

**For Sustainable Development  
of the Whole World  
by  
Renewable Energy**

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## Preface

The atmospheric carbon dioxide concentration exceeded 400 ppm which will be a threat to survival of many living things. If gentle green renewable energy is easily and sufficiently available for all people in the whole world, conflicts in the world will decrease. For prevention of global warming and for avoiding complete exhaustion of fossil fuels we have been studying since the 1980s electrolytic hydrogen production using electricity generated by renewable energy and methane formation by the reaction of hydrogen with captured carbon dioxide to supply renewable energy in the form of synthesized natural gas, methane by which the whole world can survive and keep sustainable development. Professor Emeritus Maria Janik-Czachor, Institute of Physical Chemistry, Polish Academy of Sciences kindly recommended the author to write this book for summarizing our research and development.

The detailed science of key materials for hydrogen production by water electrolysis and for methane production is written in 8. Key Materials for Global Carbon Dioxide Recycling. If the reader is not particularly interested in related chemistry in detail, the reader may skip 8. Key Materials for Global Carbon Dioxide Recycling in reading.

We are facing the critical situation in global warming because the increasing rates of atmospheric carbon dioxide concentration and global temperature are remarkably high. The recent extreme weather is frequently causing the disasters with many dead persons in the whole world. We have to convert urgently to use only renewable energy without fossil fuel combustion by the cooperation of the world. The renewable energy sources are superabundant on our planet. The author hopes for the world to understand that the current and future technologies of the world can provide sufficiently renewable energy for all people in the whole world to live peacefully and happily keeping sustainable development without fossil fuel combustion and nuclear power generation.

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## **1. The Gift of Our Planet**

Hundreds of millions of years ago, bodies of organisms were buried in sedimentary layers under high temperature and pressure, and deteriorated to fossilized matters. These are coal, petroleum and natural gas. They are the gift of our planet. They have been used from ancient time as flammable stone and flammable water, but mass consumption of coal, petroleum and natural gas was long afterward.

Industrial revolution, the process change from handicraft economy to industrial and machine manufacturing economy begun in Great Britain in the 18th century. This transition included going from hand production methods to machines, new chemical manufacturing and iron production processes, and the increasing use of steam power. Remarkable technological innovation of power sources by exploitation of steam engine enabled establishment of machine industry and mass transportation of passengers and cargos. After industrial revolution, the expansion of consumption of fossil fuel has always supported economic growth. Our activity induced a continuous increase in atmospheric carbon dioxide concentration since the industrial revolution.

We ourselves had experienced steady increase in the world fossil fuel consumption through the post world war II economic expansion until now. Living in the world of the high economic growth we became worried in the 1970s how long we can continue to consume natural resources of the Earth at such a high rate and we were afraid of complete exhaustion of all the gift of the Earth including those reserved for hundreds of millions of years for fossilization

In that era the term “minable year” begun to be used: That is how many years are minable the reserve at the current production rate. Listening to the numerical value of the minable year we were convinced that we do still no need to worry about complete exhaustion of resources. That was, however, wrong. The current rate of production that is the base of the calculation of the minable year increases every year. Thus, now we learned that the minable year is untrustworthy.

## **2. Dream of Hydrogen Energy-Based Society**

In the early 1970s we who knew some electrochemical industries such as electrochemical deposition of gold, copper, nickel and other metals, chlor-alkali

industry to form sodium hydroxide and chlorine by electrolysis of aqueous sodium chloride solutions, etc. were thinking to supply hydrogen to the whole world producing hydrogen by electrolysis of seawater using electricity generated by solar cell installed on rafts floating on sea.

At the same time we felt the difficulty to use hydrogen as fuel. As has been well known by the disaster of hydrogen airship Hindenburg on May 6, 1937, because hydrogen explodes when air includes 4.0-75 % hydrogen, the common people cannot handle hydrogen easily. Furthermore, transportation of liquefied hydrogen cannot be adopted because almost all combustion energy of hydrogen will be consumed by liquefaction: Liquefaction of hydrogen by cooling it to lower than the boiling point of hydrogen of -252.6 degrees Celsius consumes the electric power of 10-14 kWh per 1 kilogram hydrogen, that is 30-40 % of combustion energy of hydrogen, in spite of the fact that the thermal power generation efficiency itself is generally about 40 % or less. In addition, the hydrogen storage vessel must be resistant to repetitive thermal shock of cooling to -253 degrees Celsius and heating to ambient temperature.

At that time we were, however, thinking that if hydrogen were only the major fuel for survival of the whole world we have to solve these problems.

Furthermore, facing to violent human activities we ourselves begun to worry that complete consumption of resources and emissions of wastes may change nature.

### **3. Global Temperature and Atmospheric Carbon Dioxide Concentration**

We know that our planet Earth has been warmed by the Sun and is the only place in our solar system where life can and does exist on the surface. This is due to a number of factors, in particular to the Earth's position relative to the Sun. Being in the habitable zone and due to existence of an atmosphere, the Earth is able to maintain a stable average temperature 14 degrees Celsius on its surface that allows for the existence of warm circulating water on its surface, and conditions favorable to life.

If the atmosphere is not present on the Earth, the incoming radiation from the Sun is directly outgoing to space, and the average surface temperature would be minus 18 degrees Celsius.

Fortunately, our planet has the atmosphere. About 30 % of the solar energy that arrives at the top of the Earth atmosphere is reflected back to space by clouds,

atmospheric particles, or bright ground surfaces like sea, ice and snow. This energy plays no role in Earth's climate system. About 20 % of incoming solar energy is absorbed in the atmosphere by water vapor, carbon dioxide, dust, and ozone, and about 50 % passes through the atmosphere and is absorbed by the surface. Thus, about 70 % of the total incoming solar energy is absorbed by the Earth system, the oceans, the lands and the atmosphere. As the oceans, lands and atmosphere heat up, they release heat in the form of infrared thermal radiation, which passes out of the atmosphere and into space. Gas molecules in the atmosphere, water vapor, carbon dioxide, methane, nitrous oxide, other gases absorb thermal infrared radiation and affect the climate

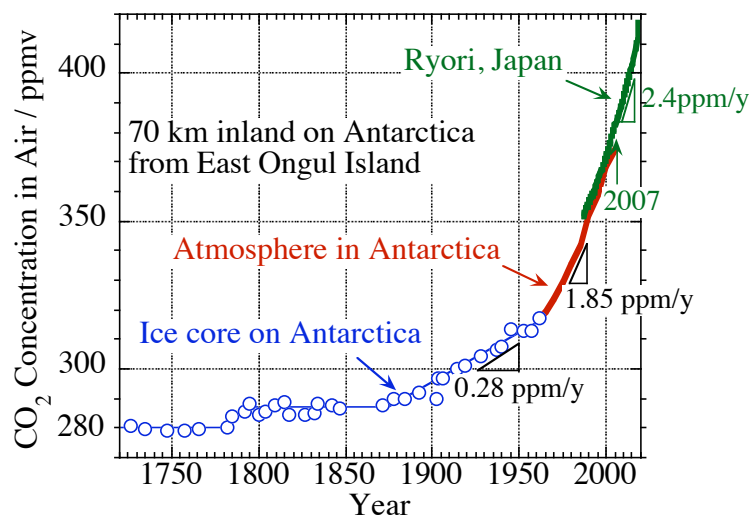


Figure 1 Historical carbon dioxide record in ice core and atmospheric carbon dioxide concentration in Antarctica at 70km north from East Ongul Island [1] and atmospheric carbon dioxide concentration in Ryori, Japan [2].

system. These types of gases are called greenhouse gasses. As far as the carbon exchange keeps a balance in biogeochemical carbon cycle among the biosphere, pedosphere, geosphere, hydrosphere, and atmosphere, the presence of carbon dioxide in the atmosphere does not induce the climate change of the world average temperature of 14 degrees Celsius.

Historical change in atmospheric carbon dioxide concentration exhibits how the current level is in the hazardous situation. The carbon dioxide analysis of air contained in ice core was carried out at 70 km inland on Antarctica from East Ongul Island in addition to the direct analysis of atmosphere [1]. Figure 1 shows the atmospheric carbon dioxide concentrations obtained by analyses of the ice core and the atmosphere on Antarctica [1] and those in a rural fisherman area, Ryori, Iwate, Japan [2]. The increasing pattern

of the atmospheric carbon dioxide concentration in Japan is almost the same as that measured on Antarctica. The difference in numerical values between Japan and Antarctica is only 3-4 ppm, indicating the fact that once carbon dioxide emitted to the atmosphere it is well mixed in all over the surface of our planet, although the atmospheric carbon dioxide concentration in warmer regions on the Earth is slightly higher because the solubility of carbon dioxide in the colder sea is higher than that in the warmer sea as will be mentioned later.

We had been living in the atmosphere containing about 280 ppm (part per million) carbon dioxide since the prehistory to the industrial revolution. After the industrial revolution the use of steam engines led to an increase in the atmospheric carbon dioxide concentration. From the 1870s to 1970 the concentration of carbon dioxide in the atmosphere increased at almost constant rate of about 0.28 ppm every year. In this period starting with the rise of imperialism and militarism in Europe and Asia, through two World Wars, and high economic growth of developed countries, industrial development continued in developed countries. Since 1970 the increasing rate of the atmospheric carbon dioxide concentration has significantly risen, because carbon dioxide emissions by developed countries are too high to be treated on our planet, and carbon dioxide has been accumulating in the atmosphere with a very high rate of about 1.85 ppm every year. After 2007 until 2017 the atmospheric carbon dioxide concentration has been increasing at a much faster rate of about 2.4 ppm every year. Thus, the current concentration of carbon dioxide in the atmosphere reached 415 ppm in 2018.

According to Intergovernmental Panel on Climate Change (IPCC) Fourth Assessment Report: Climate Change 2007 [3,4], such a high atmospheric carbon dioxide concentration dates back to 3.5-2.5 million years ago in Pliocene epoch. In the Pliocene the continents and ocean basins had nearly reached their present geographic configuration. Atmospheric carbon dioxide concentrations in the Pliocene were between 360 to 400 ppm. Mean global temperatures were about 2 degrees to 3 degrees Celsius above pre-industrial temperature, and sea level was at least 15 to 25 m above modern levels.

Regarding to Pliocene Epoch, Figure 2 [5] shows the temperature change from 5.2 million years ago to the present. The temperature is expressed by  $\delta^{18}\text{O}$ . The archaic air temperature has been estimated by the isotope analysis of oxygen or

hydrogen. The mass of an atom is determined by mass number, that is, the sum of numbers of proton and neutron in an atomic nucleus. The mass number of the most of oxygen atoms is 16,  $^{16}\text{O}$ , but the mass number of about 0.2 % of oxygen is 18,  $^{18}\text{O}$ . Thus, the water,  $\text{H}_2\text{O}$  with  $^{18}\text{O}$  is also present, which is heavier than the most of water molecule consisting of  $^{16}\text{O}$ . In general, ordinary water evaporates preferentially. At lower temperatures, evaporation of heavier water is particularly difficult in comparison with ordinary water. Thus, the higher the  $^{18}\text{O}$  in seawater the lower is the temperature in both sea and atmosphere. In paleosciences, the data of the ratio  $^{18}\text{O}/^{16}\text{O}$  from corals, foraminifera and ice cores are used as a proxy for temperature. The definition is, in "permillage " (‰, parts per thousand),  $\delta^{18}\text{O}$

$$\delta^{18}\text{O} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \times 1000 (\text{‰}) \quad (1)$$

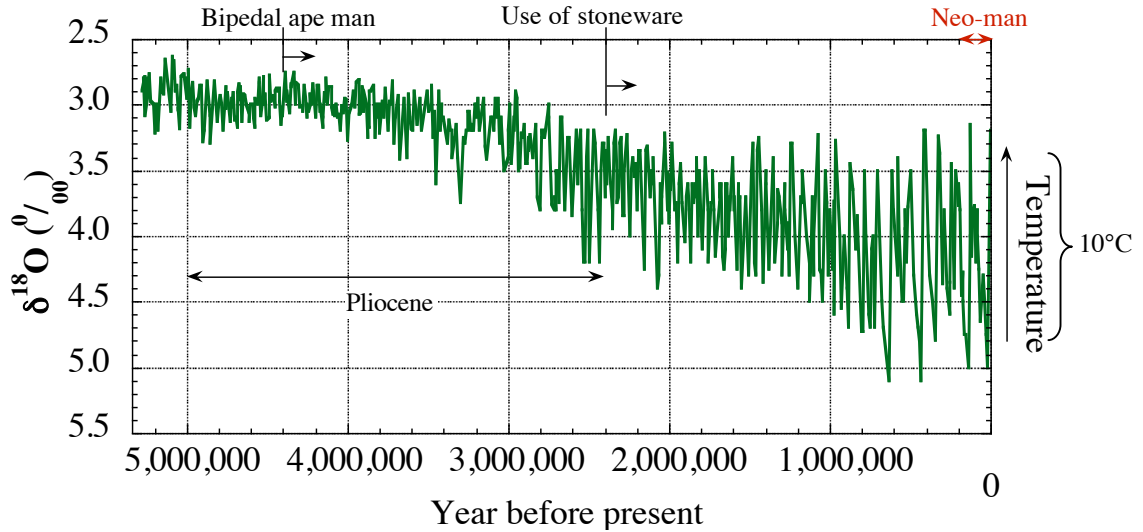


Figure 2 Analytical results of  $\delta^{18}\text{O}$  of benthic foraminiferal calcite from 57 globally distributed sites [5].

The foraminifera formed their calcite shells using water when they lived. If the  $^{18}\text{O}/^{16}\text{O}$  ratio is analyzed from foraminiferal calcite piled-up in sea bottom, the higher the  $\delta^{18}\text{O}$  value, the lower was the temperature at the time when they lived. As shown in Figure 2 [5], the temperature estimated by isotope analysis of benthic foraminiferal calcite from 57 globally distributed sites decreased from 3.5 million years ago in Pliocene spending 2.5 million years, because of a decrease in the



atmospheric carbon dioxide concentration. In Figure 2 historical temperature shows oscillation particularly after a million years ago, by which a better understanding of climate is difficult. For historical climate properties of much shorter periods from 420,000 years ago to the present, an interesting joint work by France, Russia and the United State had been performed. In 1998 they drilled ice core at the Russian Vostok station in East Antarctica to a depth of 3,623 meters to get piled up ice core samples for analysis of historical data of climate. Since the ice core formed from the incremental buildup of annual layers of snow, the ice core dating was performed using estimation of annual layers combined with a set of various age markers along the core such as  $^{10}\text{Be}$  [6]. The well known age maker for dating is  $^{14}\text{C}$ . Both radioactive  $^{14}\text{C}$  and  $^{10}\text{Be}$  are formed by the cosmic ray spallation of nitrogen and mainly oxygen, respectively, and change by  $\beta$  decay to stable nitrogen and boron. Although  $^{14}\text{C}$  having a half life of 5,730 years is used for dating of at most 26,000 years ago,  $^{10}\text{Be}$  has a half life of 1.387 million years and thus  $^{10}\text{Be}$  fallen on the snow was used as the marker of far older ages. The decrease from their new born amounts by decay corresponds to the age.

The resulting ice core samples extended to about 420,000 years ago. Gas extraction and measurements were performed by crushing the ice sample under vacuum without melting it for analysis of the carbon dioxide concentrations in the ancient air.

The air temperature was also estimated by the isotope analysis of melted ice samples. If evaporated water stays on a land in the form of deposited snow the ratio of heavier water to ordinary water is maintained in the piled up snow which formed the ice core. For estimation of ancient temperature not only the ratio of  $^{18}\text{O}/^{16}\text{O}$  but also the ratio of D/H can be used. Heavier hydrogen, Dueterium,  $^2\text{D}$ , is 0.0156 % of hydrogen, but the difficulty for evaporation of HDO in colder water, that is the fractionation factor is larger than  $\text{H}_2^{18}\text{O}$ . Thus, if the isotope analysis is carried out for oxygen,  $\delta^{18}\text{O}$  and/or hydrogen,  $\delta\text{D}$ , one can estimate the air temperature at the time when water evaporation occurred forming the ice core analyzed.

The joint research of France, Russia and the United State revealed historical changes of temperature and atmospheric carbon dioxide concentration [7-12] as shown in Figures 3 [7] and 4 [9], respectively. Figure 3 in which  $\delta\text{D}$  was used [7] exhibits 4 glacial cycles in 420,000 years. Each cycle consisted of a glacial period and a short warm interglacial period of 15,000-20,000 years. The temperature difference between glacial and interglacial periods was about 10-12 degrees Celsius. Our present

interglacial period began about 11,000 years ago.

These climatic patterns had been described by Milancovich cycles [13], where the Earth temperature is essentially determined by the density of solar irradiation on our

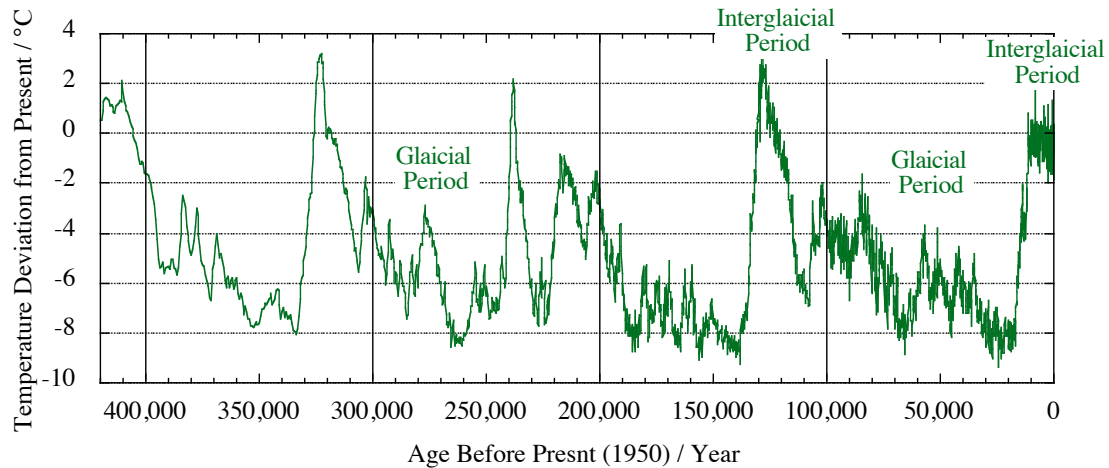


Figure 3 Historical isotope temperature estimated from Vostok ice core in Antarctica [7].

planet depending upon the distance between our planet and the Sun. Serbian geophysicist and astronomer Milutin Milancović had theorized in the 1920s that variations in orbital eccentricity, axial tilt and axial precession of the Earth's orbit strongly influence the climatic patterns. The shape of the Earth's orbit varies in time between nearly circular and mildly elliptical. The major component occurs on a period of 413,000 years. A number of other terms vary between components 95,000 and 125,000 years and loosely combine into a 100,000-year cycle. The change in distance between the Earth and the Sun of 18.27 billion meters in maximum mainly affects the amount of solar irradiation.

The angle of the Earth's axial tilt varies with respect to the plane of the Earth's orbit. These obliquity variations are roughly periodic between 21.5 and 24.5 degrees, taking approximately 41,000 years. This also affects the solar irradiation.

Precession in the direction of the Earth's axis of rotation is due to the tidal forces almost equally exerted by the Sun and the Moon with periods of 18,000-23,000 years. This further affects the solar irradiation.

The temperature pattern seen in Figure 3 has been roughly explained by these relations between the Sun and the Earth.

Figure 4 indicates that the change in carbon dioxide concentration in air was generally synchronized with the temperature change seen in Figure 3. As shown in

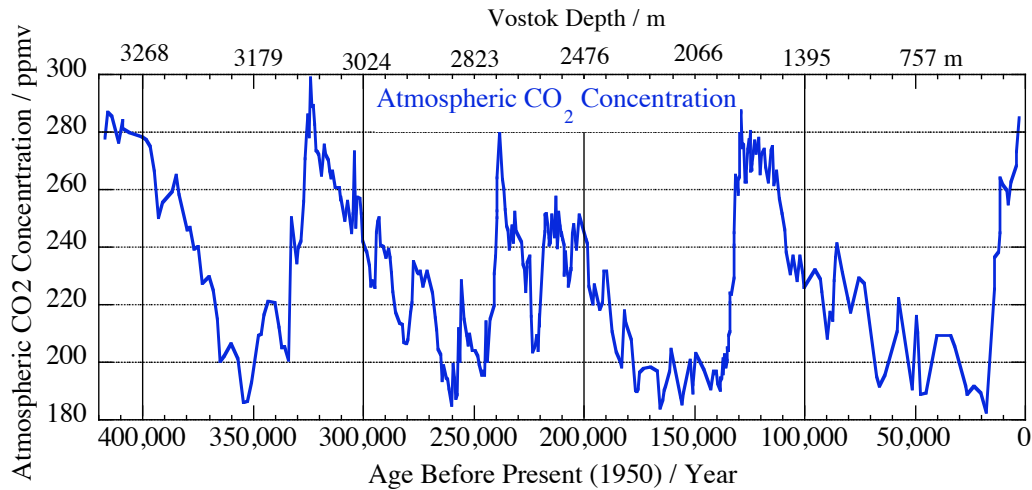


Figure 4 Historical carbon dioxide record in Vostok ice core on Antarctica [9].

Figure 5, when Figure 4 is superposed on Figure 3, changes in the atmospheric carbon dioxide concentration followed in the wake of changes in temperature. The carbon

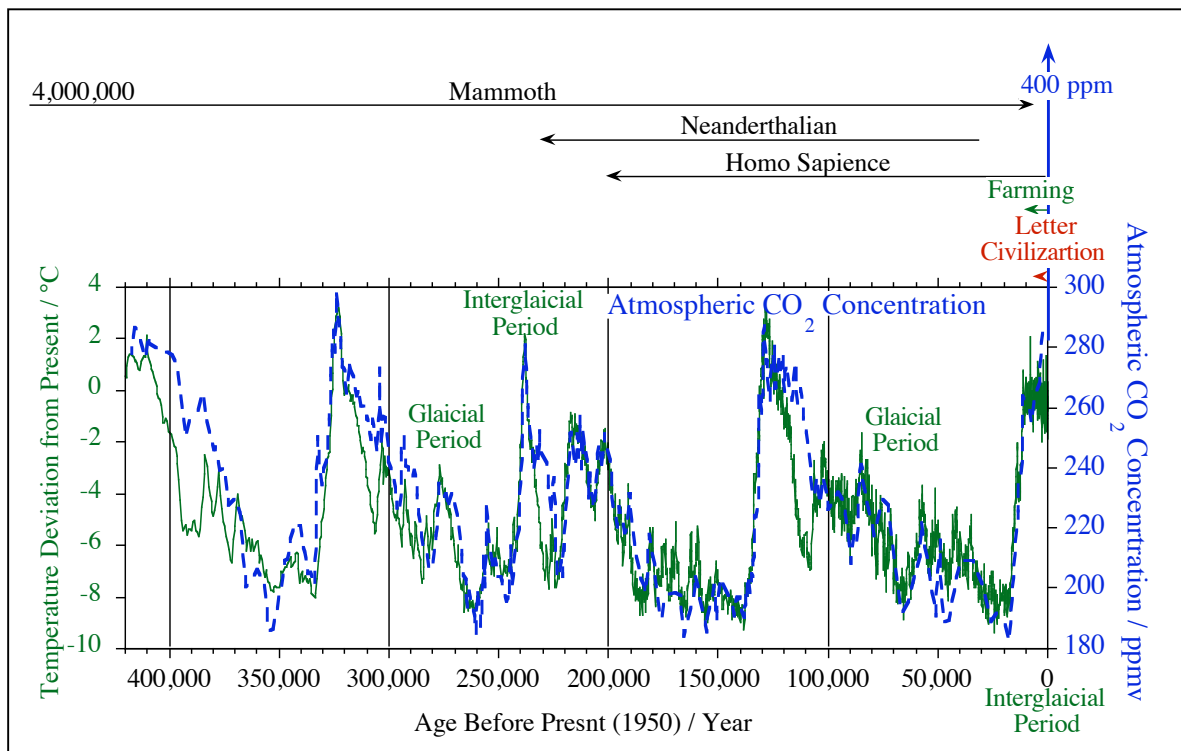


Figure 5 Superposition of Figures 3 and 4.

dioxide concentrations in atmosphere have risen and fallen between about 280 ppm in interglacial period and about 180 ppm in glacial period. These values are far lower than the current level of the atmospheric carbon dioxide concentration over 400 ppm. The atmospheric carbon dioxide concentrations are dependent upon the solubility of carbon dioxide in ocean. When the atmospheric temperature is lowered the ocean temperature is also lowered and the solubility of carbon dioxide in ocean increases just like cooled beer. The enhanced dissolution of carbon dioxide into sea leads to a decrease in the atmospheric carbon dioxide concentration. In contrast, when the carbon dioxide concentration in ocean becomes lower at higher temperatures, just like stale beer, the atmospheric carbon dioxide concentration increases. In this manner, the atmospheric carbon dioxide concentration is determined by the temperature. In Figure 5 the carbon dioxide concentration increased almost following the temperature rise but its decrease was about 10,000 years at most behind the time of temperature decrease. It is reasonable because carbon dioxide bubbles out from the volume of sea to atmosphere with the temperature rise but carbon dioxide dissolution with temperature decrease occurs from the surface of sea and it takes a time to reach the equilibrium concentrations between air and sea. Thus, changes in the atmospheric carbon dioxide concentration looked synchronized with temperature changes but followed temperature changes. Even so, the higher atmospheric concentration of carbon dioxide enhances the greenhouse effect, leading to further increases in temperature and atmospheric carbon dioxide concentration. By contrast, the lower atmospheric concentration of carbon dioxide weakens the greenhouse effect, resulting in further decreases in temperature and atmospheric carbon dioxide concentration. Thus, changes in the temperature and atmospheric concentration of carbon dioxide are functionally interdependent, although the main factor to determine the temperature and the atmospheric carbon dioxide concentration is the Earth's relation to the Sun.

