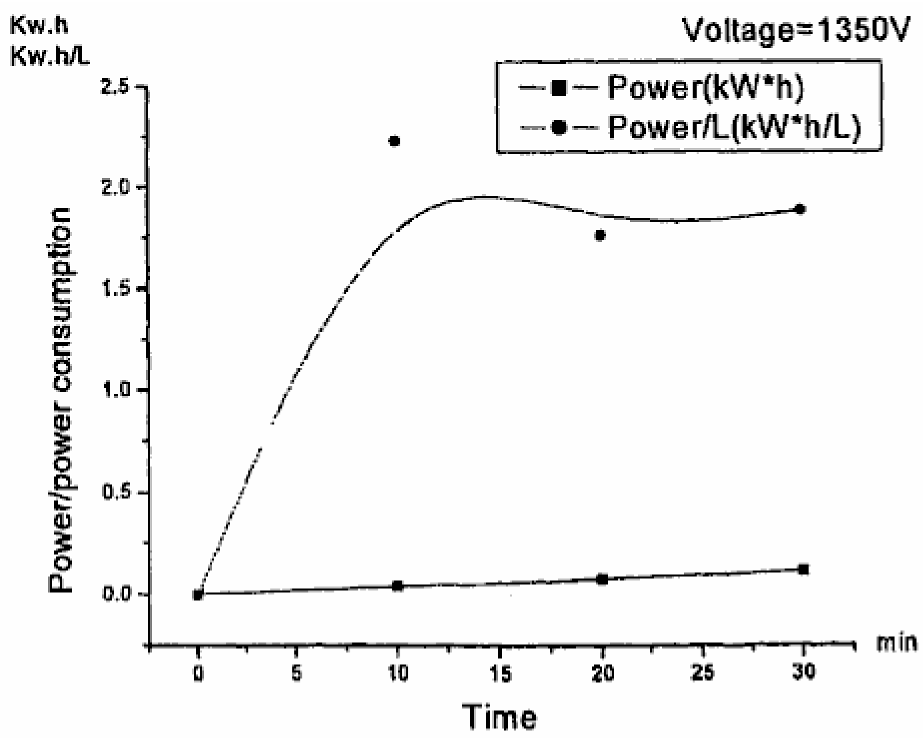

Kw.h
Kw.h/L
Voltage=1350V
—■— Power(kW*h)
—●— Power/L(kW*h/L)
Power/power consumption
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
min
Time

