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学 位 論 文 要 旨
Dissertation Summary

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論文名：高周波液中プラズマ法による高圧下におけるメタンハイドレート分解

(Dissertation Title) **High Frequency Plasma in Liquid Method for Decomposition of Methane Hydrate under High Pressure**

The search for new energy sources that are both economically viable and ecologically sustainable is becoming one of the most pressing concerns worldwide. The demand for energy has significantly increased due to the growth of world economic and global population. Alternative energy sources such as solar energy, biomass, geothermal power, and tidal power have been considered as solutions to this problem. All of these natural energy resources are believed to reduce our dependency on fossil fuel, which has increased global carbon emission.

Natural gas as an important source of future energy supply has been attracting worldwide interest as oil reserves are being exhausted. Natural gas demand is also expected to increase year to year. World natural gas production increased by 1.1% in 2013, an increase that is slightly below the growth rate of global consumption. Therefore, natural gas is performing an important role as an energy supply for electricity generation through gas turbines as well as an alternative automotive fuel, in recent times.

Hydrogen fuel provides the highest potential advantages in terms of variety of supply and lowered emission of pollutants and greenhouse gasses. It has been proposed as the answer to the problems of air pollution and global warming. It possesses all the key criteria for an ideal fuel substitute for gasoline, heating oil, natural gas, and other fuels, these critera are inexhaustibility, cleanliness, convenience, and independence from foreign control. The electrochemical property of hydrogen is one of its essential and interesting features, due to its ability to be utilized in a fuel cells. In addition, hydrogen production is a large and growing industry with the annual production estimated to be about 55 million tons along with an annual increase in consumption by about 6%.

There are a wide variety of processes is available for the purpose of hydrogen production from gaseous or liquid fuels, all of which vary according to the nature of the primary fuel and the chemical reactions involved. The application of plasma technologies to hydrocarbon reforming for the production of hydrogen has been progressively attracting attention on a global scale. Some of its characteristics that have attracted consideration are its fast ignition, its compatibility with a wide range of hydrocarbons, the removal of catalyst sensitivity to trace impurities in the gas stream, and its compactness. Within plasma there is a variety of chemically active species and energetic electrons which can greatly promote reforming chemistry. The advantages of high product selectivity by use of thermal catalysis and the fast startup from plasma technique have are combined by integrating plasma and thermal catalysis. The overall reforming reactions in plasma reformation are the same as conventional reformation, however, for the reforming reaction, energy and free radicals are provided by plasma.

In addition, plasma can be generated within a liquid by an underwater electrode providing high frequency or microwave irradiation. Plasma can exist despite the presence of a liquid via vapor generated from the liquid evaporation by the heat of plasma. In order to achieve breakdown generation as well to obtain the desired processing application of plasma discharge in liquids, HV, high-power discharges are generally required. The high energy from a power source is first used to evaporate the liquid surrounding the HV electrode, generating gas bubbles that are subsequently ionized by large electric fields produced by the HV. Furthermore, radio frequency (RF) or microwave (MW) irradiation has been applied for generating plasma in liquid in the chemical fields concerned with the direct decomposition of the liquids itself for hydrogen production. Nomura et.al in 2003 reported the establishment of plasma within bubbles created in a hydrocarbon liquid, which was simultaneously irradiated by both ultrasonic waves and microwaves.

As a fuel/energy source, however, the valuable active element of "natural gas" is methane. It can be obtained from gas hydrates. Gas hydrates are also called methane hydrate or chemical clathrates. Gas hydrates are potentially one of the most important energy sources for the future. Methane gas hydrate is a crystalline solid formed by the combination of methane and water in a low temperature and high pressure environment and enormous reserves of hydrates can be found under the oceans on continental shelves and on land in permafrost. The amount of organic carbon in gas hydrates is estimated to be twice that of all other fossil fuels. Unfortunately, methane emission as a greenhouse gas has a higher effect on global warming than CO_2 emissions with a warming potential of 21 to 25 times that of CO_2. A single cubic meter of methane hydrate may contain 170 m^3 of methane. The methane in gas hydrates is dominantly produced by bacterial degradation of organic substance in low-oxygen surroundings near the seafloor. Three processes have been recommended for dissociation of methane hydrates: thermal stimulation, depressurization, and inhibitor injection.

Because the methane hydrate resources are accumulated in ocean floor sediments at depths exceeding 400 meters at low temperature and high pressure, it is essential to generate a stable plasma in seawater under high pressure. Discharge in seawater is very difficult and requires considerably high voltage. Plasma had been generated in sea water with 5 kW power using a fourth generation plasma reactor as well as with plasma air flotation with 1.2 kW of power. Some studies have been reported about plasma generation at atmospheric pressure, but only a limited number has been investigated under high pressure.

Therefore, this dissertation proposes the main objective of producing fuel gas directly from the decomposition of methane hydrate by applying 2.45GHz microwave plasma irradiation and 27.12MHz radio frequency plasma irradiation at atmospheric pressure, also investigating the feasibility of plasma irradiation under high pressure levels for hydrogen production by applying argon plasma jets as an alternative method.

The excitation temperature in the pressure range of 0.1 to 2.0MPa increased from 4477 to 7576K with an increase of gas pressure, whereas it reduced from 3960 to 2082K with an argon flow rate in the range of 100 to 3000mL/min. When plasma was generated under high pressure in pure and artificial seawater, the excitation temperature decreased with an increase in pressure from 10 kPa to 300 kPa from about 4800K to 3500K in pure water and 3300K to 2300K in seawater. Additionally, the enthalpy required during the process tended to remain constant for the methane hydrate dissociation reaction (MHD), whereas for the other basic reactions, i.e. steam methane reforming (SMR) and methane cracking reaction (MCR) it tended to increase. At present, the steam methane reforming reaction is the dominant method for methane conversion into hydrogen.

The research in the present dissertation has determined that hydrogen production from methane hydrate is feasible under atmospheric pressure by using 2.45MHz microwave and 27.12MHz radio frequency plasma sources. Also it has become feasible under high pressure levels by applying argon plasma jets, even though the hydrogen production efficiency is less than that for radio frequency plasma in-liquid. Therefore, a process with the ultimate goal of producing hydrogen from hydrate fields on the seabed and in permafrost regions using an in-liquid plasma method is viable. From the aspect of practical use, the author believes that methane held in gas hydrates are a foreseeable source of hydrogen and could contribute to hydrogen production for the future.