In Figure 2, the cooling trend can be seen until a million years ago, but after a million years ago only the temperature oscillation due to Milancovich cycles is predominant. Thus, after a million years ago the carbon dioxide concentrations are in an equilibrium between the atmosphere and the ocean, depending upon the temperature of our planet, and the up and down change of the atmospheric carbon dioxide concentrations between 280 ppm in the interglacial period and 180 ppm in the glacial period continued for recent a million years.

In these years there were various things happened on our planet. The first known members of mammoth was from Pliocene in South Africa, chased cold dry meadows and spread throughout the world. The fossil of the mammoth survived until 4,000 years ago was found in Wrangel island in the Arctic Ocean. In about 500,000 years ago *Sinanthropus pekinensis* was making fire in caves. Neanderthalian emerged about 230,000 years ago but died out about 30,000 years ago because of scarcity of food in the glacial period. It has been explained [14] that Neanderthalian was the nearest rival of our *Homo Sapiens* with larger body and brain than *Homo Sapiens*. Because Neanderthalian was stronger, they were hunting large and medium-size animals and once they could catch a game they could eat for a while. Thus, they lived generally in a small unit such as a family just like other animals and did not need to improve hunting technology. However, in cold climate in the last glacial period, it was difficult for them to catch poor game. On the other hand, *Homo Sapiens* (Neo-man) emerged about 200,000 years ago and saw Neanderthalian in cold Europe. Weak *Homo Sapiens* lived in a large group of one hundred or more members and hence they could hunt in a group exchanging improved hunting technologies. Women caught small animals and collected edible plants exchanging their knowledge. They could share poor food. It has been said that the cooperation is the unique character of *Homo Sapiens* and has been printed to DNA of *Homo Sapiens*. Because of the cooperation *Homo Sapiens* could survive in the cold glacial period, and greet the current warm interglacial period.

A variety of living things emerged on the history of our planet because the climate of that time was the best for their life, but they died out, because they could not accommodate to the climate change.

One division of the year axis in Figures 3, 4 and 5 corresponds to 10,000 years. The climate of the current interglacial period lasting about 11,000 years has been providing the healthy life of all the current living things, and thus, after passing 1,000 years in the current interglacial period, *Homo Sapiens* started the farming of wild animals and wild plants about 10,000 years ago. The use of characters in Ancient Egyptian, Mesopotamian, and Indus Civilizations started only about 5,000 years ago, and Hwan-huou Civilization was from only 4000 years ago. Therefore, since prehistory, human beings had been living in the atmosphere containing about 280 ppm of carbon dioxide.

The decrease in the atmospheric carbon dioxide concentration from the Pliocene epoch has been explained as follows [15]. About 50 million years ago Indian Subcontinent collided with Eurasian Continent, and pushed each other. About 20 million years ago Himalayan Tibet mountain massif emerged and about 7 million years ago its height was about 3,000 m. In the Pliocene epoch of 5 to 2.5 million years ago the rise of Himalayan Tibet mountain massif was particularly intense, reaching the highest level close to 9,000 m with about 3,000 km width and strengthened the monsoon. Heavy water fall resulted in polishing out of the mountain surface, and in dissolving metallic ions into Indian Ocean from around 3.5 million years ago. The dissolved metallic cations reacted with dissolved carbon dioxide forming solid carbonate precipitates such as calcium carbonate,  $\text{CaCO}_3$  in Indian Ocean. Resultant decrease in carbon dioxide concentrations in the ocean led to dissolution of atmospheric carbon dioxide in the ocean with a consequent decrease in the atmospheric carbon dioxide concentrations, inducing global cooling, taking about 2.5 million years as can be seen in Figure 2.

Even if intense orogenesis resulted in dissolution of calcium ions from Himalayan Tibet mountain massif, the decrease in the atmospheric carbon dioxide concentration from about 400 ppm to the oscillation level between 180 and 280 ppm took 2.5 million years on our planet. It is, therefore, impossible to decrease the atmospheric carbon dioxide concentration from 400 ppm to 280 ppm by human effort. The only effort we can do is to avoid further increase in the atmospheric carbon dioxide concentration.

Figure 6 [2] shows monthly change of the atmospheric carbon dioxide concentrations in three areas in Japan. Ryori is in Iwate Prefecture about 450 km northeast north of Tokyo, where four seasons are clear: in summer temperature sometime becomes higher than 30 degrees Celsius and in winter snow falls. In a year, the atmospheric carbon dioxide concentration is lowest in August because of the highest activity of plants for photosynthesis consuming carbon dioxide, but the atmospheric carbon dioxide concentration is higher from colored leave season to leafing time, because respiration of plants to emit carbon dioxide takes predominance over photosynthesis. Minami-torisima, the easternmost island of Japan locates in 1,860 km southeast of Tokyo, and Yonagunijima, the westernmost island of Japan is in more than 1000 km southwest of the south end of Kyushu island. Both are in the subtropical zone with a smaller seasonal climate change. In spite of difference of Ryori in the temperate zone

and two islands in the subtropical zone the annual average concentration of atmospheric carbon dioxide is almost the same, suggesting again no big difference in atmospheric carbon dioxide concentrations on the surface of all over the Earth. Slightly but upwardly curved continuous increase in the atmospheric carbon dioxide concentration indicates the further rise of its increasing rate.

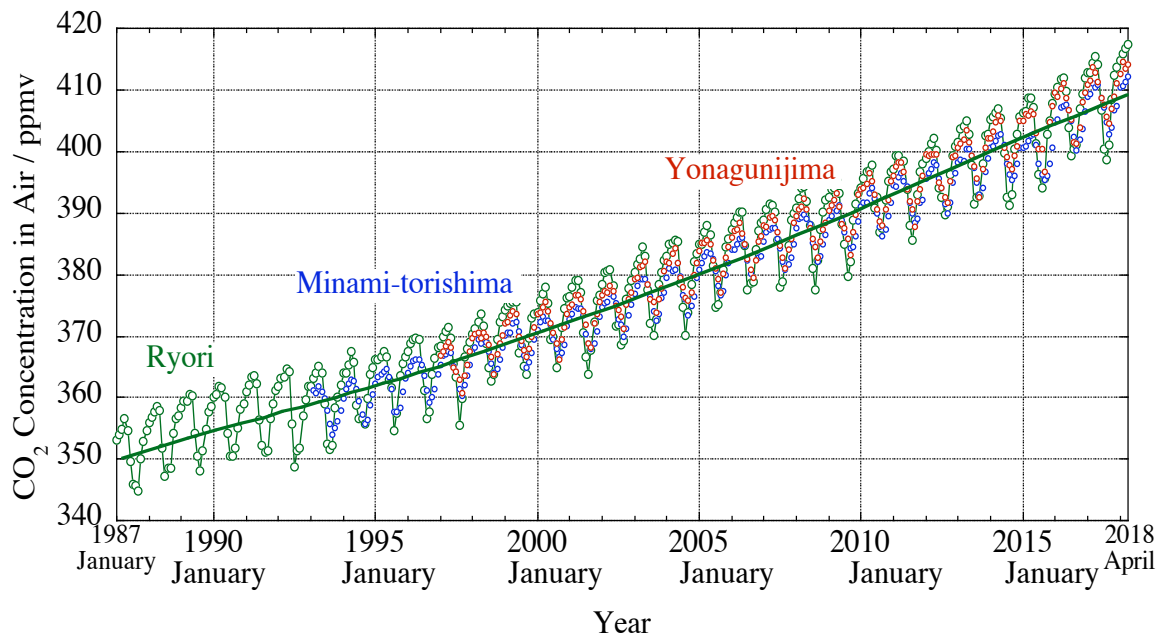


Figure 6 Monthly change in atmospheric carbon dioxide concentration at Ryori in temperate zone, and at Minami-torisima and Yonagunijima in subtropical zone in Japan [2].

As seen in Figure 6, the up and down change of the atmospheric carbon dioxide concentration by plant activities is ten to twenty ppm at most. We cannot anticipate plant activities to decrease the atmospheric carbon dioxide concentration. Only the effort we can do is to avoid further increase in the atmospheric carbon dioxide concentration.

The pressure of atmospheric carbon dioxide was more than 5 atmospheres at the birth of the Earth about 4.6 billion years ago. The atmospheric carbon dioxide had been captured mostly in the form of solid on our planet, and its final decrease to the pre-industrial level occurred from the Pliocene epoch. On the history of our planet a variety of living organisms were born accepting the climate and disappeared because

they could not accommodate to the climate change.

All current living things can live because of the climate in the current interglacial period lasting 11,000 years. However, the atmospheric carbon dioxide concentration suddenly rose exceeding 400 ppm to the level in 3.5 million years ago. If the climate dates back to that in Pliocene Epoch, the current living things have no experience to live in the climate in 3.5 million years ago, and many of them will not be able to accommodate to such climate. The time of 3.5 million years ago is far earlier than the appearance of the first *Homo erectus*, *Homo habilis* which used stone flakes to butcher and skin the animals in 2.4 million years ago. Thus, we cannot imagine the time travel to the era where Bipedal ape men were wondering to find the meat of the leftover by other animals. Such climate change will threaten survival of all current living things.

We need to understand how important is to prevent carbon dioxide emissions by converting from fossil fuel combustion to the use of renewable energy!

#### 4. Greenhouse Effect and Global Warming

Figures 7 and 8 show average temperature deviations in Southern and Northern Hemispheres from 1891 to 2017 [16]. In the Southern Hemisphere the temperature increased about 1 degree Celsius almost continuously from the beginning of the 20th century. In contrast, in the Northern Hemisphere, the temperature increased continuously to the end of the World War II but then showed a cooling trend. Thus, the temperature was not the subject of attention in the world up to the middle of the 1970s. From the second half of the 1970s the temperature in

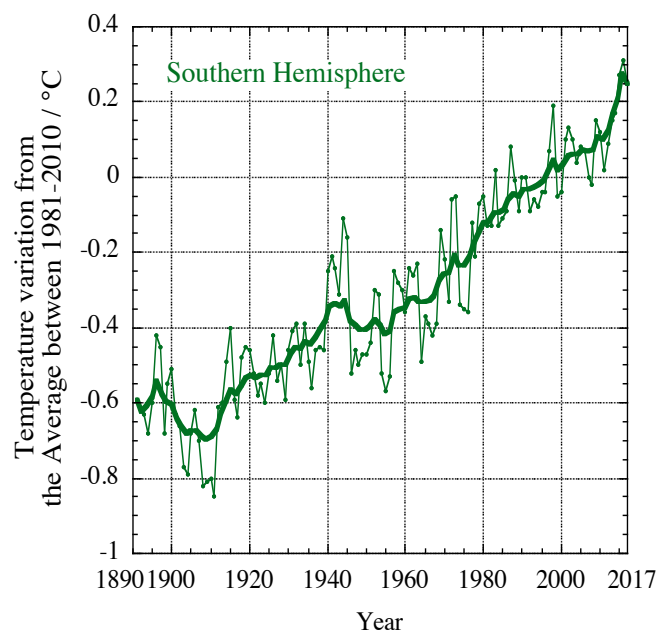


Figure 7 Mean temperature deviation from the average between 1890 and 2017 in southern hemisphere [16].



the Northern Hemisphere increased at a much higher rate in comparison with the Southern Hemisphere. Because of continuous increase in the world temperature, not

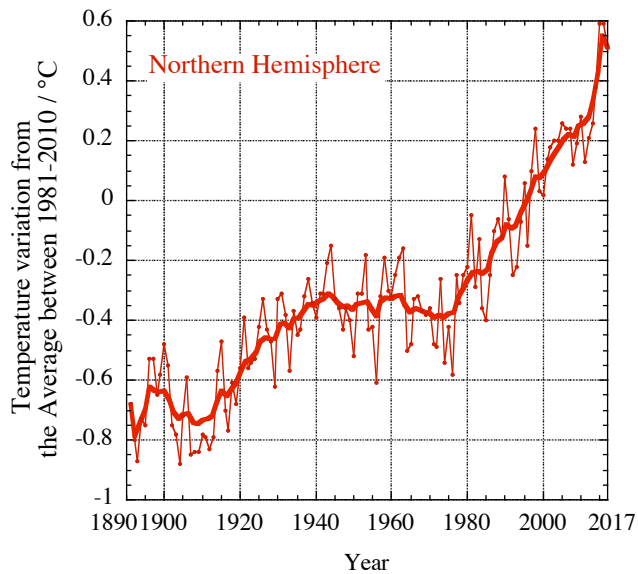


Figure 8 Mean temperature deviation from the average between 1890 and 2017 in northern hemisphere [16].

hence the temporary cooling in Northern Hemisphere until the first half of the 1970s might be induced by soaring industrial pollution in developed countries. In fact, dust and smog fall out of the atmosphere in weeks, whereas atmospheric carbon dioxide would linger for centuries. After the air pollution was almost settled in developed countries, the temperature increase by an increase in the atmospheric carbon dioxide concentration was manifested. In particular, the temperature rise became sharper after 2010 at about 0.05 degrees Celsius every year.

After the World War II, rapid development of world economy due to prosperous industrial activity has been leading to a continuous increase in atmospheric concentration of carbon dioxide which cannot be treated by biogeochemical carbon cycle. As a result, the greenhouse effect of atmospheric carbon dioxide has been enhanced with consequent rises in atmospheric temperature and in sea level of the Earth.

The temperature rise is faster in high latitudes. Figure 9 [17] shows the mean annual temperature in three cities in Alaska. Barrow is in Arctic Ocean coast,

only meteorologists but also the world became worried the influence of the world temperature increase.

The following interpretation has been given for cooling trend in the Northern Hemisphere after the World War II. The human activity puts not only carbon dioxide but also dust and smog particles into the atmosphere, and dust and smog particles can block sunlight and cool the world. After the World War II the human activity emitted ever more dust and smog particles and

Fairbanks is in inland and Anchorage is in the closed section of Cook Inlet at Southern tip. Temperature in these three cities rose much faster than global average.

It has been reported that temperature in Deadhorse in Arctic Ocean coast about 500 km east of Barrow went up to 29.4 degrees Celsius on July 13, 2016 [18]. We have to consider that the time of extinction of polar bears is approaching. The Washington Post reported on July 24, 2016 [19] that the temperature in Mitribah, Kuwait on July 21 rose to a blistering 129.2 degrees Fahrenheit (54 degrees Celsius), reading matches the hottest ever reliably measured anywhere in the world.

Not only coastlines and inlets sink into sea, but also extremely high temperature induces formation of extraordinarily strong cyclone, typhoon and hurricane in tropical sea, in addition to abnormal weather, extreme climate, heavy rain, drought, melting of glacier, ice sheet and permafrost, sea level rise, etc. The sea level rise by global warming is the serious problem for island countries, but the sign of warming was not predominant in Japan.

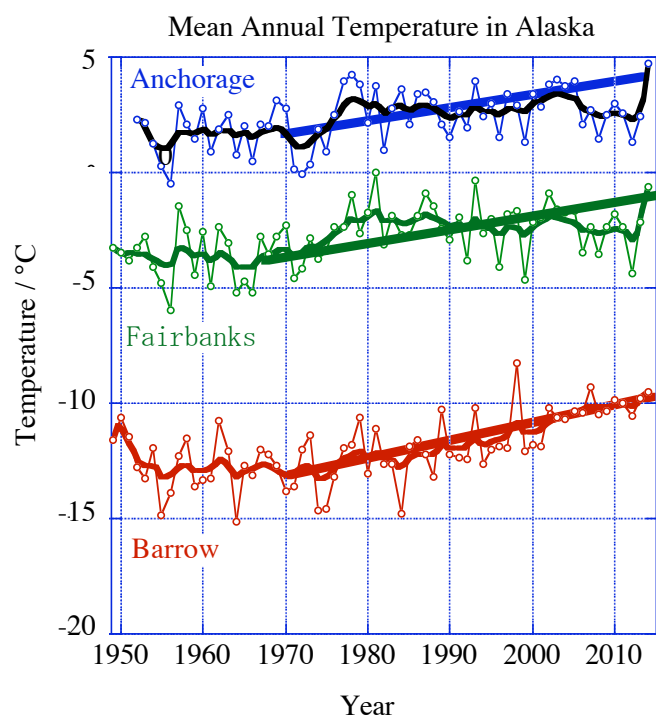


Figure 9 Mean annual temperatures in three cities in Alaska from 1949 to 2014 [17].

However, the influence of global warming is recently manifested even in Japan. In general, typhoons used to hit southwest Japan and to get weaken until typhoons come to northeast Japan. However, in August 2016, typhoons directly hit one after another small mountain villages along a small river in Iwate prefecture about 500 kilometers northeast north of Tokyo. The amount of rainfall in mountains within one hour was that of normal one month. A violent flow of water could not make turn a serpentine river, and built a dam by piling up of trees pulled out from the mountain. Thus, not only river flood but also water fall from the behind mountain hit houses, and water

instantly reached the ceiling of the ground level of buildings with a consequent death of 27 people including 9 bedridden elderly people in a nursing home. The eastern part of Hokkaido, the northernmost island of Japan never had direct hit of typhoon on history after onset of weather observation, but three typhoons hit within 10 days in August 2016. Because of floods in large area two people were killed and farm products suffered serious damage. In July 2018, the torrential rain and stream of mud left about 230 dead and missing in ancestral lands within three days in western Japan.

Unusual weather has been reported in many areas in the world. We have no way to decrease atmospheric carbon dioxide concentration and now the extraordinary weather becomes not unusual but ordinary by progress of global warming. These disasters are not local ones but generated in the whole world. The response to individual disaster is mostly done by respective countries, but implementation of no fossil fuel combustion must be done urgently by collaboration of the whole world.

## **5. Energy Consumption and Carbon Dioxide Emissions in the World**

### **5-1. Current Situation of Our World**

For prevention of global warming a better understanding of the energy-related world problems is necessary. Figure 10 [20] shows primary energy consumption and carbon dioxide emissions from 1980 in the world and three groups of countries. The units of left and right axes of the ordinate are taken as the symbols of primary energy consumption and carbon dioxide emissions of the world in 2015 coincide with each other. It is difficult to distinguish OECD countries and non OECD countries in Europe in primary energy consumption and carbon dioxide emissions per person. Thus, OECD countries in this article mean European countries and other OECD countries. Primary energy consumption and carbon dioxide emissions of the world continue to grow. Increases in primary energy consumption and carbon dioxide emissions show the same trends because nearly 90 percent of primary energy consumption was fossil fuel combustion. There were stagnation periods in some years. The stagnation in the first half of the 1980s was due to the oil crisis in the wake of Iranian Revolution in 1979 and subsequent Iran-Iraq War. The stagnation from 1990 was due to the dissolution of the USSR. In 2001 an economic activity decline occurred in developed countries. In

2008 the Lehman Brothers' bankruptcy occurred.

In this manner, only the economic depression led to suppress increases in primary energy consumption and carbon dioxide emissions of the world. Primary energy consumption and carbon dioxide emissions of developing countries increase very rapidly. Primary energy consumption

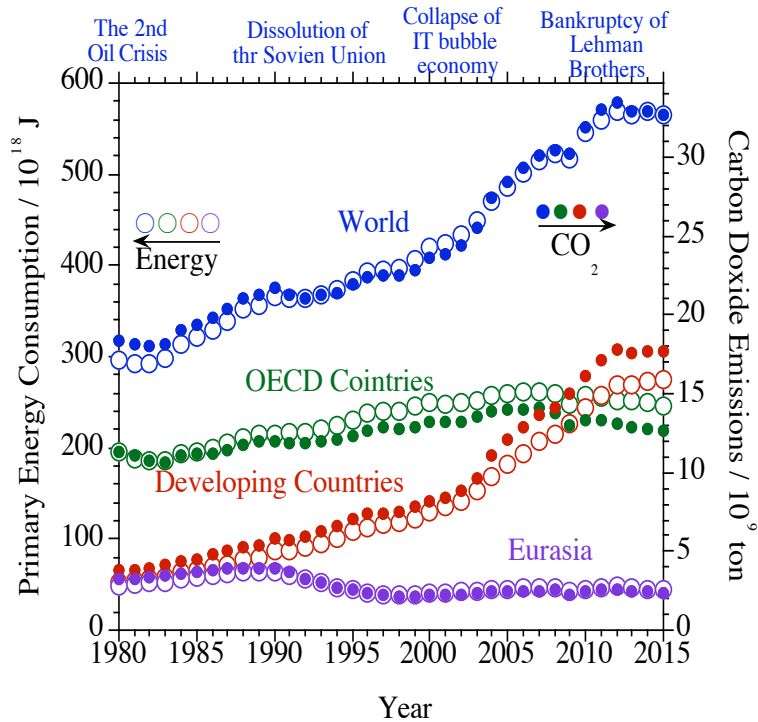


Figure 10 The history of primary energy consumption and carbon dioxide emissions of the world and three groups of countries from 1980 [20].

and carbon dioxide emissions of OECD countries also increased although OECD countries did not yet completely recover from the economic depression by Lehman Brothers' bankruptcy. The increasing trend of carbon dioxide emissions of developing countries was almost the same as world total carbon dioxide emissions and around 2010 total amounts of primary energy consumption and carbon dioxide emissions of developing countries exceeded those of OECD countries. It was, therefore considered by some developed country people that a large amount of carbon dioxide emissions of developing countries is responsible for enhancement of global warming. However, populations of developing and OECD countries are 78.2 % and 17.9 % of the world population in 2015, respectively. Thus, a simple comparison of total amounts of primary energy consumption and carbon dioxide emissions of developing countries with those of OECD countries will lead to misunderstanding of real problems.

For a further better understanding of world problems of primary energy consumption and carbon dioxide emissions we need to compare how much individual person

consumed energy and emitted carbon dioxide. The most of data are given in Reference [20] and recent data of population are given in Reference [21]. Figure 11 [20, 21] shows primary energy consumption and carbon dioxide emissions per person in the world, three groups of countries and some representative countries. The units of left and right axes of ordinate are taken as the symbols of primary energy consumption and carbon dioxide emissions per person in the world in 2015 coincide with each other. It can easily be understood how primary energy consumption and carbon dioxide emissions per person of OECD countries are higher than those of developing countries and world averages. High energy consumption per person is an indicator of fulfilling life.