FIG. 42

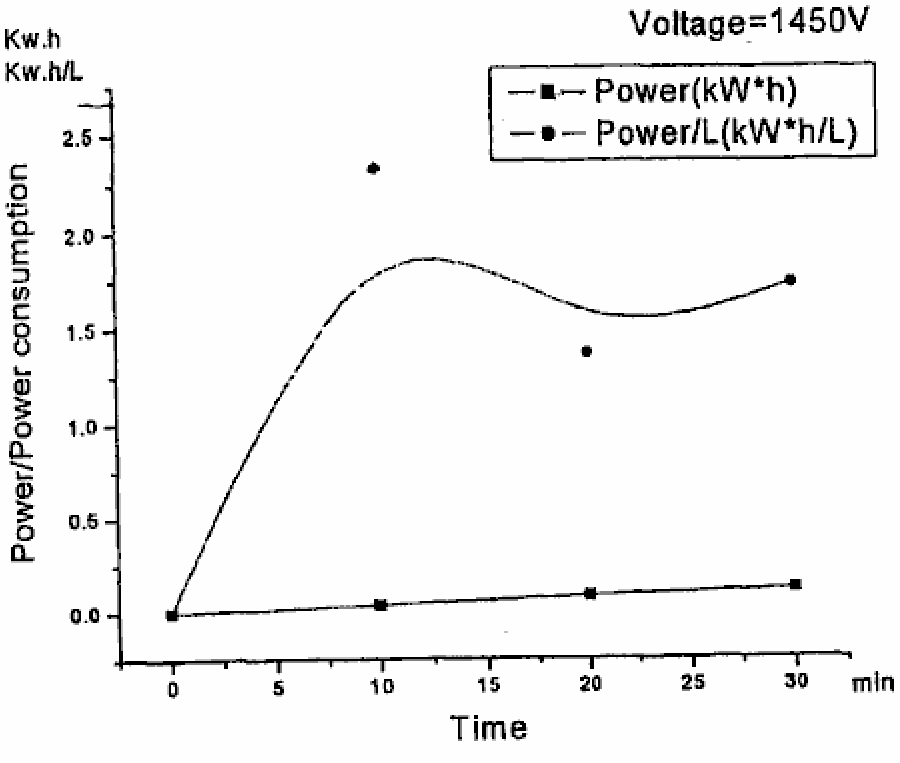

Voltage=1450V
Kw.h
Kw.h/L
—■— Power(kW*h)
—●— Power/L(kW*h/L)
Power/Power consumption
2.5
2.0
1.5
1.0
0.5
0.0
0
5
10
15
20
25
30
min
Time

FIG. 43

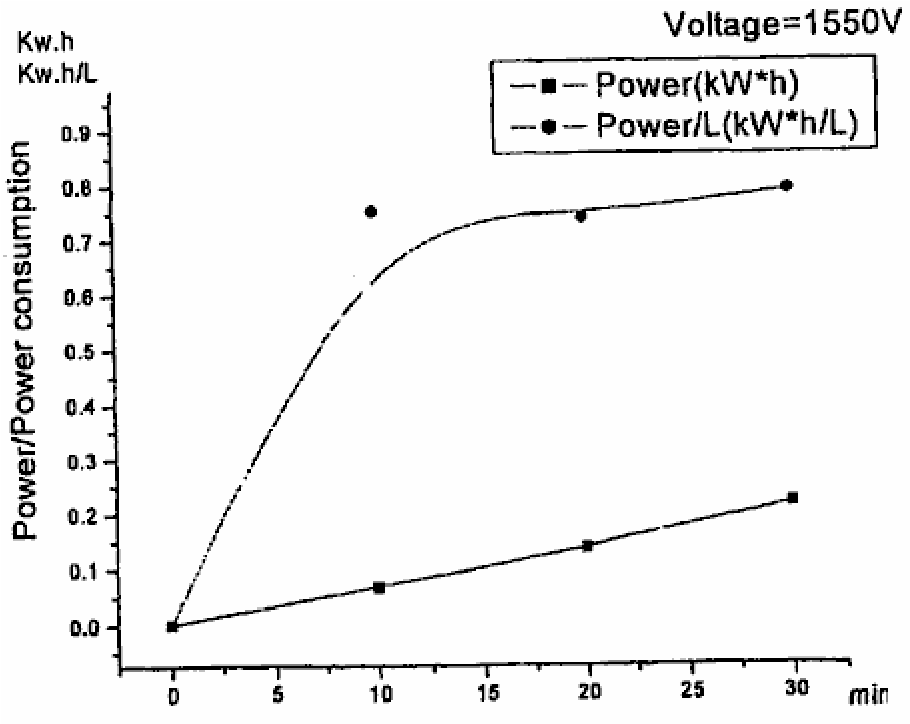

Voltage=1550V
Kw.h
Kw.h/L
—■— Power(kW*h)
—●— Power/L(kW*h/L)
Power/Power consumption
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
5
10
15
20
25
30
min
Time

