Materials and Technology for Supply of Renewable Energy and Prevention of Global Warming

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Abstract. We are proposing global carbon dioxide recycling to use solar energy for all people in the whole world. The electricity will be generated by solar cell in the deserts and used for production of hydrogen by seawater electrolysis at the nearby desert coasts. Hydrogen with no existing infrastructures for transportation and combustion will be converted to methane at the desert coasts by the reaction with carbon dioxide captured by energy consumers. Among systems in global carbon dioxide recycling, seawater electrolysis and carbon dioxide methanation have not been performed industrially. We tailored anodes for oxygen evolution without chlorine formation in seawater electrolysis, effective cathodes for hydrogen production and catalysts for methane formation by the reaction of carbon dioxide with hydrogen.

1. Introduction

Latest energy-related data of all nations and districts of the world from 1980 to 2005 in addition to world fuel reserves have been posted on the website of Department of Energy, the USA (DOE) [1]. The energy consumption by a person in developed countries in 2005 was 5.9 times as high as that by a person in developing countries. Thus the increase in the world energy consumption is inevitable. The left hand side of Fig. 1 shows the history of energy consumption for 25 years. The world energy consumption on the average during 15 years since 1990 resulted in 1.0193-fold increase every year. If we assume the 1.0193-fold increase every year for the future world energy consumption, the total energy consumption will be expressed by a bold curve shown in Fig. 1. The area under the bold curve has been filled by fuels extended following the history. The world uranium reserves in 2005 were not given in DOE data [1], and the highest estimation, that is, 4.743 M tonnes [2] was used for Fig. 1. Until 2034 the oil consumption will be 1.293 T barrels that was the world total oil reserves in 2005, and hence no more oil will be available after 2034. Both natural gas and uranium on the Earth will be completely exhausted until 2040. After 2040, the use of only coal will lead to complete exhaustion of coal reserves by 2054. One may expect finding new fuels. However, even if the amount of new fuels found are the same as the oil reserves of the world in 2005 corresponding to the area of 1.293 T barrels of oil, the area is smaller than the open area from 2054 to 2060. The real energy supply, instead of continuous increase followed by sudden running out as shown in Fig. 1, will show a maximum and then a decrease, since the fuel producing countries will try to survive without supplying their fuels to other countries. Continuous increase in primary energy consumption results in continuous increase in
carbon emissions. Such a huge carbon emissions resulting from complete exhaustion of fossil fuel reserves will induce intolerable global warming.

In order to avoid such a miserable situation of no fuel and intolerable warming, we have to establish immediately new technologies to use only renewable energy and to distribute the technologies to the world by which all people in the whole world can survive. The technology must be now within our reach. Otherwise, it will not be in time to avoid the miserable situation.

1.1. Renewable energy

We need a large amount of energy for industry, transportation, business and civic life, for which we have to use remote renewable energy sources such as deserts and/or ocean, since renewable energy available at the habitation area is very limited. The primary energy consumed in the whole world in 2005 was $488.28 \times 10^{15}$ kJyear$^{-1}$ [1]. When we use solar cell with 15 % energy conversion efficiency in deserts where 1000 Wm$^{-2}$ solar energy are available for 8 hours a day, the necessary desert area for production of energy of $488.28 \times 10^{15}$ kJyear$^{-1}$ in the form of electricity is only 1.92 % of main desert area of the Earth. Thus we can survive on the Earth.

The renewable energy is inherently intermittent and fluctuating. We need off-grid, renewable energy based systems to form fuels for which the existing efficient infrastructures for transportation and combustion can be used.