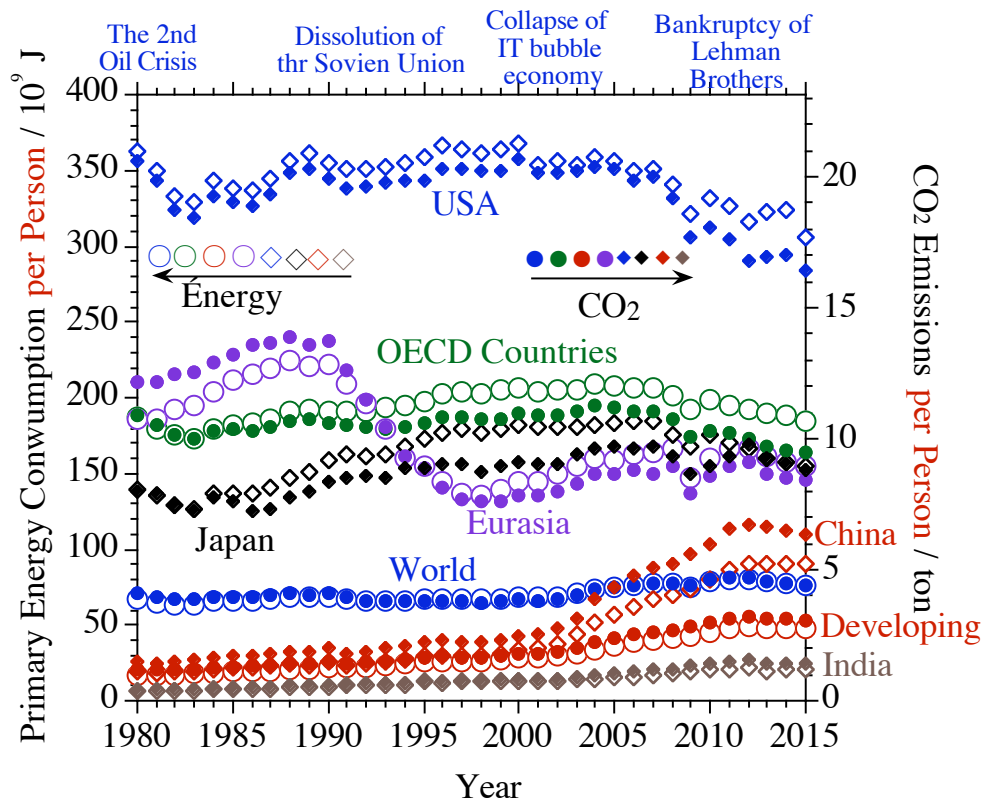


Figure 11 The history of primary energy consumption and carbon dioxide emissions per person for the world, three groups of countries and some representative countries from 1980 [20,21].

It is obvious from Figure 11 that for prevention of global warming, developed countries are necessary to decrease carbon dioxide emissions. Thus, the 3rd Session of the Conference of Parties (COP 3) to the United Nations Framework Convention on

Climate Change (UNFCCC) held in December 1997 adopted an international treaty, Kyoto Protocol recognizing that developed countries are principally responsible for the current high levels of greenhouse gases in the atmosphere as a result of greenhouse gas emissions by industrial activity for more than 150 years. The Kyoto Protocol placed a very light burden of a few percent decrease in carbon dioxide emissions on developed countries under the principle of "common but differentiated responsibilities." It is, however, clear from Figure 10 that OECD countries had never decreased carbon dioxide emissions except for that done by economic depression. This indicates that the advanced technologies of fuel combustion in OECD countries are useless in decreasing the carbon dioxide emissions. Because high energy consumption per person is the indicator of fulfilling life, even if any country promised to decrease carbon dioxide emissions, as far as economic and industrial activities are maintained by fossil fuel combustion it is impossible to decrease the carbon dioxide emissions.

Since Kyoto Protocol was not effective, global warming was seriously discussed at the COP 15 held on December 2009 in Copenhagen. U.S. President Barack Obama attending as an active leader raised that the decrease in carbon dioxide emissions by developing countries is the prerequisite for the decrease in carbon dioxide emissions by

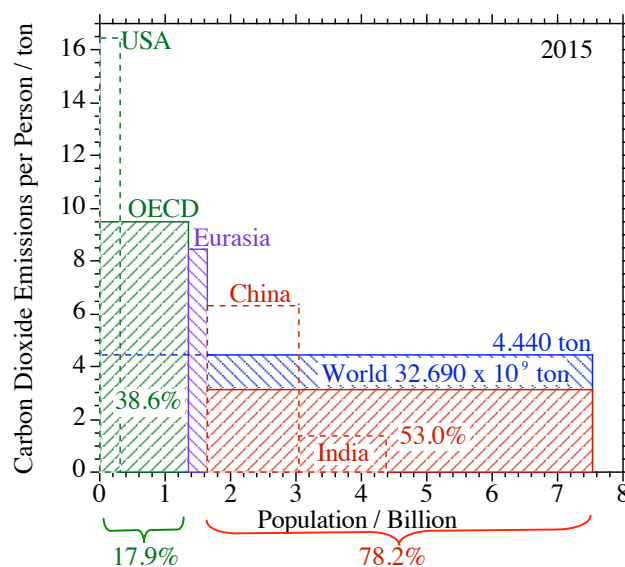


Figure 12 Relation between carbon dioxide emissions per person and population in 2015 [20,21].

developed countries. Figure 11 clearly shows the fact that such an argument was unreasonable. When the developed countries accomplish the decrease in carbon dioxide emissions per person to the level lower than the level of the carbon dioxide emissions per person in developing countries, developed countries are allowed to say for the first time that they will help developing countries to decrease carbon dioxide emissions.

Let's see more detail of carbon

dioxide emissions taking the data in 2015. Figure 12 [19,20] shows the carbon dioxide emissions per person as a function of population in 2015. The world emitted 32.690 billion tons of carbon dioxide by 7.529993 billion people in 2015. Thus, world average carbon dioxide emissions per person was 4.440 tons. The division of the world carbon dioxide emissions into three groups of countries is shown in Figure 12. The population of OECD countries was only 17.9 % of the world population. Nevertheless, OECD countries emitted 38.6 % of the world total carbon dioxide emissions. In contrast, the population of developing countries was 78.2 % of the world population, and developing countries emitted only 53.0 % of the world total carbon dioxide emissions. The US residents were included in OECD countries. However, if the U.S. residents were extracted from OECD countries, the carbon dioxide emissions of the U.S. residents were 16.1 % of the world total carbon dioxide emissions by 4.3 % of the world population.

As has been seriously discussed at a series of meetings of the COP of the UNFCCC the carbon dioxide emissions of the world were known to be too high to prevent global warming. However, if the whole world were allowed to emit the world average of 4.440 tons per person of carbon dioxide, developing country people can emit almost 1.5 times as high as that emitted by them in 2015. In contrast, the U.S. residents are necessary to decrease 3/4 of their carbon dioxide emissions. That is impossible. For OECD country people more than a half decrease in carbon dioxide emissions in average is impossible. For Eurasian people a half decrease in carbon dioxide emissions is impossible. It is clear that unless we stop fossil fuel combustion we have no solution to avoid global warming.

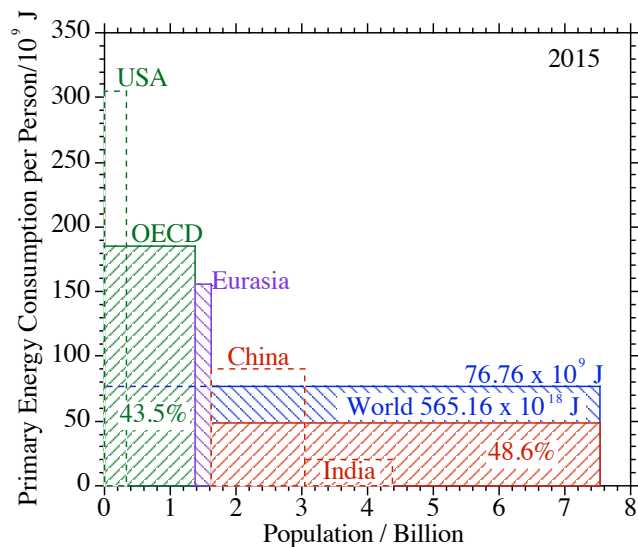


Figure 13 Relation between primary energy consumption per person and population in 2015 [20,21].

The trend of primary energy consumption of the world is the same as that of carbon dioxide emissions. Figure 13 [20,21] shows the primary energy consumption per person as a function of population in 2015. The world consumed 565.16 quintillion ( $10^{18}$ ) Joules of primary energy. Thus, world average primary energy consumption per person was 76.76 billion Joules. The OECD country people consumed 43.5 % of the world primary energy consumption. Developing country people consumed only 48.6 % of the world primary energy consumption. The primary energy consumption of the U.S. residents was 17.3 % of the world primary energy consumption. Because high energy consumption per person is an indicator of fulfilling life, to keep a high economic activity high energy consumption is necessary. The world primary energy consumption will continue to increase. Unless we convert from fossil fuel combustion to the use of renewable energy, the world carbon dioxide emissions will continue to increase.

Furthermore, if one looks at the increase in the world population, one can understand how the situation is serious. Figure 14 [21] shows the increase in the world population at a constant rate of about 83.1 millions every year.

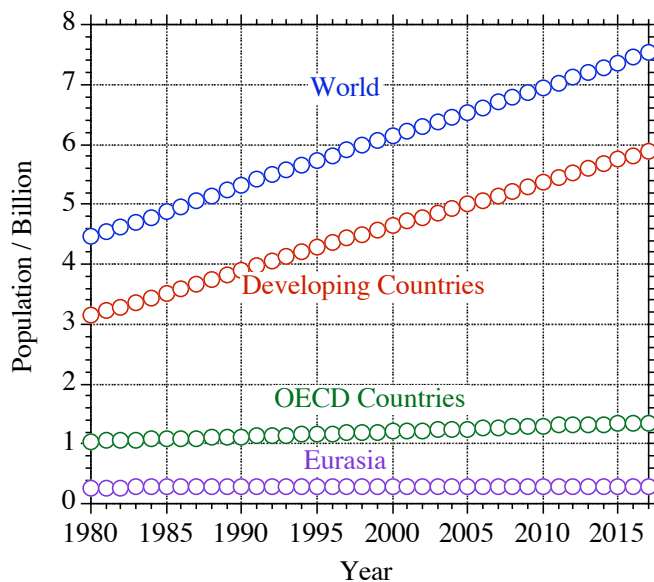


Figure 14 Linear increase in population of world and three groups of countries [21].

All these data indicates that the world energy consumption and carbon dioxide emissions will increase continuously. There are no other solutions than that we should make sustainable development only using renewable energy without combustion of fossil fuel.

In European countries for prevention of global warming the use of renewable energy was started from the early 1980s. Under the leadership of European countries the COP 21 of the UNFCCC in Paris on 12

December 2015 adopted the Paris Agreement to hold the global average temperature to



well below 2 degrees Celsius above pre-industrial levels and to pursue efforts to limit the temperature increase to 1.5 degrees Celsius above pre-industrial levels. This is quite difficult decision that we want to avoid the change in the climate to 3.5 million years ago, in spite of the fact that the atmospheric carbon dioxide concentration exceeded the level in 3.5 million years ago. Even if the ratification is done by majority of countries, unless we determine stopping combustion of fossil fuel and relying on renewable energy, the agreement will fall to the ground as the Kyoto Protocol did. In particular, countries of extraordinarily higher carbon dioxide emissions per person must not to be selfish and ought to decrease carbon dioxide emissions to the pre-industrial level. Nevertheless, on June 1, 2017, the U.S. President Donald Trump announced that he will withdraw the United States from participation in the Paris climate accord, in spite of the fact that the amount of carbon dioxide emissions per person of the U.S. is the world highest far over other OECD countries. The immediate news conveys that nearly 60 percent of Americans oppose to the removal of the U.S. from the Paris

climate agreement to a Washington Post/ABC News poll. Many state governors and mayors in the U.S. have declared continuation of their effort to decrease carbon dioxide emissions. Regardless of thinking of President Donald Trump, judicious world will make a great effort to decrease carbon dioxide emissions following the Paris climate agreement. This is the only way for the world to survive.

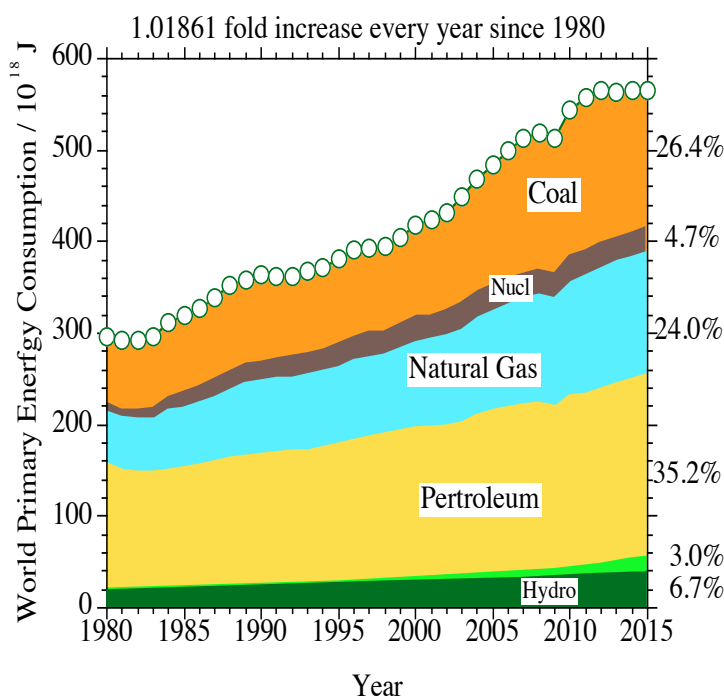


Figure 15 World history of primary energy consumption for 35 years [20].

## 5-2. The Future of Energy Consumption

Figure 15 [20] shows the world history of primary energy consumption for 35 years. In 2015, fossil fuel consumption was 85.6 % of primary energy consumed. Hydroelectric power and other renewable energy were 6.7 % and 3.0 %, respectively, and a nuclear electric power was only 4.7 %. The world primary energy consumption continued to increase. If we take the average increasing rate between 1980 and 2015, the world primary energy consumption increased by a factor of 1.01861 every year since 1980.

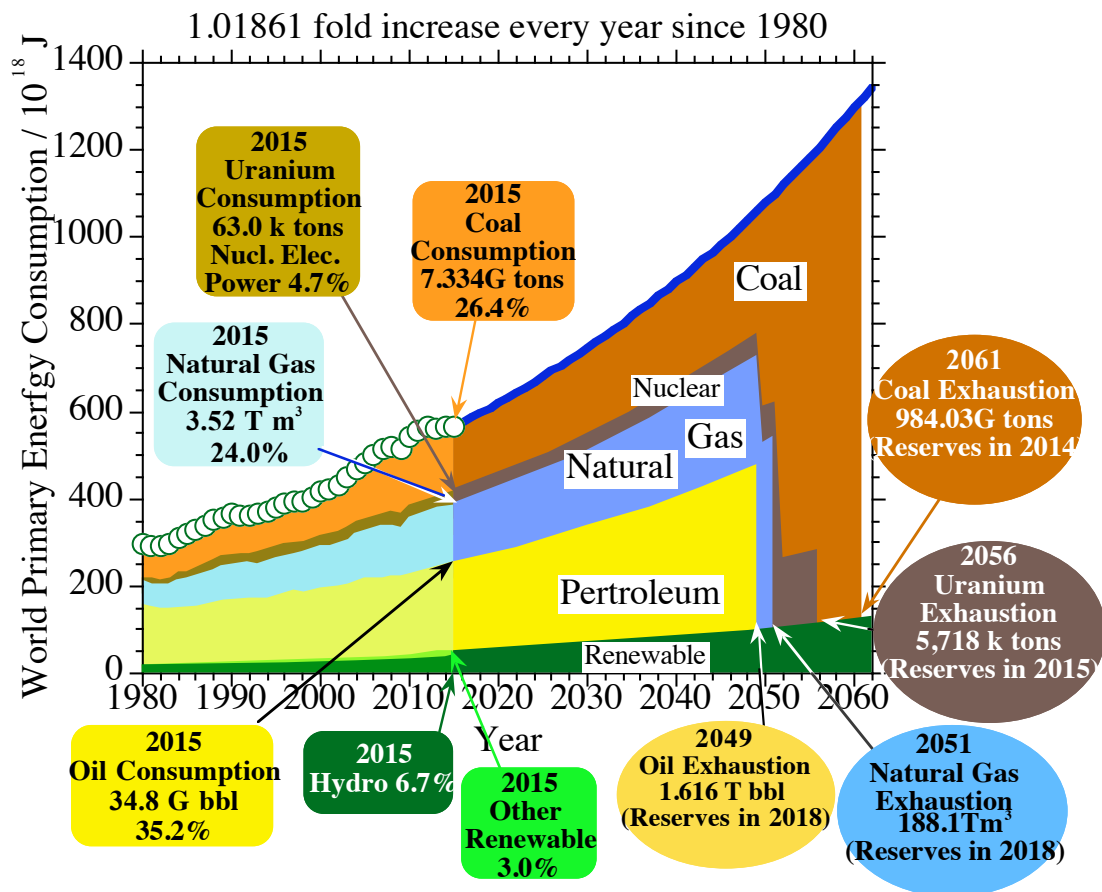


Figure 16 History and future of the world primary energy consumption [20,21].

Figure 16 [20,21] shows the history and future of the world primary energy consumption. A blue curve in the right in the figure is the extrapolation of the world primary energy consumption in 2015 by the increasing factor of 1.01861 every year. For instance, the division of the estimated world primary energy consumption in 2050

on the blue curve by the estimated world population in 2050 obtained by extrapolation of the world population shown in Figure 14 gives the estimated value of the world average primary energy consumption per person in 2050. The world average primary energy consumption per person in 2050 thus obtained is only 58.5 % of  $184.42 \times 10^9$  J that is the primary energy consumption per person in OECD country people in 2015 as shown in Figure 13. Thus, the blue curve in Figure 16 is significant underestimation. Nevertheless, if we supply fuels following the history until 2015, responding to this underestimated energy demand, the world petroleum reserves in 2018, that is 1.616 Tera barrels will be completely exhausted by 2049. If we continue to supply the remaining fuels following this demand, the world reserves of natural gas, uranium and coal will be successively exhausted. There is no meaning of minable year that is how many years is minable the reserve at the current amount of production, because the current amount of production that is the base of the calculation of the minable year increases every year.

It is clear that the all reserves of fossil fuel and uranium will be completely exhausted until the middle of this century inducing intolerable global warming. However, there are superabundant renewable energy sources on our planet as will be explained later. Before that, let's consider about nuclear power generation.

### **5-3. Nuclear Power Generation**

The nuclear power generation was started in the USA in 1951 and performed as the national project mobilizing science and technology. Nevertheless, after passing more than 60 years, the share of nuclear electric power in the world primary energy consumption was only 4.7 % in 2015. In spite of such a small amount of energy production and in spite of the fact that only small number of countries exclusively carry out nuclear power generation, the uranium resources of 5.718 million tons in 2015 will be completely exhausted until the middle of this century. (According to World Nuclear Association [22], the current cost category of uranium resources is U.S.\$ 80/ kilogram uranium and the known recoverable uranium resources to U.S.\$ 130/ kilogram uranium is 5.718 million tons.) Thus, the nuclear power generation cannot spread and is used only by limited number of countries. Its 4.7 % share of the world primary energy consumption in 2015 does not affect the prevention of global warming.

One of sales points of nuclear power generation is inexpensive. In general, if the

cost of industrial waste disposal is not included in the sales price such an industry will go bankrupt. However, radioactive waste is excluded in Waste Management and Public Cleansing Law of Japan. Because nuclear waste disposal is not carried out the price of nuclear electricity is currently inexpensive.

German environmental think tank Forum Ökologisch-Soziale [23] reported estimated costs for power generation by renewable energy, coal, brown coal, natural gas and nuclear energy in 2014 as shown in Figure 17 [23]. Power generation cost in new power

plants includes the costs not included in the current electric power charge, that is not only subsidies and financial incentives to the conventional power generation from government, but also social cost for environmental damage and cost of radioactive waste disposal, and others. The cost for power generation by renewable energy is transparent. In contrast, there are hidden costs in power generation by conventional power plants. For nuclear power generation a variety of government subsidies are given to surrounding municipalities in addition to exclusion of nuclear waste disposal. Furthermore, for the fossil and nuclear energy sources there are high follow-up costs due to environmental and climate damage as well as the risks associated with nuclear energy. This is the report of German think tank.

When we think about nuclear power generation we should not forget Chernobyl's accident. The nuclear accident occurred at 1:30 p.m. on April 26, 1986. The world has well known the accident but there is still no explanation about the cause of the

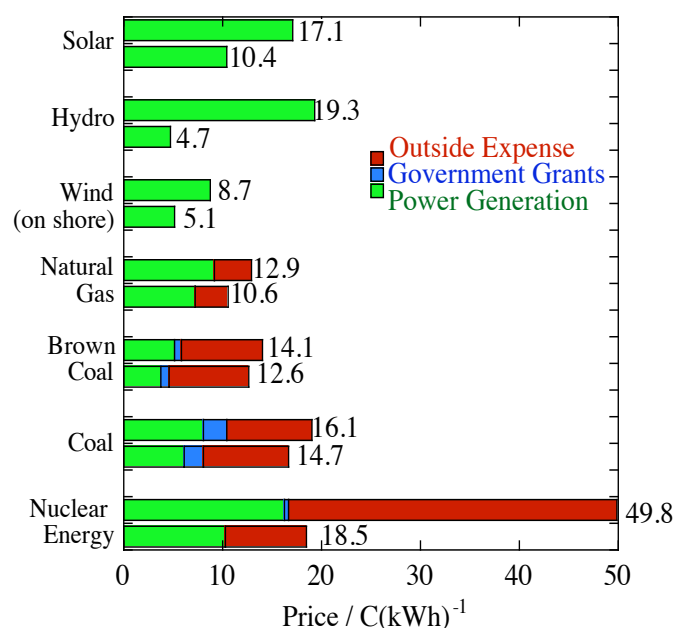


Figure 17 Cost estimation by German environmental think tank Forum Ökologisch-Soziale for power generation by renewable energy, coal, brown coal, natural gas and nuclear energy in 2014 [23].

accident. Unbelievable number of radiation victim fatalities were estimate. According to WHO, IARC (International Agency for Research on Cancer) and Green Peace in 2006, 20 years after the accident, the fatalities of radiation victims suffered cancer were 9,000 [24], 16,000 [25] and 93,000 [26] cases, respectively. Misery and agony of radiation victims have been written in the report of hearing investigation entitled “Chernobyl's Prayer” by a Belarusian journalist and non-fiction writer Svetlana Alexandrovna Alexievich in 1997 [27]. Later she received the Nobel Prize in Literature in 2015.

On September 22, 2016, Japanese TV station, BS Asahi televised the program entitled “30 years after Chernobyl’s nuclear accident, Present situation, Looking the future of Fukushima” [28]. It notified that people who have developed thyroid cancer were 6,049 cases in Ukraine. They were mostly under five years of age. There are so many handicapped children who are the second generation of radiation victims. There is a town Narodychi of 10,000 population about 70 km west of Chernobyl. After the accident USSR Government distributed a note that “Narodychi is free from radioactivity.” Nevertheless, there were many hot spots where radioactivity was very high. Many residents particularly children became radiation victims. There was an impressive scene. About 30 9-year old children were standing facing to a teacher for physical education on a schoolyard. The teacher said let’s measure the pulse rate. If the pulse rate is faster, the child is not allowed to run. After running to the center of schoolyard, the pulse rate measurement was again carried out. For practical education a health nurse with white clothing should attend because the most of children are the second generation of the radiation victims. Some children have an attack of anemia, getting giddy and nauseous. Because of weak immune strength 90 % of elementary school children suffer respiratory illness, heart disease, etc. Chernobyl disaster is not ended even 30 years after the accident and will continue to the next generation. The TV program said that in Fukushima 131 children were diagnosed with thyroid cancer. The only thing we can do now is to pray that the 131 children and their next generation will keep living in good health.