FIG. 44

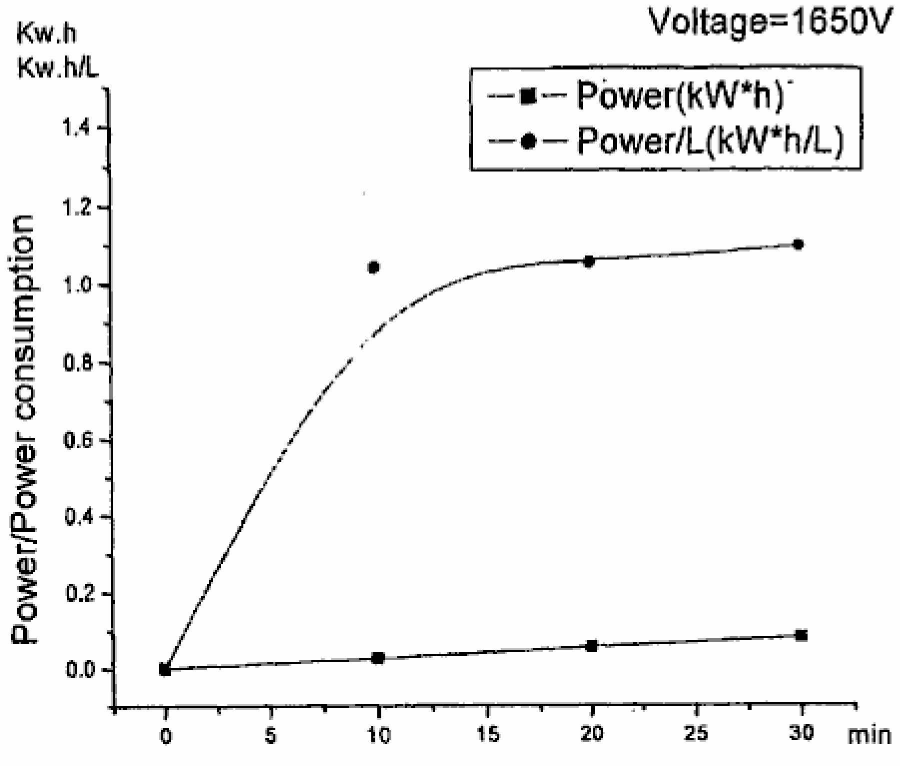

Voltage=1650V
Kw.h
Kw.h/L
—■— Power(kW*h)
—●— Power/L(kW*h/L)
Power/Power consumption
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
min
Time

FIG. 45

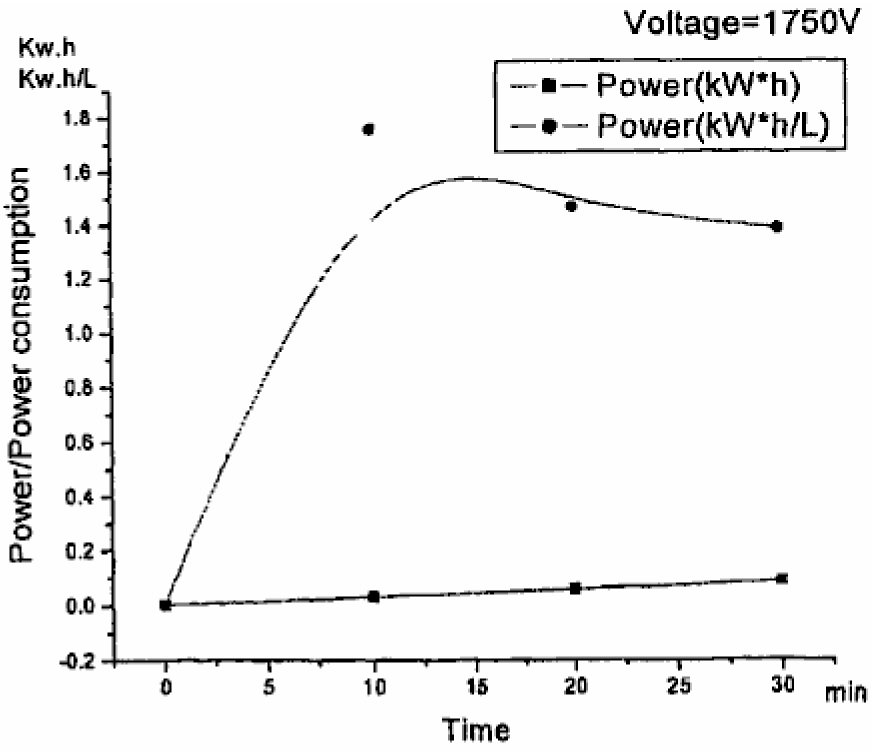

Voltage=1750V
Kw.h
Kw.h/L
Power(kW*h)
Power(kW*h/L)
Power/Power consumption
1.8
1.6
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
0
5
10
15
20
25
30
min
Time