1.2. Global carbon dioxide recycling

We found quite effective amorphous alloy catalysts [3,4] on which carbon dioxide reacts rapidly with hydrogen to form methane with almost 100% selectivity. Based on this finding we are proposing and studying global carbon dioxide recycling [5]. We will generate electricity necessary for all people in the whole world by solar cell in the deserts, where hours of sunlight are about four times as long as those in Japan. We will use the electricity for production of hydrogen by seawater electrolysis at the nearby desert coasts. However, there are no infrastructures for mass transportation and combustion of hydrogen, and the development and distribution of those infrastructures for hydrogen are impossible because of heavy burden to our world. Therefore, hydrogen cannot be the major fuel, and we will convert hydrogen thus formed to methane by the reaction with carbon dioxide at the desert coasts. Methane is the main component of world widely used fuel, natural gas, for which we have quite efficient infrastructures for transportation and combustion. Energy consumers will capture carbon dioxide after combustion of methane and transport back carbon dioxide to the desert coasts.

Fig. 1 The history of the primary energy consumption of the world in past 25 years derived from reference [1] and years of complete exhaustion of individual fossil fuel reserves of the world.
2. Materials for global carbon dioxide recycling
Among systems in global carbon dioxide recycling, hydrogen production by seawater electrolysis and methane production by the reaction of carbon dioxide with hydrogen have not been industrialized. Key materials are cathode and anode for seawater electrolysis and an effective catalyst for carbon dioxide methanation.

2.1. Cathode for hydrogen production
Energy-saving durable cathodes consisting of inexpensive elements are necessary. In electrolysis of neutral solutions hydrogen evolution leaves hydroxide ion on the cathode surface, and hence the pH around the cathode rapidly increases. The performance of the cathodes was examined under an aggressive condition, that is, 8 M NaOH solution at 90°C. Active and durable cathodes were tailored by electrodeposition. Some of them showed higher activity than platinum. The key factor for activity and durability was addition of effective elements. Those are iron and carbon. Fig. 2 shows cathodic polarization curves. The rate of hydrogen production is determined by current, and hydrogen production is carried out industrially at the current density of 1000 Am⁻². Nickel is known to be a stable electrode but the activity is insufficient. When iron and carbon are added to nickel the activity is remarkably raised. The potential of electrodeposited Ni-Fe-C alloy is less than 1/4 of nickel at 1000 Am⁻². Iron is more active than nickel and that Ni-Fe alloy is further active than iron, although the gradient \( \partial E/\partial (\log i) \) called Tafel slope is not changed as \( \partial E/\partial (\log i) = 150 \text{ mV/decade} \approx 2.3 \times 2RT/F \). For the Ni-Fe-C alloy Tafel slope becomes about 33 mV/decade, that is \( \partial E/\partial (\log i) \approx 2.3RT/2 \). The change in Tafel slope implies the change in the mechanism of hydrogen evolution. Hydrogen evolution seems to occur through the electron transfer from the electrode metal to hydrogen ion, namely, discharge of hydrogen ion, \( H^+ + e^- = H_{\text{ads}} \) (1) to form adsorbed hydrogen atom and subsequent recombination of two adsorbed hydrogen atoms to form a hydrogen molecule, \( 2H_{\text{ads}} = H_2 \) (2). The enhancement of the activity of hydrogen evolution by alloying was interpreted in terms of the modification of the electronic state for discharge of hydrogen ion. X-ray photoelectron spectroscopy revealed that the binding energy of the Ni 2p₃/₂ electrons increases with increasing iron content of the alloy, while the binding energy of the Fe 2p₃/₂ electrons decreases with increasing nickel content of the alloy [6]. This fact indicates the charge transfer from nickel to iron by alloy formation. The carbon addition significantly enhanced the binding energy change and hence the charge transfer. As shown in Fig. 2 Tafel slope of Ni, Fe and Ni-Fe alloy is the same, and Tafel slope, 2.3 \( \times 2RT/F \), suggests that the rate-determining step seems to be reaction (1), namely, discharge of hydrogen ion. The activity of Fe, that is, the current density is higher than that of Ni, and the activity of Ni-Fe alloy is further higher than that of Fe. Thus the electron transfer from iron to hydrogen ion seems faster than that from nickel and, because of charge transfer from nickel to iron the electron transfer from iron to hydrogen ion on Ni-Fe...
alloys seems further faster, although the rate-determining step is unchanged. By contrast, the alloying with both iron and carbon strongly enhances the charge transfer from nickel to iron and hence the charge transfer from iron to hydrogen ion on Ni-Fe-C alloys seems significantly fast. Because of remarkable acceleration of discharge of hydrogen ion on Ni-Fe-C alloys the discharge reaction of hydrogen (1) becomes no longer the rate-determining step and the reaction rate is determined by the rate of the essentially fast reaction (2) of recombination of adsorbed two hydrogen atoms showing the Tafel slope of 2.3RT/2F. In this manner, the addition of both iron and carbon to nickel remarkably accelerates hydrogen evolution changing the rate-determining step.