After the Fukushima nuclear accident, hundreds of thousands of people had to evacuate from their beautiful and rich rural hometowns and on February, 2018 at seven years after the accident still 50,641 people are evacuating from their hometowns in Fukushima prefecture.

Decontamination of specified local area may be possible. It is, however, impossible to avoid the presence of hot spots. Decontamination of mountains and mountain villages was not performed. Wind easily carries radioactivity from mountains to decontaminated areas. Animals, birds and insects eat plants and insects without distinction of hot spots, and they move around widely. Many deformed animals, birds and insects have been found.

There was a report that unknown new radioactive solid particles have been found [29]. Recent inspection of exposure dose of people worked at exploded nuclear power plants showed a decrease in radioactivity, but localized intense radioactive sites around chest were found. The most dangerous nuclear species, cesium  $^{137}\text{Cs}$  and  $^{134}\text{Cs}$ , the half lives of which are 30.07 and 2.062 years, respectively were scattered by explosion of nuclear power plants. Cesium salts dissolve in water. Radioactive cesium species taken into a body were generally discharged dissolving in water and the radioactivity of an adult became a half in 80-100 days. On the other hand, at melting of the nuclear fuel in the reactor, the radioactive cesium was scattered and adsorbed on heat-insulating glass fibers in the reactor. Explosion of the reactor melted glass fibers, and when cooled the glass fiber solidified in particles in which radioactive cesium was trapped. These are radioactive insoluble particles. Once these radioactive insoluble particles are taken into the human body such as lung by breathing, their discharge takes many years. It has been said that the amount of absorbed doses from the radioactive insoluble particles for an adult and an 1-7 year old child will be 70 and 180 times as high as those from the equivalent amount of soluble cesium, respectively. Even if total exposure dose is not high, no one knows the influence of the radioactive particles staying in the body for many years. Even if decontamination was carried out, wind will easily carry these particles from the contaminated zone to the decontaminated areas. In fact, it was found that furniture in houses evacuated by nuclear accident has been covered by dust including these radioactive insoluble particles.

For healthy life of all people we need to decide that the contaminated area is not habitable for several generations.

“Nevertheless, they made a great effort to live” was the title of a TV program [30]: Immediately after permission of return a couple of age thirties went home, got married and started preparation of rice farming, suffering from radioactivities from behind mountain. They made experimental rice transplanting getting help of about ten

volunteers on April 2012, 13 months later the Fukushima nuclear accident. In the autumn, no radioactivity was detected on the harvested rice and they awarded the first prize at competitive exhibition. They expanded rice field area in 2013, but in the autumn their rice was evaluated only 2/3 of the ordinary price because of the product in Fukushima. They organized tasting parties of harvested new rice inviting many people including the volunteers who helped them for rice transplanting in 2012, but there were few participants. Nothing improved. On April 2015 they made a tour with their relatives to cherry blossom viewing in Hirosaki about 500 km north of their town. They had seen happy people there. One week after came home, the couple went to behind mountain by their car and they had never come back. They killed themselves by hanging.

Younger family with children cannot go back to their hometown. Nevertheless, aged people wish. A TV program, "Travel of Alexievich" [31] reported: When evacuation was ordered just after the Fukushima accident, a 102 year old man said "this is my native town. I have lived till today. I will never leave here". In the early morning of the day of evacuation, he killed himself by hanging. His daughter in law who had lived with him left his mortuary tablet and portrait at home together with those of her husband who died before the accident, and she came whenever she was allowed to come home. She will be allowed to live there near future. She said, the radioactivity is still high, but I will live here with their souls.

A retired school principal looking after people in the town, which recently become habitable by decontamination, said that residents are mostly old and eating radioactive wild mushrooms thinking that small amounts will be safe. He also said young people do not and should not come back and after death of their old generations their town will become a ghost town keeping sunny and beautiful scenery with radioactivity which we cannot see, touch, sniff, hear and tasting.

The radioactivity inspection has been conducted for every package of all marine and agricultural products in Fukushima. Only those for which the radioactivity has not been detected come onto the market. Aged people intentionally buy such products for encouragement of people in Fukushima. However, younger families with children avoid to buy Fukushima products. It is said the risk of harmful rumors. Younger families do not want to take risks of exposure of their children to radioactivity.

In 2016 passing five years after Fukushima accident, apologize of local educational

committees and principals of elementary and high schools often made news. Children whose family moved from Fukushima to other cities were called “bacteria” by children of the city because they think or have been taught that the children from Fukushima are radioactive. Then they ordered the children from Fukushima to buy confections and toys because they think or have been taught that the families from Fukushima are getting compensation. The harassment at school some time results in suicide of harassed children. However some children from Fukushima said that so many people including their relatives were killed by Tsunami, and hence, we have to linger with a strong mind impervious to the harassment.

Even today, local government in Japan are spending public expenses for preparation of shelters and evacuation practice of hundreds of thousands of people at a nuclear accident. For instance, on July 2016, assuming the nuclear accident of power plants in Fukui prefecture on Japan Sea coast, three prefectural governments conducted evacuation practice carrying refugees from Fukui prefecture through Kyoto prefecture to Seto Inland Sea coast of Hyogo prefecture over 500 km. In Miyagi prefecture which suffered most serious Tsunami disaster on March 11, 2011, seven local governments within 30 km from Onagawa nuclear power station have been worrying how to evacuate the residents to other 27 cities, towns and villages.

On the other hand, in Germany, the Federal Ministry for the Environment published the departmental research reports on nuclear safety and radiation protection entitled epidemiological study on childhood cancer in the vicinity of nuclear power plants [32-34]. The geographical area covered by the study comprised of 41 counties in the vicinity of 16 West German nuclear power plants that had been operated normally. The study group included all children diagnosed of a malignant disease (or nonmalignant brain tumor) in 24 years from January 1, 1980 through December 31, 2003, who had been diagnosed before their fifth birthday. The study covered a total of 1592 cases including 593 leukaemia cases. The epidemiological evaluation is expressed by the odds ratio. The odds is the ratio of the number taken ill to the number not taken ill as equation (2).

$$\text{Odds} = \frac{\text{Number}_{\text{taken ill}}}{\text{Number}_{\text{not taken ill}}} \quad (2)$$

In any areas there are children diagnosed with cancer. Thus, the epidemiological study



on a disease is carried out by comparison of the odds in a selected local area with the odds of other area. The odds ratio (OR) is (Number taken ill/ Number not taken ill) in 5 or 10 km zone / (Number taken ill/ Number not taken ill) out of influence zone as shown in (3).

$$OR = \frac{\text{Odds}_{5 \text{ or } 10 \text{ km zone}}}{\text{Odds}_{\text{out of 5 or 10 km zone}}} = \frac{\left( \frac{\text{Number}_{\text{taken ill}}}{\text{Number}_{\text{not taken ill}}} \right)_{5 \text{ or } 10 \text{ km zone}}}{\left( \frac{\text{Number}_{\text{taken ill}}}{\text{Number}_{\text{not taken ill}}} \right)_{\text{out of 5 or 10 km zone}}} \quad (3)$$

Odds ratios (OR) estimated for all cancer and leukaemia cases are summarized in Tables 1 and 2 .

In these two Tables the odds ratio (OR) in 5 or 10 km zone of 16 nuclear power plant sites is clearly higher than unity, although the authors [34] wrote that acute nonlymphoid leukaemia in 10 km zone is not statistically significant (lower 95%-CL: 0.66) due to the comparatively low number (10 cases). This report exhibits that there is the risk of childhood cancer in the surrounding area even if the nuclear power plant is normally operating. This result indicates that the regulation values of the radioactivity cannot be applicable to younger children.

Even after passing more than 60 years from the first nuclear power generation, the share of the world primary consumption in 2015 was only 4.7 % in spite of the fact that nuclear power generation was carried out as the national project in all countries. Nevertheless, resources itself is limited. Thus, different from renewable energy, and even if compared with fossil fuel, we cannot expect future prospects at all for the technology of nuclear power generation.

Table 1 Results of studies on childhood all cancer and leukaemia cases (under 5 years of age) in the vicinity of nuclear power plants performed at the German Childhood Cancer Registry. 1980-2003 [33].

	OR	Lower 95%CL	Cases 5-km zone
All cancer	1.61	1.26	77
Leukaemia	2.19	1.51	37

95%-CL, one-sided 95% confidence limit.

Table 2 Estimated odds ratios (OR) for two distance categories for all leukaemias and subtypes (under 5 years of age) in the vicinity of nuclear power plants performed at the German Childhood Cancer Registry. 1980-2003 [33].

	OR	Lower 95%CL	Cases
All leukaemias			
5-km zone	2.19	1.51	37
10-km zone	1.33	1.06	95
Acute lymphoid leukaemias			
5-km zone	1.98	1.33	30
10-km zone	1.34	1.05	84
Acute nonlymphocytic leukaemias			
5-km zone	3.88	1.47	7
10-km zone	1.30	0.66	10

95%-CL, one-sided 95% confidence limit.

The nuclear power generation was meant to show off the high level of science and engineering of the countries. The virtual image of the high level of science and engineering collapsed by Chernobyl's and Fukushima's nuclear accidents. Such an industry is not allowed to exist that once accident occurs hundreds of thousands of people must evacuate from their hometowns for several tens of years or more, in addition to inevitable cancer cases of childhood and on going workers. Some governments are emphasizing no carbon dioxide emissions from nuclear power plants. However, we need to convert 100 % from fossil fuel combustion to the use of renewable energy and only 4.7 % of world primary energy consumption in 2015 does not make sense for prevention of global warming.

There is no absolutely safe technology. We have learned a lot from Chernobyl's and Fukushima's accidents. Thus, if the accident occurs again, promoters of nuclear power generation will be judged as not victims but perpetrators for a large number of casualties and heavy damages.

After Fukushima Nuclear Disaster the federal government of Germany convened the Ethics Committee for a Safe Energy Supply on April 4, 2011 with the aim of establishing a public consensus on future energy supply, discussing the risks of using

nuclear energy. On May 30, 2011, the Ethics Committee submitted its recommendations to limit the use of nuclear energy as far as possible and to phase-out the use of nuclear energy within a decade, concluding that the possibility of an accident out of control is of crucial significance in Germany. It said that the risk cannot be deduced from experience with real accidents, because the consequences of a worst-case nuclear incident are unknown or cannot be fully grasped. The ecological responsibility of human beings for nature sets out to preserve the environment and protect it, and not to destroy it for selfish purposes, but to increase its usefulness and preserve the chances for securing future living conditions. The responsibility for future generations therefore also extends in particular to the energy supply. It also said that a critical assessment is especially important, in particular when the consequences of technologies assume the character of “eternal burdens”. Based on the Ethics Committee’s recommendations Germany made decision of phasing out of nuclear energy by 2022.

In Taiwan, on October 20, 2016, President Tsai Ing Wen and her government decided the phase-out of nuclear power generation and the rise of power generation by renewable energy to 20% by 2025. The decision based on the consideration that a nuclear accident will imperil the existence of the nation surrounded by sea is reasonable.

There are a variety of technologies to generate electricity. As will be mentioned below, there are superabundant renewable energy sources for sustainable development of the whole world. There are no advantages and no positive reasons to use nuclear energy. Instead, developed countries are responsible for showing the technologies by which the whole world can survive only using renewable energy, without taking selfish attitude clinging to nuclear power generation that cannot spread to the world.

## **6. For Sustainable Development of the Whole World**

As shown in Figure 16, an extension of current global energy consumption trend will lead to complete exhaustion of fuel resources on our planet until the middle of this century, inducing intolerable global warming by complete combustion of fossil fuels. In fact, if complete exhaustion of petroleum and natural gas is predicted by fuel producing countries they will stop to export fuels one after another because they need remaining fuel for their own survival. Implementation of UNFCCC Paris Agreement is the minimum requirements for prevention of progress of global warming. Because

the atmospheric carbon dioxide concentration exceeded 400 ppm in contrast to the pre-industrial level of 280 ppm, in order to keep the temperature lower than 2 degrees Celsius above the pre-industrial level we need to suppress the carbon dioxide emissions to the pre-industrial level. At pre-industrial time we used only renewable energy. Consequently, we need to attain 100 % conversion from the fossil fuel combustion to the use of renewable energy. We have to establish technologies to use renewable energy as soon as possible and to spread the technologies for the survival and sustainable development of the whole world without consumption of any reserves of our planet as shown in Figure 18.

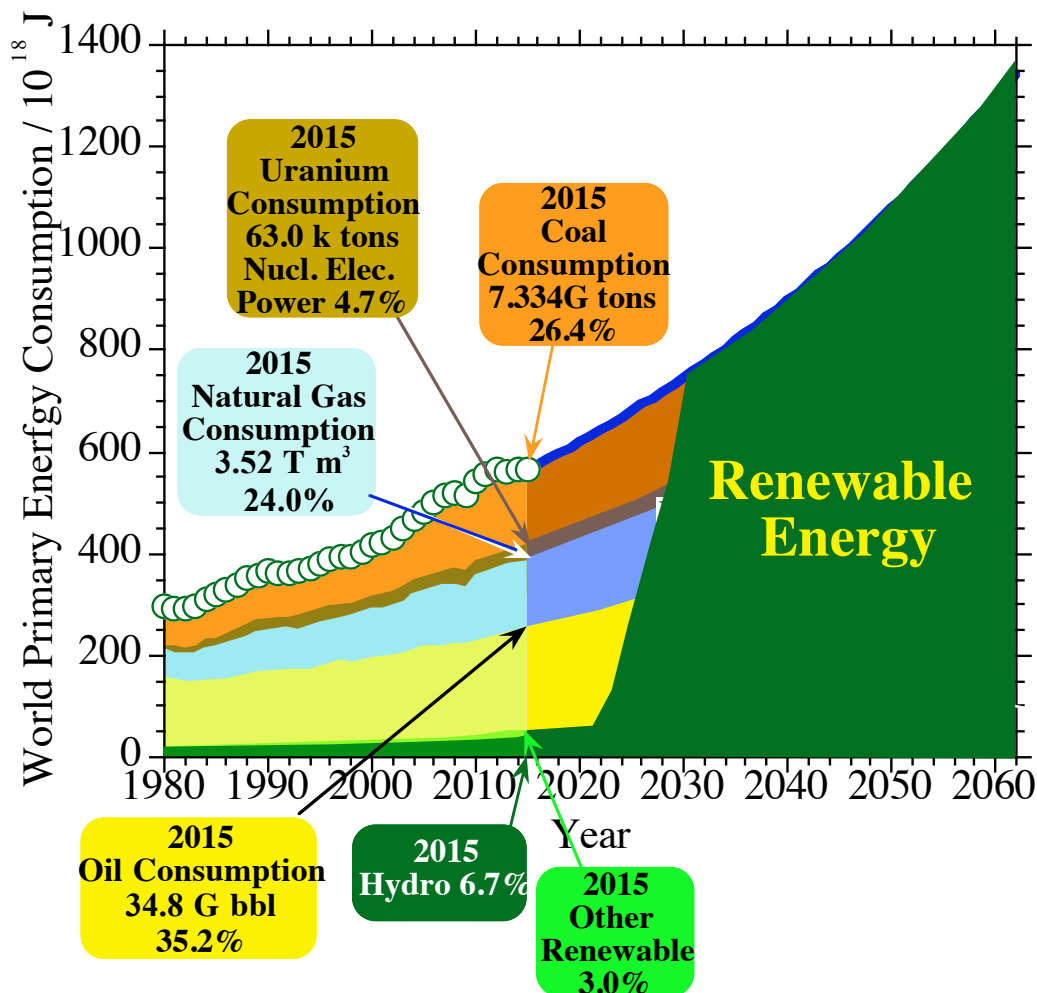


Figure 18 Necessity of development and spread of technologies to use renewable energy by which all people in the whole world can survive and can keep sustainable development.

Let us consider whether we can survive by only biomass as we were doing on pre-industrial time or not. It has been reported [35] that higher heating values of some woods are from 6,400 BTU per oven-dry pound (14.9 kilo joules per gram) for red oak, 8,000 BTU per oven-dry pound (18.6 kilo joules per gram) for red alder to 12,230 BTU per oven-dry pound (28.4 kilo joules per gram) for pitch pine. Their densities are 0.74, 0.4-0.7 and 0.67 grams per cubic centimeter, respectively [36]. Primary energy consumption of the world average in 2015 was 210.3 million joules per person per day. If we wish to generate fuel corresponding to 210.3 million joules per person per day by growing a tree with a density of 0.7 grams per cubic centimeter and with the heat of combustion of 20 kilo joules per gram, all people in the whole world should grow 47.8 cm high trees of 20 cm diameter every day. A Japanese and an American consumed 423.3 and 836.4 million joules per person per day of primary energy in 2015, respectively, and hence they need to grow 96.3 and 190.3 cm high trees of 20 cm diameter, respectively, every day. It is, therefore, impossible to survive relying only on biomaterials as has been so until pre-industrial time.

However, renewable energy sources are superabundant on our planet. The world consumed 565.16 quintillion ( $10^{18}$ ) joules of primary energy in 2015. Let's consider to generate this amount of energy in the form of electricity on deserts by solar cell of 20 % energy conversion efficiency under sunlight of 1000 W per  $\text{m}^2$  for 8 hours every day. The necessary desert area is  $0.2688 \times 10^6 \text{ km}^2$ , which corresponds to only 1.18% of  $22.69 \times 10^6 \text{ km}^2$  of the main desert area on our planet. This corresponds to only 8.0 % of the desert area in Australia. The whole world can survive even if we use only solar cell on a very limited desert area for power generation. Consequently, there are superabundant renewable energy sources on our planet.

There are a variety of renewable energy sources and we have various technologies for conversion of renewable energy to electricity. However, distant transmission of electricity is impossible. Furthermore, major renewable energy sources are wind and sunlight. Both are characterized by fluctuating and intermittent nature. It is not always possible to meet variable energy demands by supplying the power generated from fluctuating and intermittent renewable energy. We have no batteries to store a large amount of electricity. Although direct use of electricity generated from renewable energy is most effective, we need to convert the surplus electricity generated from renewable energy to fuel for direct use and regeneration of stable electricity which

will be used in supplying the deficit of electricity generated from renewable energy and in leveling of fluctuating and intermittent electricity.

As mentioned previously, in the 1970s we had been considering to form hydrogen by seawater electrolysis using fluctuating and intermittent electricity generated from renewable energy. However, we have no spread technologies for storage, transportation and combustion of hydrogen. There are no houses equipped with hydrogen cooking stoves. We, therefore, understood that we need to convert fluctuating and intermittent electricity to currently used fuel for which widespread infrastructures and technologies for storage, transportation and combustion exist.

## **7. Carbon Dioxide Recycling**

From ancient times we have been using fuel obtained simply by picking up the dead branches or digging the ground. Those are the fuel used in the whole world. Thus, the fuel that can be used world-widely should be synthesized by simple method; fuel must be formed by passing simply just the necessary reactant gas mixture through a simple reactor at ambient pressure. If sophisticated system is necessary for fuel production such fuel cannot be used in the whole world. For production of currently used fuel from renewable energy we need to use carbon dioxide as the feedstock in addition to hydrogen formed by water electrolysis using electricity generated from renewable energy. The authors were very fortunate. We could find extremely effective catalysts on which hydrogen reacts rapidly with carbon dioxide to form methane with almost 100% methane selectivity without forming other substances [37]. Methane is the main component of natural gas for which very efficient combustion systems and infrastructures for storage and transportation exist in the whole world.

On the basis of the finding of the catalyst for carbon dioxide methanation by the reaction with hydrogen at ambient pressure we made a proposal of global carbon dioxide recycling [38,39] about 25 years ago as shown in Figure 19. The intermittent and fluctuating power generated from renewable energy will be used for hydrogen production by seawater electrolysis at nearby coasts, and subsequently hydrogen will be converted to methane by the reaction with carbon dioxide. The synthesized natural gas, methane, will be supplied to the whole world using infrastructures and technologies for transportation of natural gas and then consumed with combustion systems of natural gas.

One thing different from the current situation is that we need to capture carbon dioxide from the exhaust gas and send carbon dioxide back to the place where hydrogen is available from renewable energy. If we realize the carbon dioxide recycling, the world can use renewable energy forever without emitting carbon dioxide into atmosphere.

For realization of global carbon dioxide recycling, we have technologies of power generation from renewable energy, and transportation and combustion systems for methane. Alkanolamine absorption and/or pressure swing adsorption can be applied to carbon dioxide capture from chimney. The properties of liquefied carbon dioxide are

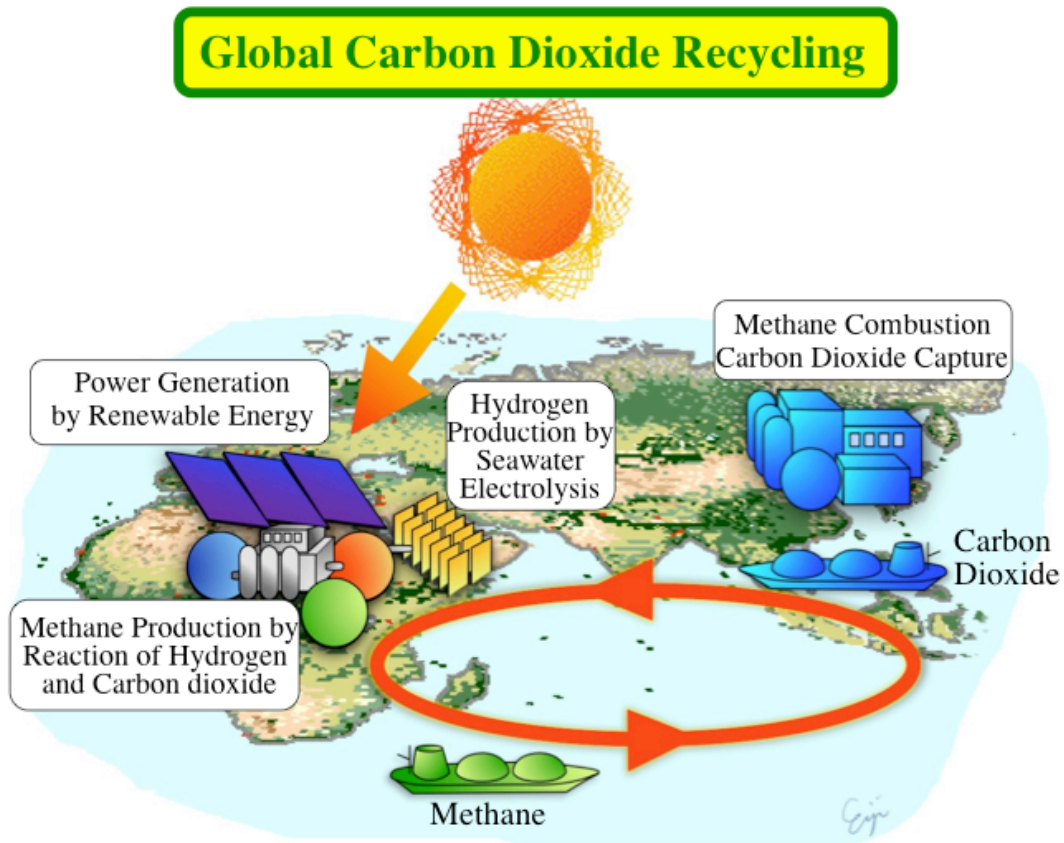


Figure 19 Schematic of global carbon dioxide recycling for survival and sustainable development of whole world [38,39].

almost the same as those of liquefied petroleum gas (LPG), and hence LPG transportation systems can be used if necessary for long distance transportation of liquefied carbon dioxide.