FIG. 46

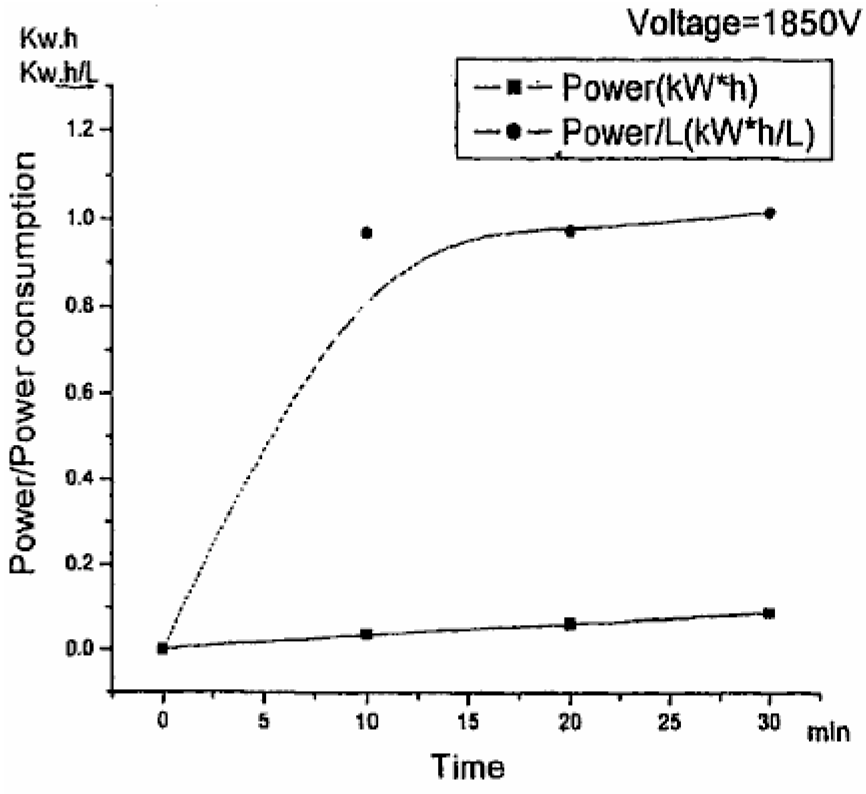

Voltage=1850V
Kw.h
Kw.h/L
Power(kW*h)
Power/L(kW*h/L)
Power/Power consumption
1.2
1.0
0.8
0.6
0.4
0.2
0.0
0
5
10
15
20
25
30
min
Time

FIG. 47

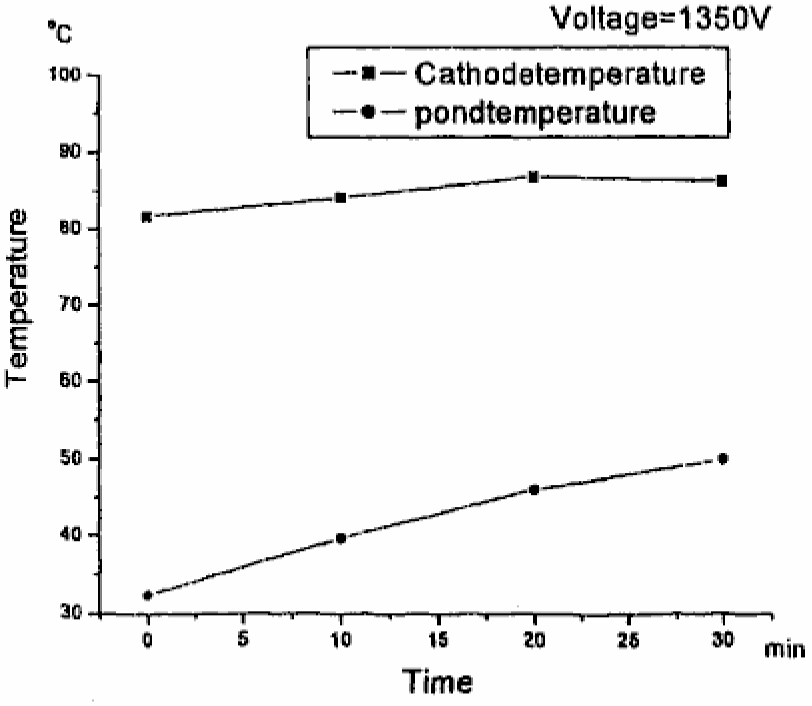

Voltage=1350V
°C
—■— Cathodetemperature
—●— pondtemperature
100
90
80
70
60
50
40
30
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 48