The enhancement of the activity and durability for hydrogen evolution is one of decisive factors to determine the price of the final product, methane, and hence the study of the cathode materials with high activity and durability is in progress.

2.2. Anode for oxygen evolution in seawater electrolysis

The industrial seawater electrolysis has so far been conducted not to form hydrogen on the cathode but to form chlorine on the anode in chlor alkali industry and for sterilization of seawater at the inlet in various plants using seawater as coolant. However, formation of poisonous chlorine on the anode at an enormous amount of hydrogen production is not allowed. A variety of γ-MnO₂ type double and triple oxides for electrocatalysts of anodes were tailored by anodic deposition on the electro-conductive substrate. Anodically deposited MnO₂ anode had a fairly high activity for oxygen evolution but more than 8% of electricity was consumed for chlorine evolution at a current density of 1000 Am⁻²[7]. The 100 % oxygen evolution efficiency was attained through the formation of multiple oxides containing manganese, such as MnₓMoO₆₋ₓ [7]. MnₓW₂O₆₋ₓ [8], Mnₓ-₀.₅ₓFe₂O₆₋ₓO₂₋ₓ [9], Mnₓ⁺₂MoₓWₓO₂ₓ+y [10] and Mnₓ⁺₂SnₓO₂ₓ+y [11]. Some of Mnₓ⁺₂MoₓWₓO₂ₓ+y and Mnₓ⁺₀.₅ₓSnₓO₂ₓ+y triple oxide anodes showed 98% oxygen evolution efficiency for more than 3000 hours at 1000 Am⁻² in 0.5 M NaCl solutions of pH 2 [11] and 1 [12], respectively.

Fig. 3 Change in the durability with the composition of the intermediate layer of the anode for oxygen evolution in 0.5 M NaCl of pH 1 at 1000 Am⁻² [12].

The oxygen evolution anode for seawater electrolysis is composed of three layers of an outer electrocatalyst layer, an intermediate layer and a punched titanium net. Corrosion-resistant titanium under anodic polarization in aggressive NaCl solution is used as the substrate. However, anodic polarization of titanium readily results in the formation of the insulating oxide, TiO₂, rutile, and hence the electro-conductive oxide layer with the same crystal structure as rutile which is able to form double oxide with titanium is required between the titanium substrate and the electrocatalytic oxide for
prevention of the growth of insulating TiO\textsubscript{2}. We had been using IrO\textsubscript{2} as the intermediate layer; IrO\textsubscript{2} has the same rutile structure as TiO\textsubscript{2}. However, the use of precious iridium is not practical for worldwide production of hydrogen and hence an attempt was made to substitute IrO\textsubscript{2} with SnO\textsubscript{2}, having the same rutile structure as IrO\textsubscript{2} and TiO\textsubscript{2}, the electronic conductivity of the intermediate SnO\textsubscript{2} layer being enhanced by inclusion of Ir\textsuperscript{III} and Sn\textsuperscript{IV}. Fig. 3 shows the results of durability experiment [13]. The intermediate layer was prepared by brushing of coating solution and subsequent calcination. The coating solutions were butyl alcohol solution of H\textsubscript{2}IrCl\textsubscript{6}·6H\textsubscript{2}O·SnCl\textsubscript{4}·5H\textsubscript{2}O·SbCl\textsubscript{4}, in which the total concentration of metallic cations was kept at 0.1 M, although the protective IrO\textsubscript{2} intermediate layer had been prepared using 0.52 M H\textsubscript{2}IrCl\textsubscript{6}·6H\textsubscript{2}O butyl alcohol solution. The intermediate layer thus formed was composed of a rutile-type single phase triple oxide, Sn\textsubscript{13.3}Ir\textsubscript{5}Sb\textsubscript{0.55}O\textsubscript{2}. The anodes with SnO\textsubscript{2}-rich intermediate layers kept the 99.7% oxygen evolution efficiency for 3375 hours showing no degradation. The life of the anode with 100% IrO\textsubscript{2} intermediate layer is significantly shorter than that of the anode with SnO\textsubscript{2}-rich intermediate layer. The thickness of 100% IrO\textsubscript{2} in Fig. 3 was only 1/5.2 of that of the protective 100% IrO\textsubscript{2} intermediate layer, on which the 98% oxygen evolution efficiency was kept for 3200 hours [12]. The IrO\textsubscript{2} intermediate layer with insufficient thickness is not protective against TiO\textsubscript{2} growth on the substrate titanium under the anodic polarization condition. Nevertheless, the anodes with thin SnO\textsubscript{2}-rich intermediate layers did not show degradation. Less noble metal oxide, SnO\textsubscript{2} is more stable than IrO\textsubscript{2} and hence the oxidation of underlying titanium is well prevented.