Thus, if we establish industrial technologies for hydrogen production by seawater

electrolysis and methane production by the reaction of hydrogen with carbon dioxide, we can realize global carbon dioxide recycling. Consequently, we started the study of key materials for global carbon dioxide recycling about 30 years ago.

## 8. Key Materials for Global Carbon Dioxide Recycling

Key materials toward realization of a global carbon dioxide recycling are effective cathode and anode for water electrolysis to form hydrogen and a catalyst for conversion of hydrogen to methane through the reaction with carbon dioxide.

### 8-1. Water Electrolysis

The electrolysis of water  $\text{H}_2\text{O}$  is carried out to form hydrogen  $\text{H}_2$  and oxygen  $\text{O}_2$ . In water electrolysis hydrogen production occurs on a cathode and oxygen production occurs on an anode. The electrolysis is schematically shown in Figure 20. The reaction is written as



We use a diaphragm between anode and cathode in the electrolyzer for separation of hydrogen and oxygen formed. Hydrogen ion  $\text{H}^+$  carrying a positive charge is able to pass through the diaphragm so as to transfer the positive charge from the anode compartment to the cathode compartment through the diaphragm.

Water just partially dissociates into hydrogen ion  $\text{H}^+$  and hydroxide ion  $\text{OH}^-$  as



Hydrogen production reaction on a cathode is

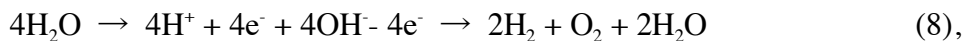


where  $\text{e}^-$  is an electron contributing to the reaction, provided from the anode to the cathode through the electric circuit and given from the cathode to a hydrogen ion  $\text{H}^+$ . Oxygen production reaction on an anode is



where four electrons are taken from four hydroxide ions  $4\text{OH}^-$  by the anode.

Total reaction can be written as



The volume ratio of hydrogen to oxygen formed by water electrolysis is always 2:1.



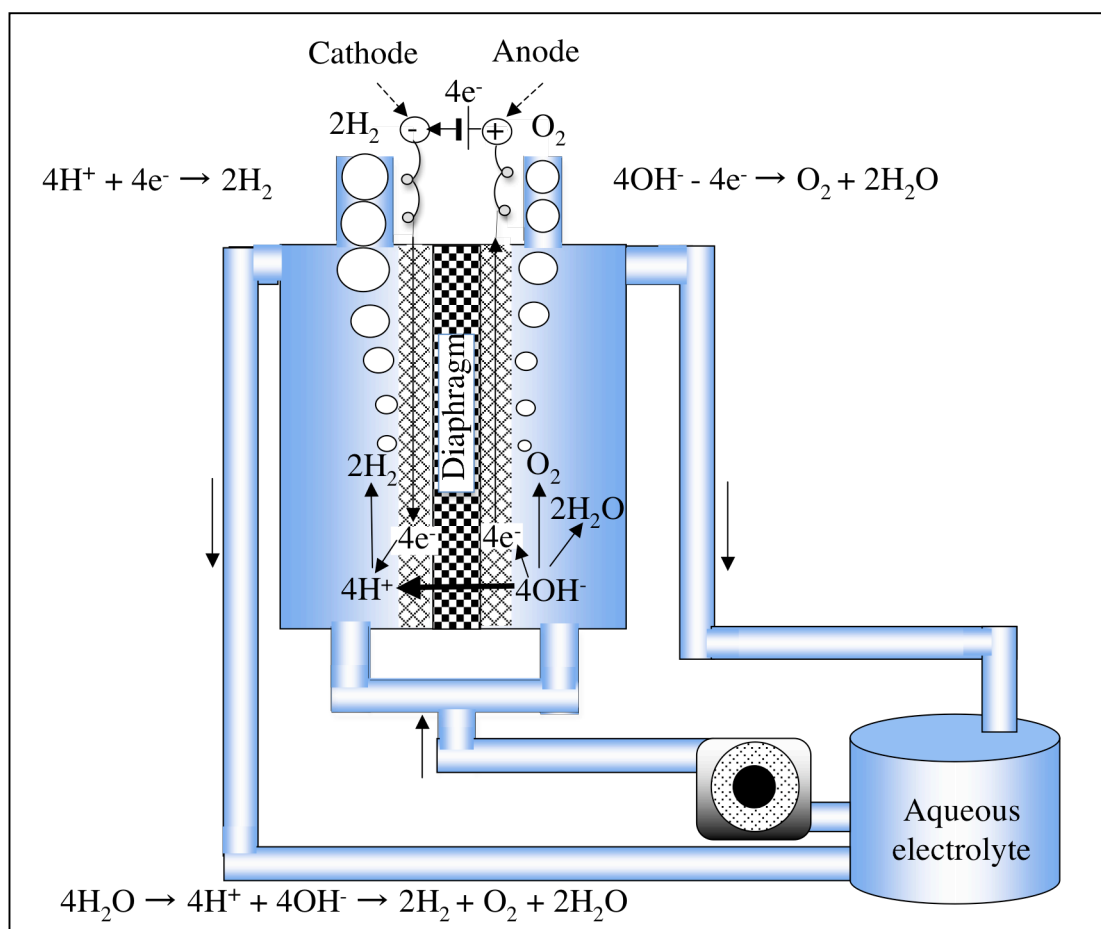


Figure 20 Schematic representation of water electrolysis.

The minimum potential required to split water into hydrogen and oxygen by electrolysis at 25 degrees Celsius is 1.228 V in a solution having the buffering action avoiding the pH change. When we apply the potential higher than 1.228 V between the cathode and the anode in an aqueous solution containing some ions called an aqueous electrolyte solution, electrons taken from hydroxyl ions by the anode move to the cathode through the electric circuit while the current passes in the solution by movement of mostly hydrogen ions from the anode compartment to the cathode compartment through the diaphragm, and forms hydrogen on the cathode and oxygen on the anode.

The production rates of hydrogen and oxygen are proportional to the current, that is, the number of electron passed, following Faraday's laws of electrolysis. For industrial

production of hydrogen and oxygen sufficiently high production rates of hydrogen and oxygen are required. For instance, in the electrolysis using the cathode and the anode having both 1 m<sup>2</sup> surface area we wish to pass the current of 6000 amperes, that is 6000 A per m<sup>2</sup> (A/m<sup>2</sup>), by which we can produce 2.5 Nm<sup>3</sup> of hydrogen on a cathode of 1 m<sup>2</sup> surface area for one hour, that is 2.5 Nm<sup>3</sup> per m<sup>2</sup> per hour and its half volume of oxygen. Because the volume of a fixed amount of gas is dependent on the temperature and atmospheric pressure, we use the symbol N for the gas volume, in which N means the gas volume at 0 degree Celsius and 1 atmosphere.

For sufficiently high gas production rate using a high current density we need to increase the potential applied between the anode and the cathode. The energy consumption for gas production is the product of current and potential that is wattage. We have to minimize the potential for passing 6000 A/m<sup>2</sup> between the anode and the cathode for industrial electrolysis. Our target was 1.8 V at 6000 A/m<sup>2</sup> at which the power consumption for production of 1 Nm<sup>3</sup> of hydrogen is 4.3 kWh per Nm<sup>3</sup> of hydrogen, H<sub>2</sub>. Thus, this potential of 1.8 V must be realized setting a diaphragm between anode and cathode compartments in the electrolyzer for separation of hydrogen and oxygen. If we use a cathode and an anode with lower activities for hydrogen and oxygen production, the higher applied potential is required with a consequent unnecessarily higher energy consumption. It is, therefore, most important for industrial electrolysis to get active anode and cathode.

### **8-1-1. Direct seawater electrolysis**

It is not always possible to use fresh water everywhere for electrolysis to form hydrogen in the world so that we at first considered to electrolyze directly seawater.

#### **8-1-1-1. Cathode for seawater electrolysis**

We succeeded to create the remarkably active Ni-Fe-C alloy cathode using a quite simple method of electrodeposition [40]. The hydrogen production reaction (6) consumes hydrogen ion. Formation of hydrogen ion is the result of dissociation of water (5), and hence the consumption of hydrogen ion leaves hydroxide ion OH<sup>-</sup> in the vicinity of the cathode surface. The increase in hydroxide ion concentration induces

the increase in the alkalinity. In neutral seawater, the supply of a hydrogen ion to a hydroxide ion to form water by the backward reaction of the reaction (5) is not easy, and because of rapid enrichment of hydroxide ion around the cathode, the pH around the cathode rapidly increases forming alkaline solution. Thus, the performance of the cathodes was examined in an alkaline solution of 8 M NaOH at 90°C.

Figure 21 shows the relationship between current density and applied potential for hydrogen generation [40]. As schematically shown in Figure 20, in the hydrogen production (6) hydrogen ions receive electrons from the cathode. For drawing the relationship between

current density and applied potential, the applied potential for the hydrogen production is written in negative number. In contrast, in the oxygen production (7) electrons are taken from hydroxide ions by the anode and hence the applied potential for the oxygen production is written in positive number.

It is clear in Figure 21

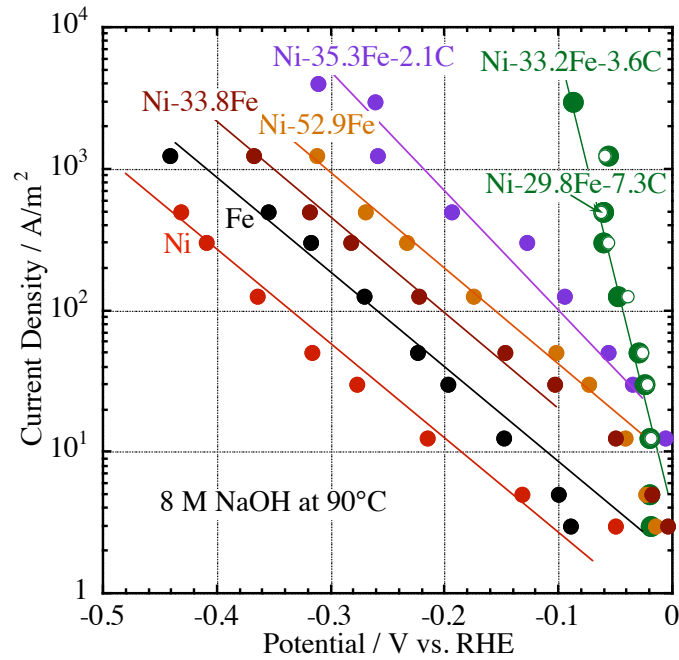


Figure 21 Relationship between current density and applied potential for hydrogen generation [40].

that there is a linear relation between the logarithmic current density and the applied potential: One order

of magnitude increase in the current density, that is hydrogen production rate, requires a linear increase in applied potential. If the mechanism of electrochemical reaction of hydrogen formation by electrolysis is not changed with applied potential, the relation between the current density,  $i$  and the applied potential,  $E$  of the electrochemical reaction for production of hydrogen in 1 second can be generally written as

$$i/F = K \exp(E/\beta) \quad (9),$$

where  $F$  is the Faraday constant,  $K$  is the constant including concentrations of species related to the reaction such as hydrogen ion and  $\beta$  is the constant depending upon the electrochemical reaction mechanism and the temperature of the electrolyte. If such a relation is obtained between the applied potential and the current density, the potential increase requiring one order of magnitude increase in the current density,  $\partial E/\partial(\log i)$ , is called Tafel slope and expressed by V/decade.

$$\partial E/\partial(\log i) = 2.303\beta \text{ V/decade} \quad (10),$$

where 2.303 is the conversion factor from natural logarithm,  $\ln i$  to base-10 logarithm,  $\log i$ .

Nickel, Ni is known to be a stable electrode but requires the high applied potential for the high hydrogen production rate, that is the high current density. This means that the hydrogen production on the nickel cathode requires higher electricity consumption because of lower activity of nickel for hydrogen production. At a fixed applied potential, iron, Fe shows higher current density than Ni, and Ni-Fe alloys further higher current density. Thus, iron has a higher activity for hydrogen production than nickel and Ni-Fe alloys have further higher activity. Although their current densities at a fixed potential are different, for these cathodes about 150 mV increase in the polarization potential is required for one order of magnitude increase in the current density. Thus, Tafel slope is about -150 mV/decade for nickel, iron and Ni-Fe alloys.

$$\partial E/\partial(\log i) \approx -150 \text{ mV/decade} \quad (11).$$

The increase in the Fe content of binary Ni-Fe alloys results in the increase in the current density at a fixed applied potential, but Tafel slope is not changed with the increase in the Fe content of Ni-Fe alloys.

In contrast, as in our cathode when iron and carbon, C are added to nickel the activity for hydrogen production is remarkably raised. For the Ni-Fe-C alloys with a sufficient addition of carbon an increase in 100 mV of the polarization potential results in about three orders of magnitude increase in the current density. Thus, Tafel slope becomes about -33 mV/decade.

$$\partial E/\partial(\log i) \approx -33 \text{ mV/decade} \quad (12).$$

The change in Tafel slope occurs due to change in the hydrogen evolution mechanism. Hydrogen evolution does not occur by a single reaction (6) but through a series of two elemental reactions. The first reaction (13) is discharge of a hydrogen ion,  $H^+$  receiving an electron from the cathode metal to form a hydrogen atom adsorbed

on the cathode surface,  $H_{ads}$



Subsequent reaction is either the recombination of two adsorbed hydrogen atoms to form a hydrogen molecule (14) or discharge of a hydrogen ion beside an adsorbed hydrogen atom to form a hydrogen molecule (15).



If the total reaction occurs through a series of elemental reactions, the total reaction rate is determined by the rate of the slowest elemental reaction. This slowest elemental reaction called the rate-determining reaction.

When we write the reaction rate equation in the case that the discharge of hydrogen ion (13) is the rate-determining reaction, the kinetic equation is

$$i/F = k_{13}[H^+] \exp(-FE/2RT) \quad (16),$$

where  $i$  is the current density,  $E$  is the applied potential,  $F$  is the Faraday constant,  $k_{13}$  is the rate constant of forward reaction of reaction (13),  $[H^+]$  is the activity of hydrogen ion, corresponding to  $pH$ ,  $R$  is the gas constant and  $T$  is the absolute temperature. Since

$$-\log [H^+] = pH \quad (17)$$

if  $pH$  of the solution is unchanged the Tafel slope  $\partial E / \partial (\log i)$  at  $90^\circ C$  is

$$\partial E / \partial (\log i) = -2.303 \times 2RT/F = -144 \text{ mV/decade} \approx -150 \text{ mV/decade} \quad (18).$$

This value is nearly the same as Tafel slope of nickel, iron and Fe-Ni alloys, and hence the rate-determining reaction of hydrogen evolution on them is the discharge of hydrogen ion (13). Because the discharge of hydrogen ion (13) on nickel, iron and Ni-Fe alloys is slower than much faster reaction (14) or (15), the high current density, that is the high rate of hydrogen production requires the high applied potential. As shown in Figure 21, at a fixed applied potential, the current density of iron is higher than nickel and the current densities of Ni-Fe alloys are further higher than iron. Thus, the discharge of hydrogen ion on the iron cathode is faster than that on the nickel cathode. The Ni-Fe alloy formation further accelerates the discharge of hydrogen ion. Nevertheless, the acceleration of discharge of hydrogen ion by Ni-Fe alloy formation is not sufficient to change the rate-determining reaction from the discharge of hydrogen ion (13) to much faster reaction (14) or (15).

If we can improve the electrode to accelerate the discharge of hydrogen ion (13) to

be faster than reaction (14) or (15), the rate determining reaction will be reaction (14) or (15).

If the reaction (14) is the rate-determining reaction, the kinetic equation is

$$i/F = k_{19}[H^+]^2 \exp(-2FE/RT) \quad (19),$$

where  $k_{19}$  is the rate constant including the rate constants of the forward reactions of (13) and (14) and the rate constant of backward reaction of reaction (13), because the forward and backward reactions of reaction (13) is in the equilibrium when the reaction (14) is the rate-determining reaction. When the reaction (14) is the rate-determining reaction and if pH of the solution is unchanged the Tafel slop at 90°C is

$$\partial E / \partial (\log i) = -2.303RT/2F = -36 \text{ mV/decade} \approx -33 \text{ mV/decade} \quad (20).$$

Thus, if the hydrogen molecule formation by the recombination of two adsorbed hydrogen atoms (14) is the rate-determining reaction, Tafel slope is -36 mV/decade at 90°C. This is the case of Ni-Fe-C alloys. Consequently, the addition of sufficient concentrations of iron and carbon to nickel led to remarkable acceleration of electrolytic hydrogen generation due to a significant increase in the rate of discharge of hydrogen ion (13) so as to change the rate-determining reaction from discharge of hydrogen ion (13) to the recombination of two adsorbed hydrogen atoms (14).

On the other hand, if the reaction (15) is the rate-determining reaction, the kinetic equation is

$$i/F = k_{21}[H^+]^2 \exp(-3FE/2RT) \quad (21),$$

where  $k_{21}$  is the rate constant including the rate constants of the forward reactions of (13) and (15) and the rate constant of backward reaction of the reaction (13), and Tafel slope at a constant pH and at 90°C is

$$\partial E / \partial (\log i) = -2.303 \times 2RT/3F = -48 \text{ mV/decade} \quad (22).$$

If the reaction (15) is the rate-determining reaction Tafel slope is about -48 mV/decade at 90°C. This is not our case.

In conclusion, our Ni-Fe-C cathodes have the mechanistically highest activity for hydrogen production.

As shown in Figure 21, at a fixed applied potential, the current density of the iron cathode is higher than the nickel cathode and the current densities of Ni-Fe alloy cathodes are further higher than the iron cathode. Because the rate-determining reaction for hydrogen generation on nickel, iron and Ni-Fe alloy cathodes is discharge of a hydrogen ion (13) the electron transfer from the iron cathode to hydrogen ion is

faster than that from the nickel cathode, and that from Ni-Fe alloy cathodes is further faster.

The discharge of a hydrogen ion occurs by transfer of a negative charge, an electron, from the cathode to a hydrogen ion. The discharge of hydrogen ion will become faster if the negative charge transfer from the cathode become easier by the change in cathode composition. The electron transfer to hydrogen ion is affected by the state of valence electron of the atom which gives an electron to a hydrogen ion, and the state of valence electron of the atom is characterized by the binding energy of the core electron. Thus, we examined the binding energies of core electrons by X-ray photoelectron spectroscopy [40]. As shown in Figure 22 the formation of Ni-Fe alloys led to an increase in the binding energy of Ni  $2p_{3/2}$  core electron and to a decrease in the binding energy of Fe  $2p_{3/2}$  core electron. As a result of Ni-Fe alloy formation a part of valence

electron in the Ni atom is transferred to the Fe atom, and thereby, Ni  $2p_{3/2}$  core electron is further strongly attracted to the nucleus of the Ni atom, while Fe  $2p_{3/2}$  core electron becomes weakly attracted to the nucleus of the Fe atom, leading to an increase in the binding energies of Ni  $2p_{3/2}$  electrons and to a decrease in the binding energies of Fe  $2p_{3/2}$  electrons. As shown in Figure 21, at a fixed potential the current density of Fe

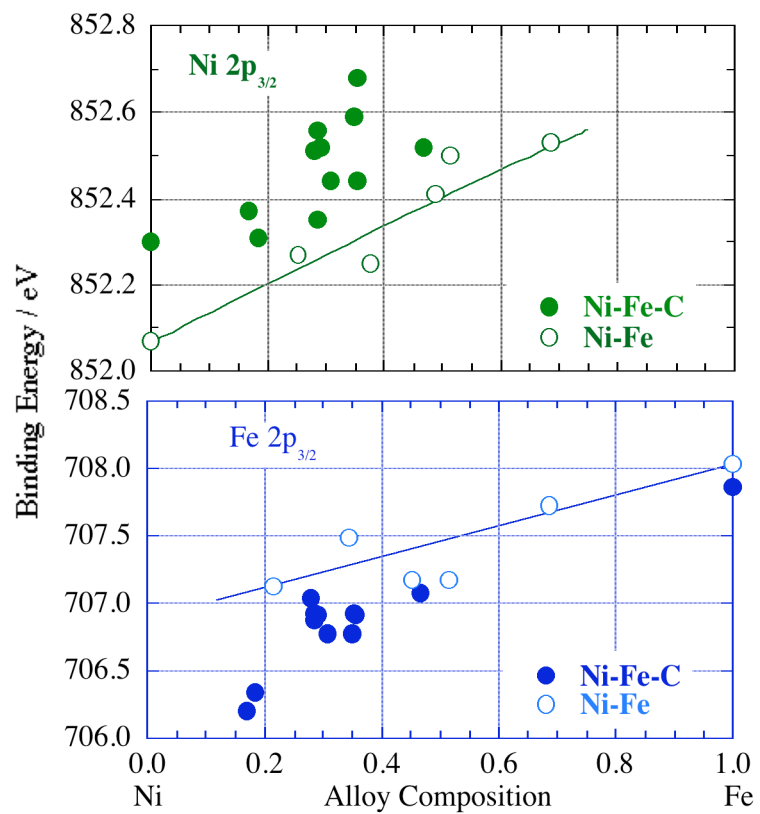


Figure 22 Change in binding energies of Ni  $2p_{3/2}$  and Fe  $2p_{3/2}$  electrons by Ni-Fe and Ni-Fe-C alloy formation [40].

for hydrogen evolution was higher than that of Ni, indicating that the electron transfer

from Fe to hydrogen ion was easier than that from Ni. Because the formation of Ni-Fe alloys resulted in charge transfer from Ni to Fe, the charge transfer from Fe in the Ni-Fe alloy cathode to hydrogen ion becomes faster than that from the Fe cathode, and the current density of hydrogen formation on the Ni-Fe alloy cathode becomes higher than that on the Fe cathode.

As shown in Figure 22 the formation of Ni-Fe-C alloys by the addition of carbon to Ni-Fe alloys increased further the binding energies of Ni  $2p_{3/2}$  electrons and decreased further the binding energies of Fe  $2p_{3/2}$  electrons. Thus, the electron transfer from Fe atom to hydrogen ion was further accelerated by Ni-Fe-C alloy formation and the discharge of hydrogen ion (13) became faster than the recombination of two adsorbed hydrogen atoms (14).

Consequently, we succeeded to create the Ni-Fe-C cathode by electrodeposition having the mechanistically highest activity for hydrogen production.

Further better cathodes for hydrogen production have been obtained by production of Co-Ni-Fe-C alloys which showed the same mechanism for hydrogen formation as that of Ni-Fe-C alloys [41].

### **8-1-1-2. Anode for seawater electrolysis**

There is a difficult problem for anode in direct seawater electrolysis. Seawater is a sodium chloride NaCl solution. If chloride ion  $Cl^-$  is present in the electrolyte solution its electrolysis results in the chlorine formation reaction (23) on the anode along with oxygen formation reaction (7) as



Although the equilibrium potential of the oxygen formation (7) is 0.167 V lower than that of the chlorine formation (23), because the oxygen formation is the 4 electron reaction while the chlorine formation is the 2 electron reaction, the chlorine formation becomes predominant at high overpotentials. Electrolysis of concentrated sodium chloride solutions has long been carried out in chlor alkali industry for electrolytic production of chlorine on the anode and sodium hydroxide NaOH and hydrogen on the cathode. In an aqueous NaCl solution,  $Na^+$ ,  $Cl^-$ ,  $H^+$  and  $OH^-$  ions exist. If hydrogen production (6) and chlorine formation (23) occur, remaining sodium ion  $Na^+$  and hydroxide ion  $OH^-$  form sodium hydroxide NaOH as





Chlor-alkali industry has been conducted to produce sodium hydroxide NaOH on the cathode and chlorine Cl<sub>2</sub> on the anode and hydrogen formed on the cathode is a by-product. The electrolysis in chlor-alkali industry is carried out using a diaphragm between cathode and anode compartments for separation of Cl<sub>2</sub> formed on the anode and H<sub>2</sub> formed on the cathode.