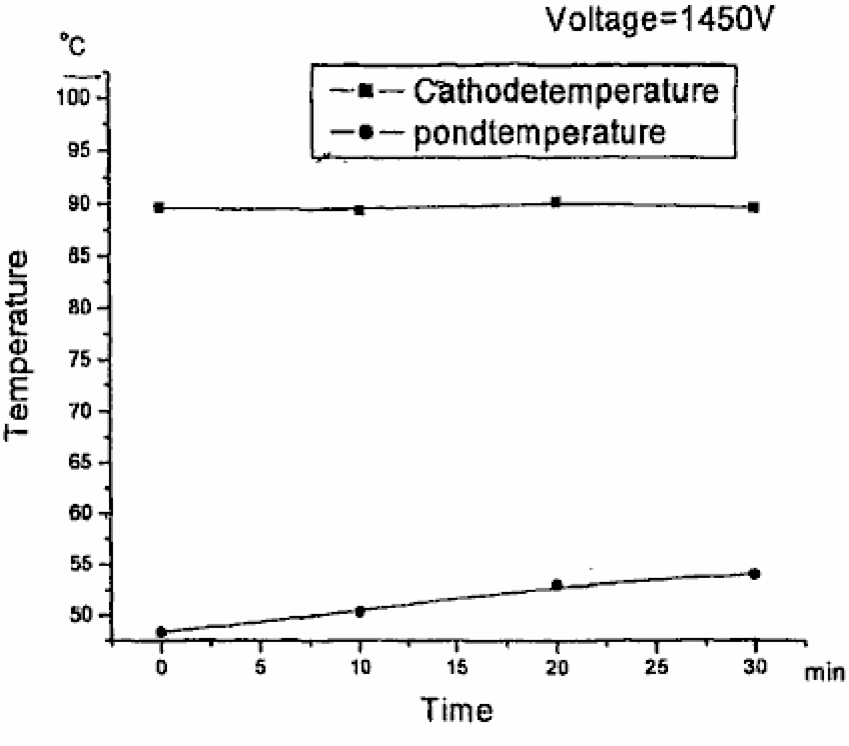

Voltage=1450V
°C
—■— Cathodetemperature
—●— pondtemperature
100
95
90
85
80
75
70
65
60
55
50
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 49

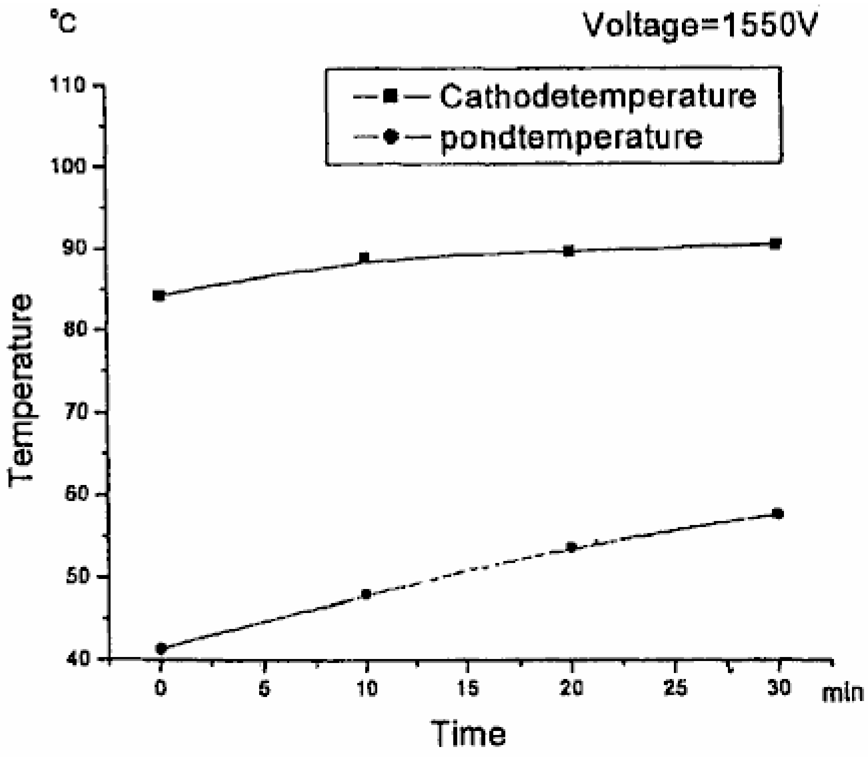

°C
Voltage=1550V
—■— Cathodetemperature
—●— pondtemperature
110
100
90
80
70
60
50
40
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 50