In addition, industrial direct seawater electrolysis has been carried out to form sodium hypochlorite, NaClO for sterilization of the cooling seawater at a water intake of plants such as power plants for prevention of clogging of the cooling system by marine life. For this objective seawater electrolysis is carried out with a narrow gap between the anode and cathode without using a diaphragm so as to form sodium hypochlorite by the reaction of sodium hydroxide formed on the cathode and chlorine formed on the anode as



Products of industrial electrolysis of aqueous NaCl solutions in both chlor-alkali industry and direct seawater electrolysis for sterilization of seawater are the same sodium hydroxide and hydrogen on the cathode and chlorine on the anode.

In direct seawater electrolysis for our mass production of hydrogen the emission of chlorine of the same amount as hydrogen are not allowed. Thus, we needed to have an anode on which only oxygen evolution reaction occurs without forming any chlorine in direct seawater electrolysis. Oxygen formation (7) and chlorine formation (23) are competitive reactions. The preferential reaction depends on the anode materials.

Both reactions (7) and (23) occur under a strongly oxidizing condition. In chloride ion solutions ordinary metal anodes other than precious metals readily suffer corrosive degradation under oxidizing condition. When precious metal anodes with high corrosion resistance are used in chloride containing solutions, not oxygen evolution but chlorine formation preferentially occurs.

Consequently, our first target was to create a new anode on which oxygen formation exclusively occurs with no formation of chlorine in direct seawater electrolysis.

Anodes used for chlorine Cl<sub>2</sub> formation for production of sodium hypochlorite NaClO in industrial seawater electrolysis generally consist of a titanium substrate covered with an iridium dioxide electrocatalyst, IrO<sub>2</sub>/Ti, where the electrocatalyst has high activity for production of necessary substance Cl<sub>2</sub> by electrolysis of an aqueous

NaCl solution. In practical seawater electrolysis for sterilization of seawater, the chlorine formation efficiency often decreased by deposition of manganese dioxides on the anode surface from seawater. Seawater generally contains manganese ion  $Mn^{2+}$ . Deposition of manganese dioxides on the  $IrO_2/Ti$  anode reduced the chlorine formation but enhanced the oxygen evolution.

We, therefore, performed to enhance further the oxygen evolution on manganese dioxide by adding various elements to manganese dioxides in  $MnO_2/IrO_2/Ti$  anodes. The addition of tungsten [42] or molybdenum [43] to manganese dioxide was particularly effective in enhancing the oxygen evolution in sodium chloride solutions. As shown in Figure 23 [43], in electrolysis of 0.5 M NaCl of pH 8 at a current density of  $1000\text{ A/m}^2$  on the  $MnO_2/IrO_2/Ti$  anode, 92 % of electricity is used for oxygen evolution but 8 % of electricity is consumed for chlorine formation.

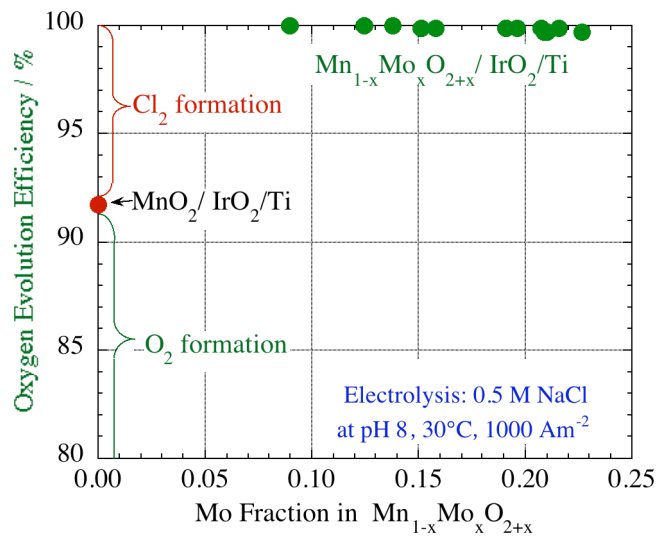


Figure 23 Oxygen evolution efficiency of  $MnO_2/IrO_2/Ti$  and  $Mn_{1-x}Mo_xO_{2+x}/IrO_2/Ti$  anodes in electrolysis of 0.5 M NaCl of pH 8 at  $1000\text{ A/m}^2$  [43].

However, when small fractions of  $Mn^{4+}$  in  $MnO_2$  was substituted with  $Mo^{6+}$  the resultant  $Mn_{1-x}Mo_xO_{2+x}/IrO_2/Ti$  anodes show 100 % oxygen evolution efficiency.

In an  $IrO_2/Ti$  anode the titanium substrate acts as a hard solid which passes the current from an electric circuit to  $IrO_2$ . Thus, the surface  $IrO_2$  can act as an electrocatalyst for evolution of chlorine in aqueous solutions containing chloride ion and for evolution of oxygen in aqueous solutions without containing chloride ion. Titanium itself cannot be used directly as the anode in electrolysis of any aqueous solutions, because, under the anodically oxidizing condition, titanium is readily oxidized and covered with an insulating titanium dioxide,  $TiO_2$ , which does not pass the current so that titanium cannot receive an electron from a hydroxide ion. In contrast,

iridium dioxide, IrO<sub>2</sub>, has a good electric conductivity. Thus, IrO<sub>2</sub> covered Ti, IrO<sub>2</sub>/Ti, can act as the anode to take electrons from chloride ion Cl<sup>-</sup> and hydroxyl ion OH<sup>-</sup>. If the surface IrO<sub>2</sub> layer is sufficiently thick, oxidation of titanium can be avoided, and the IrO<sub>2</sub>/Ti anodes are used not only for the chlorine formation in seawater electrolysis but also for the oxygen evolution in aqueous solutions without chloride ion in industrial metal plating at high current densities, such as high speed Ni plating on automobile steel sheet.

The IrO<sub>2</sub>/Ti anode is produced by heating in air for titanium coated with a butanol solution containing iridium ion, Ir<sup>4+</sup>. When the IrO<sub>2</sub>/Ti anode is used for oxygen evolution in an aqueous solution containing manganese ion, Mn<sup>2+</sup>, the IrO<sub>2</sub>/Ti anode is covered with manganese dioxide, MnO<sub>2</sub>, forming the MnO<sub>2</sub>/IrO<sub>2</sub>/Ti anode. This is anodic deposition of MnO<sub>2</sub> on the IrO<sub>2</sub>/Ti from a Mn<sup>2+</sup> solution as shown in reaction (26).



For instance, in electroplating of nickel Ni from a nickel ion, Ni<sup>2+</sup> solution (27)



a nickel ion receives two electrons from the cathode, forming neutral metal, and hence this is cathodic deposition. In contrast, in reaction (26) two electrons are taken from a magnesium ion, Mn<sup>2+</sup> by the anode forming Mn<sup>4+</sup>O<sub>2</sub><sup>2-</sup>. Thus, this is anodic deposition.

In the resultant MnO<sub>2</sub>/IrO<sub>2</sub>/Ti anode, IrO<sub>2</sub> is an intermediate layer between the electrocatalyst MnO<sub>2</sub> for oxygen formation and the substrate Ti and prevents oxidation of Ti. The enhancement of oxygen evolution efficiency and durability of the MnO<sub>2</sub>/IrO<sub>2</sub>/Ti anode was performed by modifying compositions and preparation methods [44-52]. Figure 24 [52] shows examples of performance of anodes, on which the same electrocatalyst Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub> was prepared by the same procedure from the same solution but the intermediate layers were different.

When an IrO<sub>2</sub> layer was used as an intermediate layer, the Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub>/IrO<sub>2</sub>/Ti anode, in which the IrO<sub>2</sub> layer was prepared from 0.52 M Ir<sup>4+</sup> butanol solution, showed the best performance. In order to extend the life of the anode we added tin, Sn in IrO<sub>2</sub> layer, and we found the Mn<sub>1-x-y</sub>Mo<sub>x</sub>Sn<sub>y</sub>O<sub>2+x</sub>/Ir<sub>1-z</sub>Sn<sub>z</sub>O<sub>2</sub>/Ti anode, in which the intermediate layer was prepared from 0.04 M Ir<sup>4+</sup>-0.06 M Sn<sup>4+</sup> butanol solution, showed the best performance, in spite of the fact that the concentration of Ir<sup>4+</sup> in the 0.04 M Ir<sup>4+</sup>-0.06 M Sn<sup>4+</sup> butanol solution was only 1/13 of that in 0.52 M Ir<sup>4+</sup> butanol solution.

On the  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}/\text{Ir}_{1-z}\text{Sn}_z\text{O}_2/\text{Ti}$  anode 99.9 % or more electricity was used for oxygen evolution for 4,200 hours.

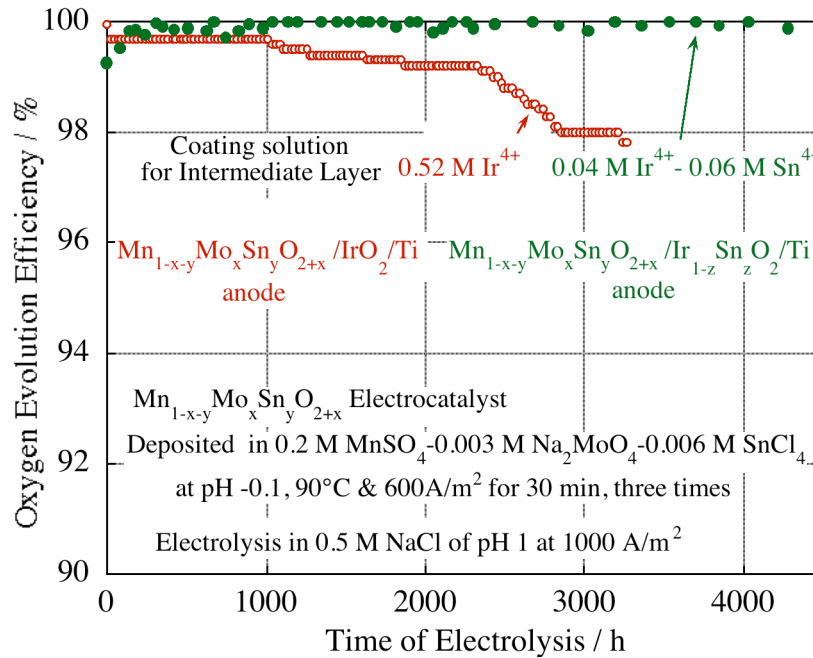


Figure 24 The performance of  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}/\text{IrO}_2/\text{Ti}$  and  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}/\text{Ir}_{1-z}\text{Sn}_z\text{O}_2/\text{Ti}$  anodes in electrolysis of 0.5 M NaCl of pH 1 at 1000 A/m<sup>2</sup> [52].

The main role of the intermediate  $\text{IrO}_2$  layer is prevention of oxidation of the substrate titanium. During electrolytic oxygen evolution on the anode, some oxygen atoms formed on the  $\text{MnO}_2$ -type oxide electrocatalyst surface migrate inward through the  $\text{MnO}_2$ -type oxide and  $\text{IrO}_2$  layers to the substrate Ti surface and form  $\text{TiO}_2$  layer on the Ti surface. Because of a high electric resistance of  $\text{TiO}_2$ , for oxygen production at a constant production rate, that is at a constant current density the potential applied to the electrolyzer increases with the growth of  $\text{TiO}_2$ . Even if 99.9% oxygen evolution efficiency is kept, higher applied potential, that is the higher electricity consumption is not allowed in industrial electrolysis.

For industrial high speed Ni plating thick  $\text{IrO}_2$  layer has been used for the  $\text{IrO}_2/\text{Ti}$  anode for prevention of oxidation of titanium. Industrial Ni plating is not big industry and hence a thick  $\text{IrO}_2$  layer can be used. However, for hydrogen energy production in the whole world, the requirement of precious metals for the electrode is not practical but

high electricity consumption by  $\text{TiO}_2$  formation is not allowed.

Consequently, although we found the effective electrocatalyst, such as  $\text{Mn}_{1-x-y}\text{Mo}_x\text{Sn}_y\text{O}_{2+x}$  for oxygen evolution without forming chlorine in direct seawater electrolysis we need further improvement of the anode for direct seawater electrolysis.

In this manner there remain several problems to be solved in direct seawater electrolysis. However, industrialization of electrolytic hydrogen production is urgent. Thus, we decided to use hot alkaline water electrolysis creating energy-saving anode and cathode for industrial application.

### 8-1-2. Anode and cathode for alkaline solution electrolysis

In comparison with direct seawater electrolysis using the above-mentioned anodes, the alkaline solution electrolysis is economically feasible for hydrogen generation, even if fresh water is used after desalination of seawater by a reverse osmotic membrane method and subsequent ion exchange.

Thus, for immediate industrialization we adopted alkaline solution electrolysis using newly created anode and cathode. Nickel alloys were effective for the cathode. Because the most of metals other than precious metals dissolve under anodic polarization condition in hot alkaline solutions, only nickel and cobalt could be candidate materials for the anode.

Figure 25 shows the performance of newly created anodes and cathodes for alkaline solution electrolysis. Our immediate target of an applied potential of 1.8 V at a current density of  $6000 \text{ Am}^{-2}$  has been already attained using a diaphragm for separation of hydrogen and oxygen.

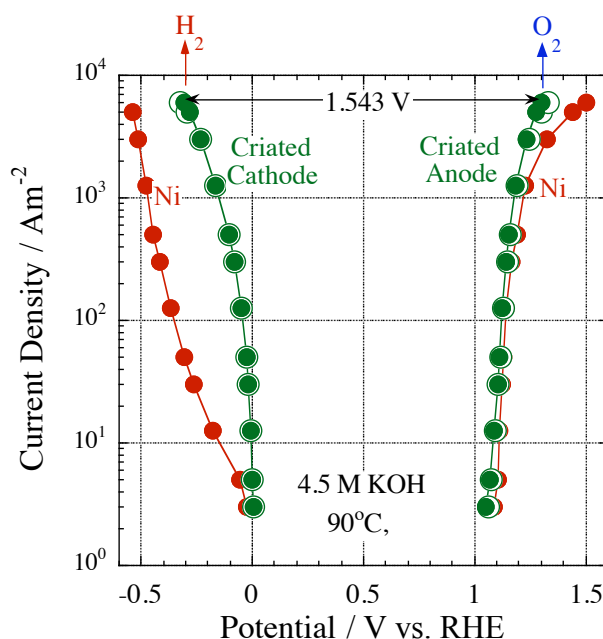


Figure 25 Relationship between current density and applied potential for hydrogen and oxygen generation in electrolysis of 4.5 M KOH at 90°C.

Industrial electrolyzers are constructed using these electrodes to produce hydrogen and oxygen for practical carbon dioxide methanation.

## 8-2. Catalyst for Carbon Dioxide Methanation

Reaction formula (28) of formation of methane by the catalytic reaction of carbon dioxide and hydrogen is very simple, which can be written easily even by junior high school students.



However, the real reaction at ambient pressure is very difficult. When conventional catalysts were used for the reaction of carbon dioxide and hydrogen at ambient pressure, the product was not generally methane but carbon monoxide (29).



In addition, the reaction (29) is very slow and the reaction rate easily decreases by contamination of catalyst with CO.

In contrast, our objective is rapid formation of methane at ambient pressure using a simple reactor by the reaction (28) with almost 100% methane selectivity without forming carbon monoxide.

For catalytic reaction, an oxygen in carbon dioxide must adsorb to a special site on the surface of catalyst so as to weaken the bond strength between oxygen and carbon in carbon dioxide. At the same time hydrogen must adsorb on another special site within the atomistic distance to the adsorption site of the oxygen in carbon dioxide in the surface of catalyst. If these situations occur hydrogen atoms react with

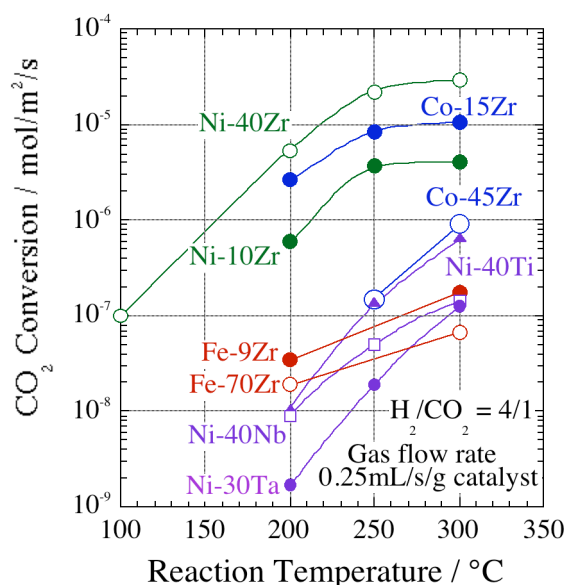


Figure 26 Analytical result of conversion of carbon dioxide by passing a gas mixture of 4 volumes of H<sub>2</sub> and 1 volume of CO<sub>2</sub> on Ni-ZrO<sub>2</sub>, Co-ZrO<sub>2</sub>, Fe-ZrO<sub>2</sub>, Ni-TiO<sub>2</sub>, Ni-Nb<sub>2</sub>O<sub>3</sub>, Ni-Ta<sub>2</sub>O<sub>3</sub> catalysts at a flow rate of 0.25 mL/s on 1 g of catalyst [37].

adsorbed carbon dioxide and leads finally to the formation of methane. In general, carbon dioxide adsorbs on the oxidized metal surface while hydrogen adsorbs on the metal surface in the metallic state. Thus, the catalyst for methane formation from carbon dioxide and hydrogen must consist of a uniform mixture of oxide and metal. For the formation of the uniform mixture of oxide and metal we used alloys as the catalyst precursor. In those alloys some of components are readily oxidized in the methane formation environments but other components stay in the metallic state.

As shown in reaction (28), the reactant gas is the mixture of one volume of carbon dioxide and four volumes of hydrogen. The forward reaction (28) is exothermic. Because the reaction releases heat, the lower temperature is better for conversion of all carbon dioxide to methane, but if the reaction temperature is lower, the reaction is slower. For industrial production of methane, rapid production at higher temperature is required. However, at higher temperatures the endothermic reverse reaction of (28) is enhanced. Thus, the reaction temperature will be 250 to 500 degrees Celsius. In the mixture of carbon dioxide and hydrogen

at 250-500 degrees Celsius, easily oxidized metals such as titanium, zirconium, niobium and tantalum will be converted to oxides but metals with lower susceptibility to oxidation, such as nickel will stay in the metallic state. Based on this expectation we used nickel, cobalt and iron alloys with titanium, zirconium, niobium and tantalum: Ni-Ti, Ni-Zr, Ni-Nb, Ni-Ta, Co-Ti, Co-Zr, Co-Nb, Co-Ta, Fe-Ti, Fe-Zr, Fe-Nb and

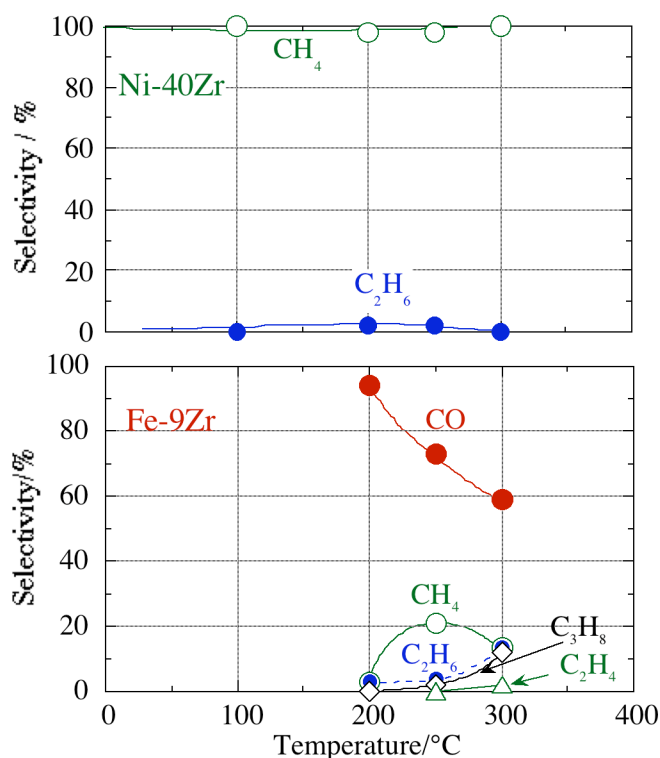


Figure 27 Analytical results of reaction products after passing a gas mixture of 4 volumes of H<sub>2</sub> and 1 volume of CO<sub>2</sub> on Ni-ZrO<sub>2</sub> and Fe-ZrO<sub>2</sub> catalysts at a flow rate of 0.25 mL/s on 1 g of catalyst [37].

Fe-Ta alloys of various compositions. We prepared solid solution alloys consisting of a single phase by rapid quenching of alloy liquid of a homogeneous mixture of atoms. These alloys have no crystallographic structure, and are called amorphous alloys. After oxidation in air and reduction in hydrogen we got the metal-oxide mixture of Ni-TiO<sub>2</sub>, Ni-ZrO<sub>2</sub>, Ni-Nb<sub>2</sub>O<sub>3</sub>, Ni-Ta<sub>2</sub>O<sub>3</sub>, etc.

Figure 26 [36] shows results of gas analysis after removal of water from the effluent gas of a tubular gas reactor through which a gas mixture of 20% carbon dioxide and 80% hydrogen was passed at the flow rate of 0.25 mL/s on 1 g of catalyst. The rate of conversion of carbon dioxide was particularly high when the catalyst prepared from the Ni-40Zr alloy was used.

Figure 27 [37] is analytical results of reaction products. The methane selectivity of the Ni-40Zr alloy catalyst is almost 100 % and a minor by-product is ethane, while on the catalysts showing low conversion the main product is carbon monoxide. Thus, the Ni-ZrO<sub>2</sub> type catalysts prepared from Ni-Zr alloys are evaluated as the ideal catalysts for carbon dioxide methanation.

The unique characteristics of the Ni-ZrO<sub>2</sub> type catalysts prepared from Ni-Zr alloys have been clarified by detailed examination [53,54]. As shown in Figure 28 [53] when binary Ni-Zr alloys were used for preparation of catalysts the maximum activity appeared at about medium concentration of nickel. The stable crystallographic structure of pure zirconium oxide ZrO<sub>2</sub> at temperatures for catalyst

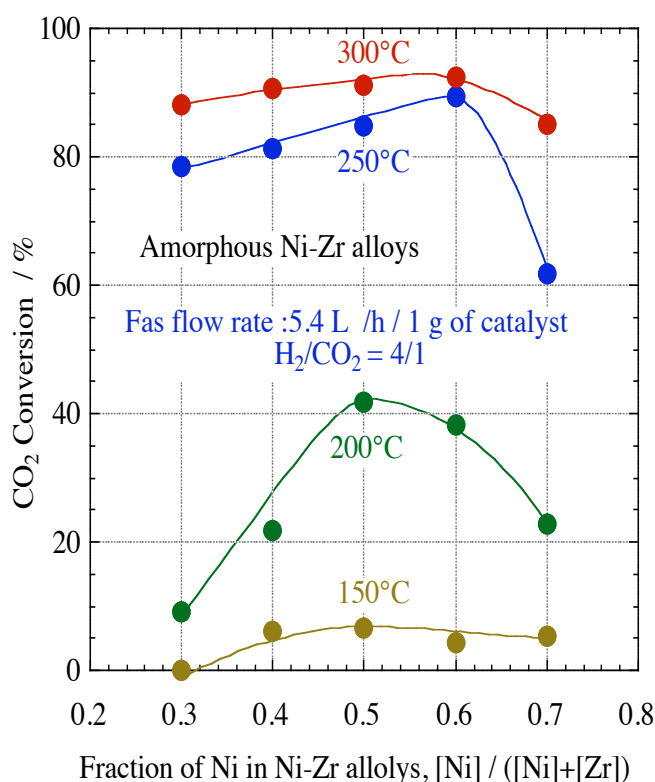


Figure 28 CO<sub>2</sub> conversion efficiency for methanation of gas mixture of 4 volumes of H<sub>2</sub> and 1 volume of CO<sub>2</sub> at a flow rate of 5.4L/h on 1 g of catalyst as a function of Ni fraction of Ni-Zr alloy precursors [53].



preparation and methanation reaction is monoclinic. However, both monoclinic and tetragonal  $\text{ZrO}_2$  were present in the catalysts prepared from Ni-Zr alloys. As shown in Figure 29 [53,54] the relative amount of tetragonal  $\text{ZrO}_2$  increased with an increase in concentration of nickel in Ni-Zr alloys. Although the number of surface Ni atoms effective for methanation decreased with an increase in concentration of nickel in Ni-Zr alloys due to decrease in the surface Ni dispersion by coagulation, the turnover number, the number of methane formed on a surface Ni atom in one second, increased with concentration of nickel in Ni-Zr alloys. Consequently, with an increase in tetragonal  $\text{ZrO}_2$  with the increase in alloy Ni content, the turnover number, the catalytic activity for methanation reaction increased. In fact, the maximum activity was found at about medium concentration of nickel in Ni-Zr alloys. This corresponded to the maximum amount of tetragonal  $\text{ZrO}_2$  in the catalyst. Further increase in the nickel content of precursor Ni-Zr alloys increased the ratio of tetragonal  $\text{ZrO}_2$  to monoclinic  $\text{ZrO}_2$ , but of course decreased the total amount of  $\text{ZrO}_2$  to form tetragonal  $\text{ZrO}_2$ . Thus, the highest activity for  $\text{CO}_2$  methanation appeared at the highest amount of tetragonal  $\text{ZrO}_2$ . It was, therefore, found that Ni-tetragonal  $\text{ZrO}_2$  is the effective catalyst.

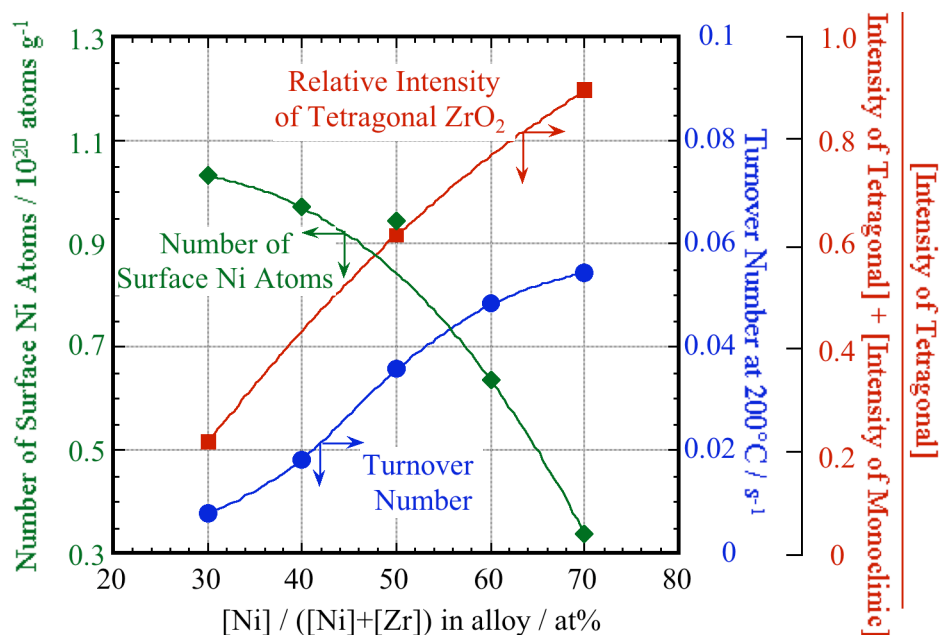


Figure 29 Turnover number of  $\text{CH}_4$  formation on a surface Ni atom, number of surface Ni atoms and relative amount of tetragonal  $\text{ZrO}_2$  as a function of Ni fraction of Ni-Zr alloy precursors [53,54].

In fact, tetragonal  $\text{ZrO}_2$  is not pure  $\text{ZrO}_2$ . The oxidation of the Ni-Zr alloy to form

ZrO<sub>2</sub> leads to inclusion of some Ni<sup>2+</sup> in the ZrO<sub>2</sub> crystal lattice. ZrO<sub>2</sub> consists of a Zr<sup>4+</sup> and two O<sup>2-</sup>, while nickel oxide is NiO, consisting of a Ni<sup>2+</sup> and an O<sup>2-</sup>. If divalent nickel Ni<sup>2+</sup> is included in the ZrO<sub>2</sub> crystal lattice, the number of O<sup>2-</sup> in ZrO<sub>2</sub>-type oxide becomes less than 2 and the deficiency of O<sup>2-</sup> from 2 is the same as the number of Ni<sup>2+</sup> included in the ZrO<sub>2</sub> lattice. The resultant oxide is Zr<sup>4+</sup><sub>1-x</sub>Ni<sup>2+</sup><sub>x</sub>O<sub>2-x</sub>. The O<sup>2-</sup> vacant sites in ZrO<sub>2</sub>-type oxide crystal is called oxygen vacancies. The resultant Zr<sup>4+</sup><sub>1-x</sub>Ni<sup>2+</sup><sub>x</sub>O<sub>2-x</sub> consists of a single phase, in which x corresponds to the number of oxygen vacancies in the ZrO<sub>2</sub> lattice. Because of the presence of oxygen vacancies in the ZrO<sub>2</sub> lattice, monoclinic structure is not stable and the resultant ZrO<sub>2</sub> is stabilized in the form of tetragonal structure.

It has been known that the oxygen vacancy in tetragonal ZrO<sub>2</sub>-type oxide strongly attracts oxygen in environments. For instance, the exposure of tetragonal Zr<sup>4+</sup><sub>1-y</sub>Y<sup>3+</sup><sub>y</sub>O<sub>2-0.5y</sub> in steam at an elevated temperature such as 250°C resulted in mass increase by inclusion of H<sub>2</sub>O, whose number was almost the same as the number of the oxygen vacancies, with a consequent transformation of tetragonal Zr<sup>4+</sup><sub>1-y</sub>Y<sup>3+</sup><sub>y</sub>O<sub>2-0.5y</sub> to monoclinic structure [55]. The detail of the transformation was explained later [56].

The strong affinity of the oxygen vacancies in the tetragonal ZrO<sub>2</sub>-type oxide to oxygen in carbon dioxide enhances the adsorption of carbon dioxide. This is the reason why Ni-tetragonal ZrO<sub>2</sub>-type oxide catalysts are effective for methane formation by hydrogenation of carbon dioxide.

In this connection, Takano [57] in studying the methanation reaction of the mixture of four volumes of hydrogen and one volume of carbon dioxide on the Ni-tetragonal ZrO<sub>2</sub>-type oxide catalysts by infrared diffuse reflectance spectroscopy identified bidentate carbonate and bidentate formate as intermediate species, and suggested the estimated path of conversion of carbon dioxide to methane on a Ni-ZrO<sub>2</sub>-type catalyst as shown in Figure 30 [57]. The finding of the intermediate bidentate formate suggests that the rate determining reaction is the transformation from bidentate formate to formaldehyde and indicates that the catalyst for methanation of carbon dioxide is necessary to have the ability to form the bidentate adsorption of carbon dioxide on its surface. Thus, there must be the adsorption site of an oxygen in a carbon dioxide on the catalyst surface and at the same time the catalyst surface must provide an oxygen to which carbon in the carbon dioxide is bound.

As shown in Figure 30, bidentate carbonate adsorption can be done by binding an

oxygen in a carbon dioxide to the oxygen vacancy site in tetragonal  $\text{ZrO}_2$  type oxide and at the same time binding of carbon in the carbon dioxide to an oxygen in tetragonal  $\text{ZrO}_2$  type oxide.

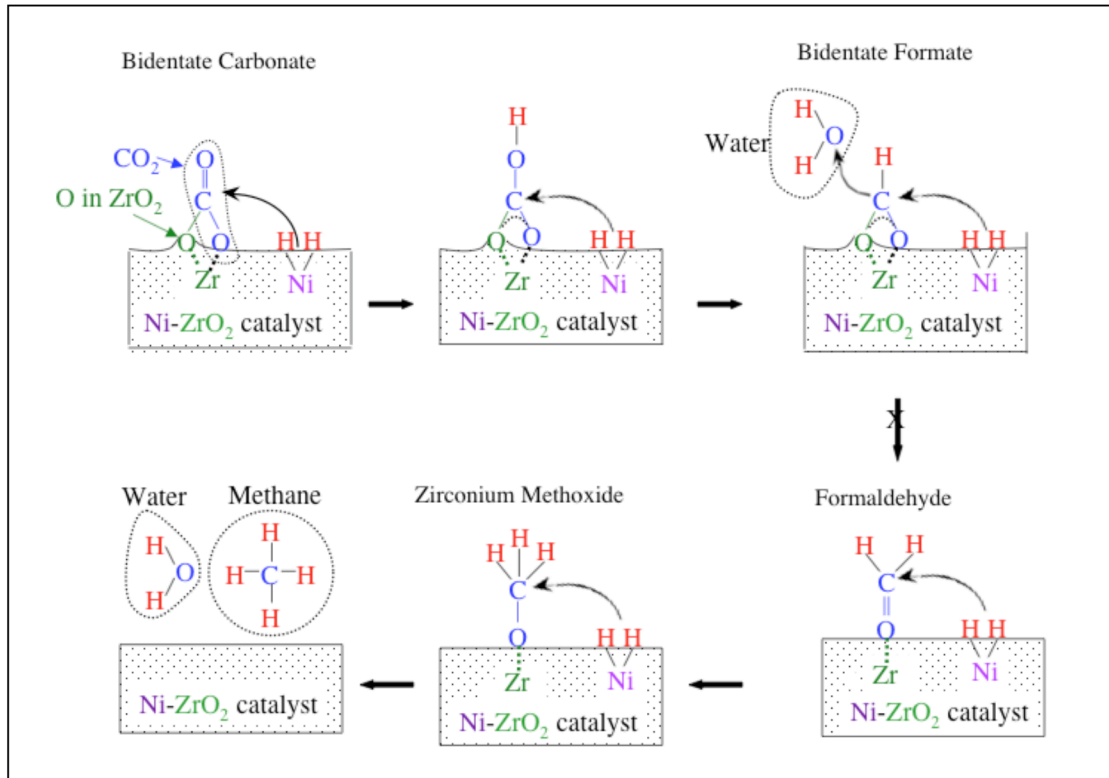


Figure 30 Estimated path of conversion of carbon dioxide to methane by the reaction with hydrogen on a  $\text{Ni-ZrO}_2$ -type catalyst [57].

The Ni-tetragonal  $\text{ZrO}_2$ -type oxide catalysts is exactly the substance to provide the sites for the bidentate adsorption of carbon dioxide. The formation of bidentate carbonate accelerates hydrogenation of carbon dioxide to form methane and water.

Further increase in the catalytic activity was expected by an increase in the relative amount of the tetragonal  $\text{ZrO}_2$ -type oxide. In Ni-Zr alloys, an increase in the nickel content increases the relative amount of tetragonal  $\text{Zr}^{4+}_{1-x}\text{Ni}^{2+}_x\text{O}_{2-x}$ , but decreases the absolute amount of  $\text{ZrO}_2$ -type oxide including tetragonal  $\text{Zr}^{4+}_{1-x}\text{Ni}^{2+}_x\text{O}_{2-x}$  in addition to a decrease in the surface dispersion of Ni atoms. It is, therefore, necessary to increase the amount of the tetragonal  $\text{ZrO}_2$ -type oxide without an increase in nickel content of the catalyst. As shown in the above-mentioned example of  $\text{Zr}^{4+}_{1-y}\text{Y}^{3+}_y\text{O}_{2-0.5y}$ , the tetragonal  $\text{ZrO}_2$ -type oxide can be stabilized by inclusion oxidized rare earth elements in

the crystal lattice. Thus, we prepared amorphous Ni-Zr-rare earth element alloys as the catalyst precursors [58]. Figure 31 [58] shows the beneficial effects of the addition of rare earth elements on the activity of catalysts for carbon dioxide methanation. The addition of rare earth elements not only stabilized the tetragonal  $\text{ZrO}_2$ -type oxide but

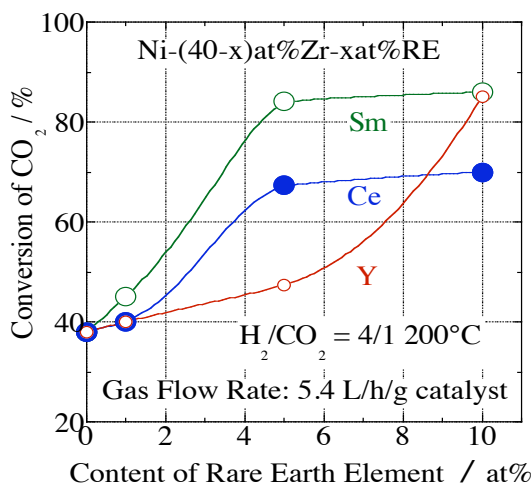


Figure 31 Effects of rare earth elements in Ni-Zr-Sm, Ni-Zr-Ce and Ni-Zr-Y catalysts on conversion of carbon dioxide by passing a gas mixture of 4 volumes of  $\text{H}_2$  and 1 volume of  $\text{CO}_2$  at a flow rate of 5.4L/h on 1 g of catalyst [58].

also significantly enhanced the methanation activity.

Amorphous alloys were effective for basic study as the catalyst precursors but not suitable for mass production of catalysts. As has been explained, the prerequisite for catalyst is not the presence of alloys but the formation of metallic nickel supported on tetragonal  $\text{ZrO}_2$ -type oxide. We created such catalysts in the form of powder [59]. Aqueous zirconia sol was used as zirconium source in which salts of nickel and rare earth elements were dissolved. After drying, heating in air at 300-650 degrees Celsius was carried

out to form the oxide mixture of NiO and tetragonal  $\text{ZrO}_2$ -type oxide containing  $\text{Ni}^{2+}$  and rare earth element cations. Heating the oxide mixture in hydrogen stream to reduce the surface NiO to Ni led to the formation of the catalyst consisting of Ni supported on tetragonal  $\text{ZrO}_2$ -type oxide. The performance of the catalyst powder was almost the same as that of the catalyst obtained from the amorphous Ni-Zr-rare earth element alloy precursors.

In order to produce catalysts using inexpensive abundant elements, calcium was used to stabilize tetragonal  $\text{ZrO}_2$  type oxide instead of rare earth elements. Although the calcium addition to any metallic alloys was impossible, calcium salts can be added to zirconia sol. Figure 32 [60,61] shows the catalytic performance of Ni-Zr-Ca and Ni-Zr-Sm catalysts. The Ni-Zr-Ca catalyst exhibits the further higher activity than the

Ni-Zr-Sm catalyst for carbon dioxide methanation reaching the chemical equilibrium. The forward reaction of reaction (28) is accelerated by temperature increase, but the maximum conversion is limited by the fact that the endothermic reverse reaction of reaction (28) is also accelerated by temperature increase as shown by the curve of the chemical equilibrium. The conversion of carbon dioxide to methane on the Ni-Zr-Ca catalyst reaches the chemical equilibrium at 400 degrees Celsius and higher temperatures at the used space velocity that is the flow rate of reactant gas passing a unit volume of the catalyst.

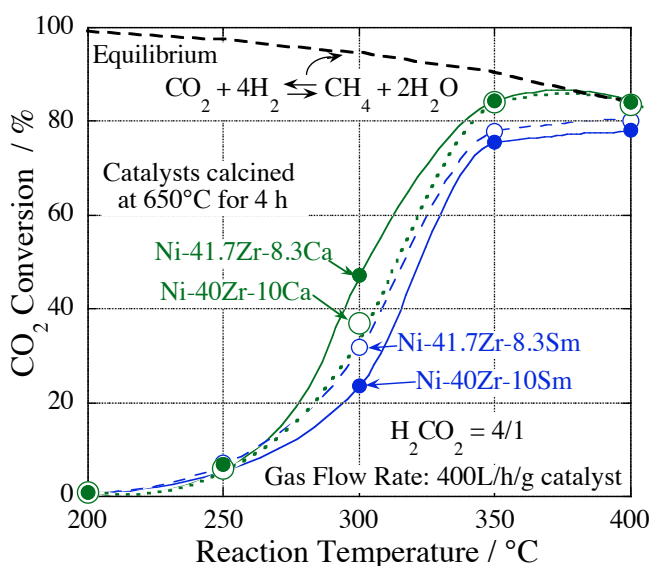


Figure 32 Catalytic performance of Ni-Zr-Ca and Ni-Zr-Sm catalysts for production of methane from 4 volumes of H<sub>2</sub> and 1 volume of CO<sub>2</sub> at a flow rate of 400 L/h on 1 g of catalyst [60,61].

If the use of a significant amounts of rare elements and/or precious metals is necessary, the wide spread of such technologies are difficult. In contrast, the Ni-Zr-Ca catalyst for carbon dioxide methanation can be used widely in the world. For wide use of renewable energy we need to spread our technology to the world. It is, particularly important for industrialization of ecological technologies to avoid the use of large amounts of rare elements and precious metals.

## 9. Prototype Plant and Pilot Plant

On the basis of our success in creating these key materials, we were awarded a special fund in 1994, and built a prototype plant of global CO<sub>2</sub> recycling in 1995 for substantiation of our idea on the rooftop of a building of the Institute for Materials Research, Tohoku University as shown in Figure 33. The plant connects a solar cell

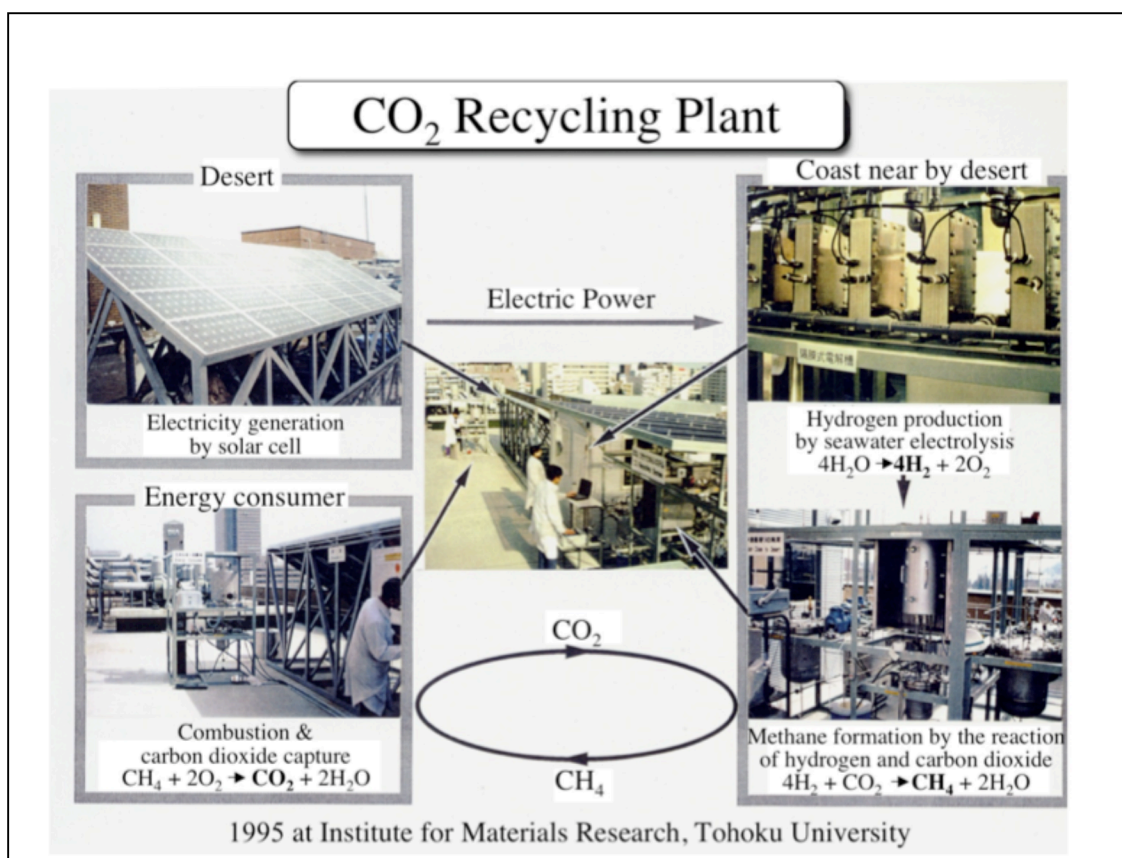


Figure 33 Prototype plant for global carbon dioxide recycling built on the rooftop of Institute for Materials Research, Tohoku University in 1995.

unit, electrolytic cells for hydrogen production, a reactor for conversion of carbon dioxide to methane by the reaction with hydrogen, a combustor of methane with oxygen, and piping for methane supply from the methanation reactor to the methane combustor and for carbon dioxide transfer from the combustor to the methanation reactor. This plant proved that the energy consumer can really use distant solar energy in the form of synthesized natural gas, methane without emitting carbon dioxide into atmosphere.

As shown in Figure 34, in 2003, we could construct the industrial scale pilot plant at Tohoku Institute of Technology consisting of a seawater electrolyzer and a carbon dioxide methanation system, by which methane was formed at a rate of 1 Nm<sup>3</sup>/h.

After the construction of pilot plants, joint work with many universities, institutes and industrial companies was conducted for practical application of water electrolysis and carbon dioxide methanation in combination with wind power generation. In Japan, good locations for wind power generation are limited and sea around Japan is too deep

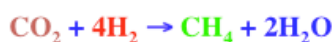


## Pilot Plant of Industrial Scale 2003

**Hydrogen Production**  
by Seawater Electrolysis



**Methane Production**  
by the reaction of  
Carbon Dioxide with Hydrogen



2003 at Tohoku Institute of Technology

Figure 34 Pilot plant of industrial scale consisting of seawater electrolysis and carbon dioxide methanation built in Tohoku Institute of Technology in 2003.

to construct off-shore wind power generators in addition to the attack of typhoons. Thus, we considered power generation on sailing raft. As shown in Figure 35, we examined conversion of renewable energy to methane by wind power generation, water electrolysis and methane production on a sailing raft. We can search the good wind condition sites by sailing and escape from typhoon. Final answer was as follows: For effective wind power generation, 11 wind power generators of five mega watts each stand in a line on a 1880 m long raft of 70 m width, at the four corners of which four sails stand. Simulation of this type of raft operation showed that the power generation efficiency was 42.6 % at most around Japan by searching good wind sites escaping from typhoon.

Our methane production from renewable energy had become technologically feasible, but industrialization for business progressed slowly. Natural gas is the primary energy available from gas wells. In contrast, our methane is the quaternary energy; renewable energy, electricity, hydrogen, and methane. It was not easy for our methane to

compete with natural gas on cost. Thus, technological development other than basic research was slow.