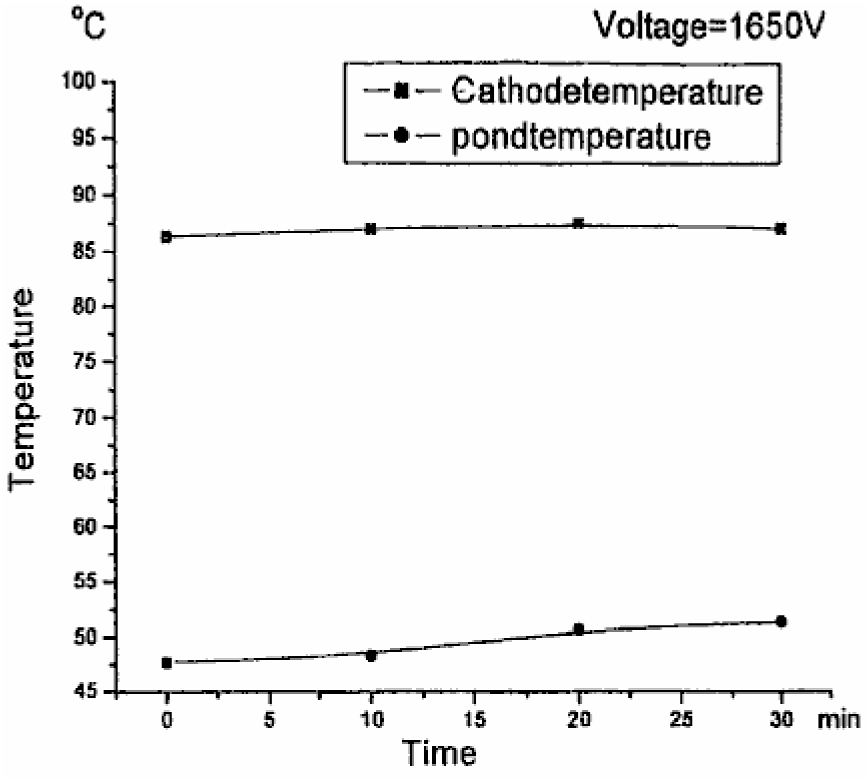
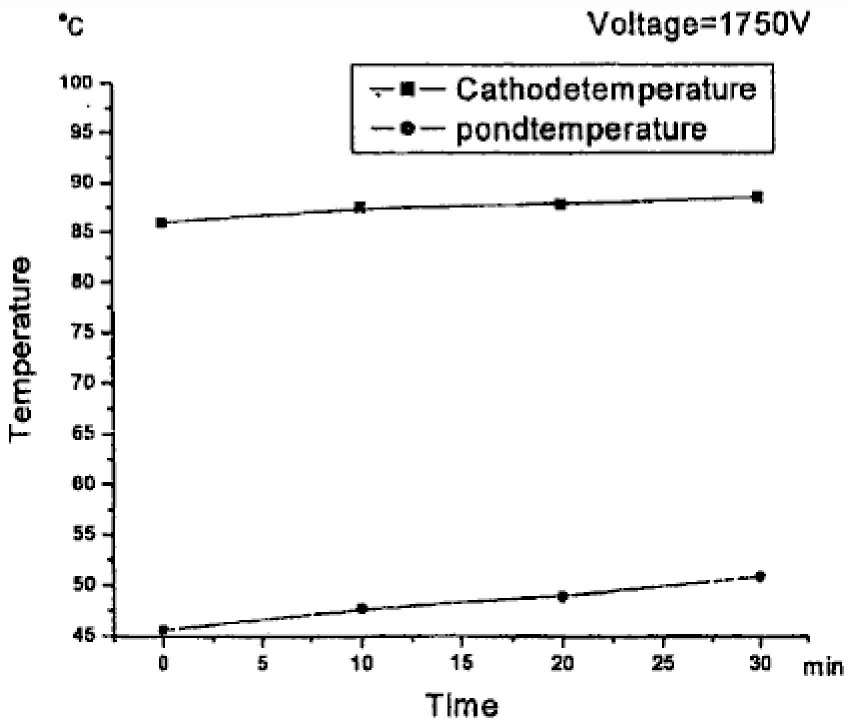
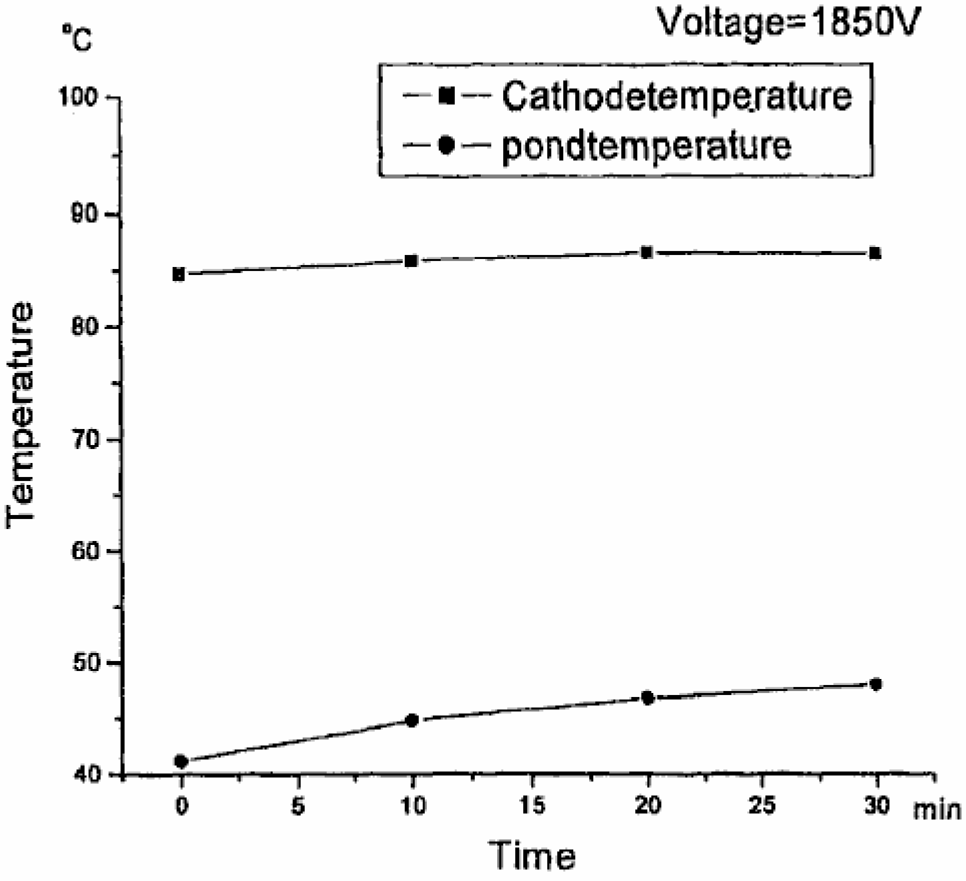

°C
Voltage=1650V
—■— Cathodetemperature
—●— pondtemperature
100
95
90
85
80
75
70
65
60
55
50
45
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 51



°C
Voltage=1750V
Cathodetemperature
pondtemperature
100
95
90
85
80
75
70
65
60
55
50
45
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 52



°C
Voltage=1850V
Cathodetemperature
pondtemperature
100
90
80
70
60
50
40
Temperature
0
5
10
15
20
25
30
min
Time

FIG. 53