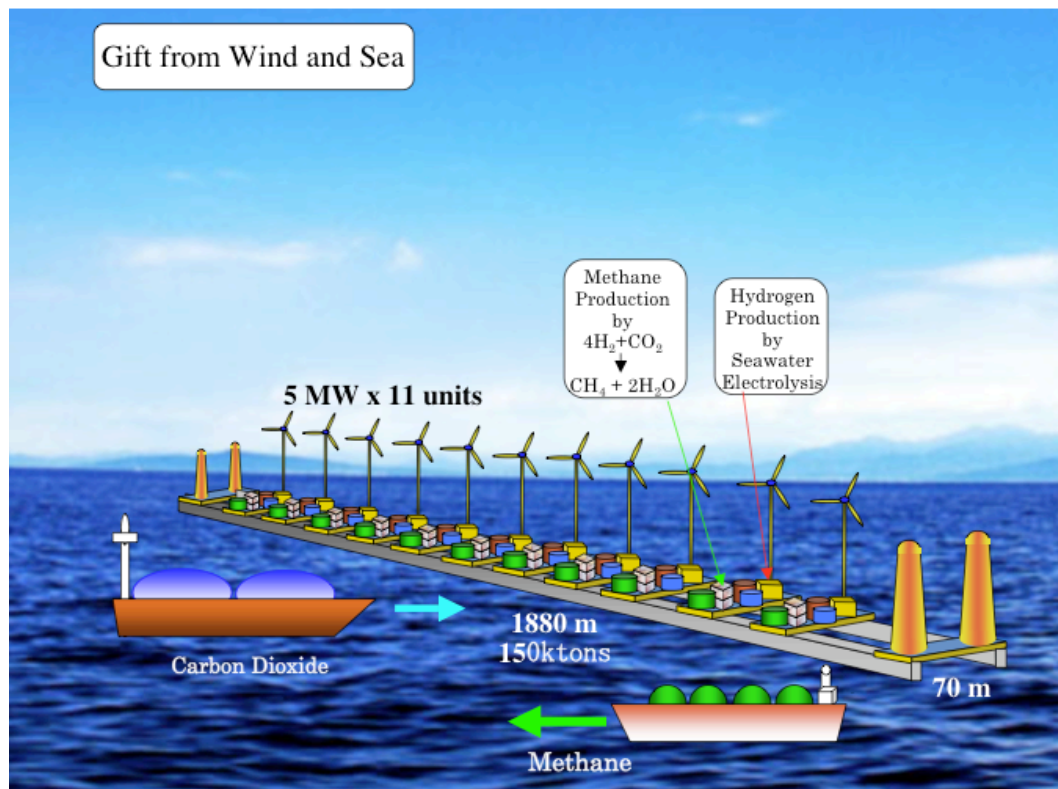


Figure 35 Wind power generation, electrolytic hydrogen generation and carbon dioxide methanation on a sailing raft.

However, just after the earthquake and tsunami disaster in the east Japan on March 11, 2011, a foreign oil and natural gas company made contact with one of our colleagues, the executive officer of an industrial company, and proposed: “Natural gas well contains a mixture of methane and carbon dioxide. In extreme cases three quarters are carbon dioxide and a quarter is methane. For purification of natural gas we are emitting carbon dioxide into atmosphere. However, now the use of renewable energy is carried out instead of fossil fuel combustion for prevention of global warming. We feel that we are not allowed to emit carbon dioxide into atmosphere for purification of fossil fuel. We made world search and found only you have the technology by which carbon dioxide from gas wells can be converted to methane using renewable energy. Your technology must be used immediately in the whole world. Let us make collaboration for industrialization of your technology”. Since then, industrialization of our



technology made big progress by international and domestic collaboration of industrial companies. In particular, deep insight of European people for prevention of global warming have been strongly supporting us.

## **10. Bright future prospect**

European people have been making the effort to decrease carbon dioxide emissions for prevention of global warming from early time of the 1980s. According to EU Renewable Energy Directive 2009/28/EC [62], by 2020, the European Union aims to reduce its greenhouse gas emissions by at least 20%, to increase the share of renewable energy to at least 20% of consumption, and to achieve energy savings of 20% or more. All EU countries must also achieve a 10% share of renewable energy in their transport sector.

The European Union agreed in Directive 2010/31/EU of the European Parliament and of the Council on the energy performance of buildings [63] that Member States shall ensure that: by 31 December 2020, all new buildings are nearly zero-energy buildings and after 31 December 2018, new buildings occupied and owned by public authorities are nearly zero-energy buildings.

Germany has been performing “Energiewende” since 2010 to convert from fossil fuel consumption to renewable energy use by which 80% carbon dioxide emissions will be cut together with 100% electric power generation from renewable energy by 2050. Germany also decided to end nuclear power generation by 2022 because Fukushima nuclear accident disclosed that the nuclear power generation is the most dangerous power generation technology. Germany has a long experience of the research and development for the use of renewable energy as exemplified by the electric power feeding law “Stromeinspeisungsgesetz” for Feed-in tariff of electricity generated from renewable energy since 1991. In fact, the power generated from renewable energy was 84.1% of domestic power consumption and 65.4% of total power generation at 1 p.m. on August 23, 2015, and covered 32.5 % of total power consumption in the first half of 2015. At 12 a.m. on April 30, 2017, the power generated from renewable energy covered 77.6 % of the total power generation.

This fact suggests that we can use the electricity without considering the fluctuating and intermittent nature even if the power formed from renewable energy covers more

than 70% of the total power generated. There are many countries importing power from Germany, and Germany can export the electricity excess of the domestic consumption. However, nuclear, coal and lignite power generators require continuous operation regardless of power demand because of difficulty of shut-down and resumption of operation. Thus, sometime they need to stimulate power consumption with incentive pay, and the term “negative price” has been used. For instance, it has been said that electrolytic hydrogen production for carbon dioxide methanation has been carried out only when the power price is lower than 2 cent per kWh. In contrast, natural gas power generation is characterized by easy shut-down and resumption of operation, if our synthesized natural gas, methane is used for regeneration of stable power. Germany is one of the most advanced countries in industrial activity. Nevertheless, Germany is performing “Energiewende” even changing the industrial structure and the civic life for accomplishment of power generation only from renewable energy.

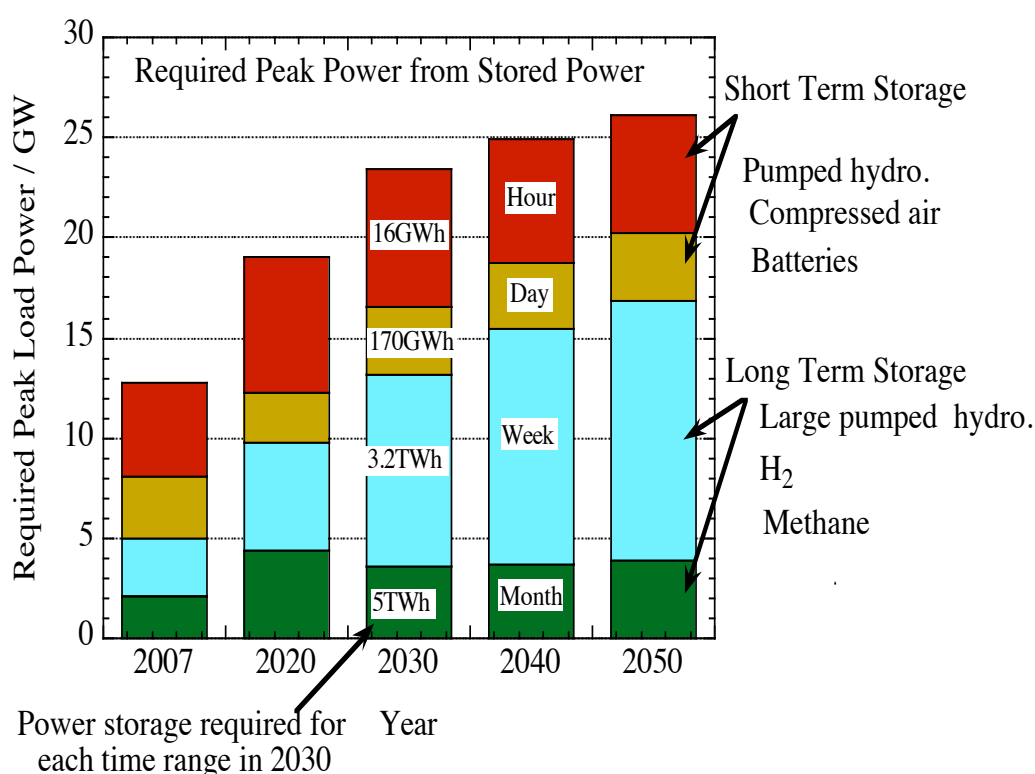


Figure 36 Power supply from stored electrical energy required for attainment of “Energiewende”[64].

We can learn a great deal from “Energiewende” for the use of renewable energy, enhancement of energy efficiency and energy saving, and we can visualize the future world keeping the sustainable development only by renewable energy. For survival and sustainable development only by renewable energy we need to generate total necessary energy from renewable energy. Direct use of the electricity from renewable energy is most effective.

Figure 36 [64] shows power supply from stored electrical energy required for attainment of “Energiewende”. For power supply after short term storage for several hours to a day we can use various conventional technologies such as batteries, pumped hydraulic power, compressed air, and so on. However, major portion of storage must be done for weeks and months. If we consider seasonal change in energy demand and power generation we may need to store surplus electricity for a half a year.

The storage in the form of currently used fuel is most effective. We need to form the necessary amount of fuels in considering the energy conversion efficiency for regeneration of steady electricity. The most convenient technology is our one that is conversion of renewable energy to methane. Regeneration of electricity by methane combustion will be easily done by conventional gas power plants combined with cogeneration system for exhaust warm water use because of excellent characteristics of gas power plants for easy shut-down and resumption of operation.

On the other hand, a significant decrease in total amounts of energy consumption and energy loss is necessary in “Energiewende” as shown in Figure 37 [65]. In particular, the decrease in the large energy loss at energy conversion such as power generation is necessary. The energy efficiency of thermal power generation by fossil fuel is generally 40% or less and that by nuclear power generation is less than 35 %. More than 60% of combustion energy is exhausted in rivers and sea in the form of warm waste water or directly in the atmosphere. The solution is power generation from renewable energy substituting coal, lignite and nuclear power generation. The power generation from renewable energy is not accompanied by energy conversion loss and carbon dioxide emissions. Even if primary energy source is only renewable energy, power regeneration is necessary for supply of deficiency of electricity generated from renewable energy every moment and for leveling of intermittent and fluctuating electricity generated from renewable energy. However, the energy efficiency of power regeneration from synthesized natural gas is also only 40 %. Thus, “Energiewende”

requests cogeneration, that is combined use of power and heat. The heat will be used for various objectives. By these efforts in “Energiewende” the high conversion losses will be reduced to 6 % of those in 2010 by electricity generation from renewable energy, and the increase in the proportion of cogeneration.

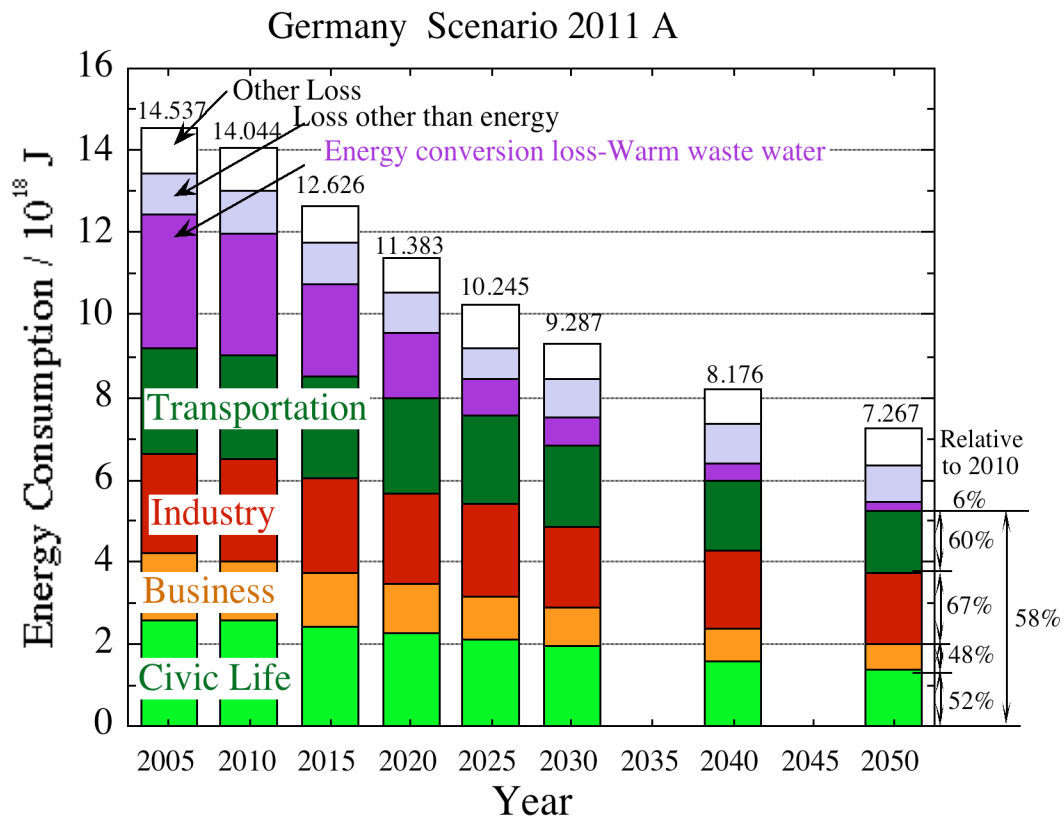


Figure 37 Requirement of energy consumption decrease for attainment of “Energiewende”[65].

As seen in Figure 37, energy consumption in business and civic life sectors in Germany is more than 40 % of total energy consumption. In fact, almost 90% of energy consumption in business and civic life sectors is for heating and hot water supply. “Energiewende” not only requests nearly zero-energy new buildings but also is encouraging renovation of existing buildings for the application of minimum requirements to the energy performance such as effective thermal insulation, double window, the use of LED and so on.

Energy saving in transportation sector is to change into electric and plug-in-hybrid vehicles from gasoline and diesel vehicles, using electricity generated from renewable

energy. For instance, the energy efficiency of gasoline car is less than 15 %, while that of electric car is around 70 % for driving and charging without emitting carbon dioxide. In this way, energy consumption in transportation, industry, business and civic life will be decreased as shown in Figure 37, and the total energy consumption in 2050 will be 58% of the value in 2010.

The success of “Energiewende” of Germany will lead whole world to follow their success, ending the dependency on fossil fuels and nuclear power.

Because hydrogen is attractive clean fuel, some politicians want to use hydrogen constructing hydrogen stations combined with electrolytic hydrogen production using electricity generated even by coal power plants emitting a large amount of carbon dioxide. It is, however, difficult to use hydrogen. As mentioned earlier there are no widely used technologies of storage, transportation and combustion of hydrogen. Only a major application considered to use hydrogen fuel is the fuel cell car at the moment. Oxidation of hydrogen and reduction of oxygen in fuel cell cars occur on platinum atom on the surface of electrodes of the fuel cell. It has been said that platinum required for compact, medium and large-sized cars is about 32, 60 and 150 g, respectively.

The world platinum reserves estimated are 56,000-60,000 tons. Platinum produced in the world in 2015, 2016 and 2017 were about 190, 189 and 185 tons, respectively. Total four wheel cars in the world in the end of 2016 were 1.324 billions. Four wheel cars produced in the world in 2017 were 97.302 millions.

Although the use of 18 t/year of platinum for construction of fuel cell cars is impossible, even if it is allowed, the number of cars produced requiring 30 g of platinum each is 600,000. This number is only 0.6 % of four wheel cars produced in the world in 2017. This clearly indicates that it is impossible to spread fuel cell cars as far as the fuel cell for the car requires platinum.

Consequently, hydrogen will not be the major fuel, unless new hydrogen combustion systems to be spread in the world are found.

If a new technology requires a large amount of precious metals and/or rare elements, unless precious metals and rare elements are substituted with inexpensive abundant elements, the technology must not be developed for industrial application, although the use of any kinds of precious metals and rare elements is allowed for basic study. Instead of pursuing unrealistic subjects, we need to realize the world using only

renewable energy keeping the sustainable development.

## 11. Creation of Paradise

The use of renewable energy will be particularly effective in localized area as illustrated in Figure 38. The direct use of the electricity generated from renewable energy is most effective. The surplus electricity from renewable energy will be used for water electrolysis to form hydrogen and oxygen. Hydrogen formed will be used for the formation of methane by the reaction with captured carbon dioxide. For combustion of synthesized methane for regeneration of steady electricity by conventional natural gas power plant, instead of air, oxygen formed by water electrolysis will be used after dilution with captured carbon dioxide. (A simple mixture of methane and oxygen is the detonating gas and the burning temperature is too high to use at any conventional natural gas power plant.)

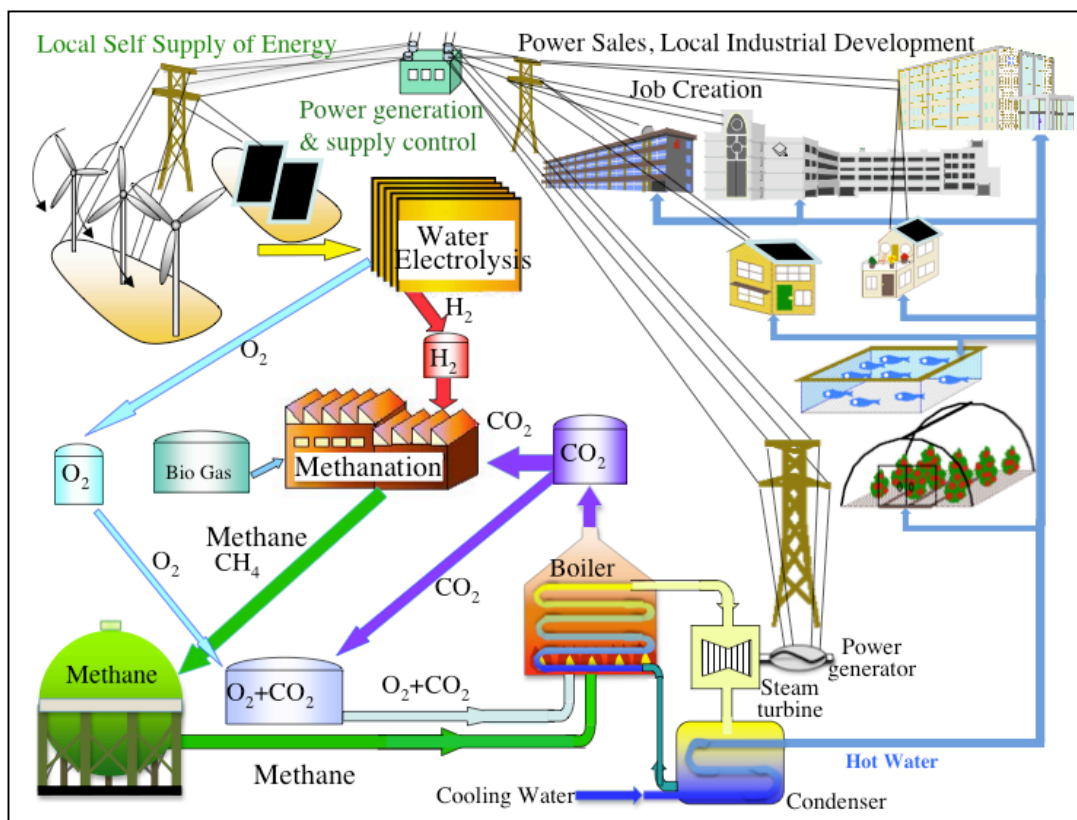


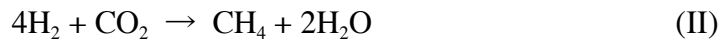
Figure 38 Illustration of wealthy local area of self supply of renewable energy.

In this system for regeneration of steady electric power chemical reactions are as follows:

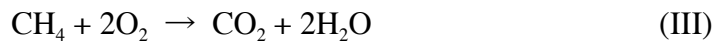
Water electrolysis



Methane formation

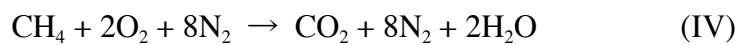


Electricity regeneration by methane combustion



The amount of methane formed by reaction (II) is a quarter of hydrogen formed by reaction (I). The amount of oxygen necessary for combustion of the methane in reaction (III) is the same as the amount of oxygen formed by reaction (I). The amount of carbon dioxide necessary for formation of the methane in reaction (II) is the same as the amount of carbon dioxide formed by combustion of the methane by reaction (III). In this way, the same amount of carbon is recycled between methane and carbon dioxide. Water consumed for formation of hydrogen and oxygen in reaction (I) is regenerated by reactions (II) and (III). Thus, in this system, as far as the electricity is available from renewable energy, carbon and water are recycled without adding any feedstocks, although water capture is not practically necessary in most of areas on our planet.

If air is used for combustion of methane, as shown in reaction (IV), the mixture of carbon dioxide and nitrogen remain in the exhaust gas after removal of steam by cooling. Furthermore, some nitrogen oxides are formed (V). The amount of nitrogen is 8 times as high as that of carbon dioxide in the exhaust gas.



The capture of carbon dioxide by separation from nitrogen in the exhaust gas needs though work.

By contrast, oxygen diluted with captured carbon dioxide can be used for combustion of methane as reaction (III)' in conventional natural gas power plant.



Because of no presence of nitrogen after combustion in the exhaust gas, carbon dioxide capture becomes quite easy after removal of steam by cooling. Just 1/9 of captured carbon dioxide will be sent for regeneration of methane and remaining 8/9 of captured

carbon dioxide will be used again dilution of oxygen. In order to cover carbon dioxide deficit by leaking, we will be able to add biogas and others. Shut-down and resumption of operation are easy in conventional natural gas power plant. In this area, the dairy control of power generation, estimating energy demand depending upon the weather and climate, will be important task of the power generation association.

Furthermore, in addition to simple power generation by a steam turbine with about 40 % energy efficiency, the remaining 60% of combustion energy of methane in the hot water should be used for agriculture, fish-culture, stock-farming, and air-conditioning of houses and other buildings. In such an area a variety of new jobs will be created and the wealth generated will stay in the inside of this area, the excess wealth being sold in the outside. This area will become the very wealthy local area.

## **12. Conclusions**

Current increasing rates of atmospheric carbon dioxide concentration and global temperature are in the critical situation. The atmospheric carbon dioxide concentration is increasing at the rate of about 2.4 ppm every year for eleven years from 2007, and the global temperature rise is about 0.05 degree Celsius every year since 2010. The current atmospheric concentration of carbon dioxide and the outlook of fuel reserves on our planet indicate that we need urgently to convert the whole world to survive and keep sustainable development only by renewable energy. The world history after Kyoto Protocol of COP 3 of the United Nations Framework Convention on Climate Change in 1997 indicates that the advanced technologies in developed countries for energy consumption and energy saving were not effective for the decrease in the world energy consumption and carbon dioxide emissions.

For prevention of further global warming and complete exhaustion of fossil fuel on our planet, the whole world will follow the German effort of “Energiewende” aiming 80% decrease in carbon dioxide emissions by 2050 by the 100% conversion from fossil fuel consumption to renewable energy use.

For such an energy revolution the most convenient and easily applicable key technology to store the surplus electricity from renewable energy is the formation of methane by the reaction of carbon dioxide captured from exhaust gas with hydrogen generated from renewable energy.



We have been performing research and development of the carbon dioxide recycling for almost 30 years to use the renewable energy in the form of methane. Methane is formed using carbon dioxide captured from exhaust gas as feedstock by the reaction with hydrogen obtained by water electrolysis using electricity generated from renewable energy. We created the effective cathode and anode for hydrogen generation by water electrolysis and the best catalyst for methanation of carbon dioxide by the reaction with hydrogen. Industry for production and supply of methane from renewable energy is in progress by domestic and international cooperation of industrial companies.

The whole world can survive and can keep sustainable development by means of current and future technologies to use renewable energy of the world without relying on fossil fuels and nuclear power.

## Acknowledgements

I owe above work to use renewable energy in the form of methane to Dr. Naokazu Kumagai, Dr. Koichi Izumiya, Dr. Hiroyuki Takano and Dr. Hiroyuki Shinomiya, Hitachi Zosen Corporation, Prof. Zenta Kato, Tohoku Institute Technology, Prof. Hiroki Habazaki, Graduate School of Engineering, Hokkaido University, and Prof. Eiji Akiyama, Institute for Materials Research, Tohoku University for their continuous collaboration.

I also obliged to retired Prof. Katsuhiko Asami and Prof. Asahi Kawashima, Institute for Materials Research, Tohoku University for their cooperation.

I express sincere acknowledgement to Professor Emeritus Tsuyoshi Masumoto, Tohoku University, Professor Emeritus Norio Sato, Hokkaido University, Professor Emeritus Maria Janik-Czachor, Institute of Physical Chemistry, Polish Academy of Sciences, Professor Emeritus Ronald M. Latanision, Massachusetts Institute of Technology, and Professor Emeritus Jacques Amouroux, Pierre and Marie Curie University for their consistent support and encouragement.

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