In addition to substitution of rare elements with abundant elements, improvement of anodes to decrease the electricity consumption and to increase the durability is in progress.

2.3. Catalyst for carbon dioxide methanation

Fig. 4 The activity for conversion of carbon dioxide to methane on catalysts with Ca or Mg.

The use of amorphous Ni-40Zr alloy as the catalyst precursor revealed a very high reaction rate of carbon dioxide with hydrogen to methane with the almost 100% selectivity [4]. This was quite different from usual catalysts on which the conversion was very slow and the main product was carbon monoxide. The amorphous Ni-Zr alloys were converted to metallic nickel supported on ZrO\textsubscript{2} type oxide during catalytic reaction. Furthermore, the maximum activity was found at medium concentration of nickel in Ni-Zr alloys [5,6]. Both tetragonal and monoclinic ZrO\textsubscript{2} were found, although the stable form is monoclinic. Increasing nickel content definitely increased the relative amount of tetragonal ZrO\textsubscript{2}; the tetragonal ZrO\textsubscript{2} type oxide being stabilized due to inclusion of Ni\textsuperscript{II} in the ZrO\textsubscript{2} lattice. The turnover number increased with the alloy nickel content. Thus we concluded that nickel supported on tetragonal ZrO\textsubscript{2} was the active site for carbon dioxide methanation. On the other hand, the number of nickel atoms on the catalyst surface decreased with the alloy nickel content due to surface aggregation of nickel atoms. In this manner, increasing nickel content of precursor alloy led to the increase in the relative amount of active nickel site supported on tetragonal ZrO\textsubscript{2}, but

![Fig. 4 The activity for conversion of carbon dioxide to methane on catalysts with Ca or Mg.](image)

![Fig. 5 X-ray diffraction patterns of calcined oxides with Ca or Mg.](image)
to the decrease in total number of surface nickel atoms. Since further increase in the activity is expected by an increase in the relative amount of the tetragonal ZrO$_2$ and since the tetragonal ZrO$_2$ can be stabilized by inclusion of oxidized rare earth elements in the lattice, amorphous Ni-Zr-rare earth element alloys were prepared as the catalyst precursors [14]. The addition of rare earth elements not only stabilized the tetragonal ZrO$_2$ but also significantly enhanced the methanation activity [15]. Amorphous alloys were effective as the catalyst precursors but not suitable for mass production of catalysts. Prerequisite for catalyst is not the amorphous structure but the formation of metallic nickel supported on tetragonal ZrO$_2$. We tailored such catalysts in the form of powder [16]. Aqueous zirconia sol was used as zirconia source in which salts of nickel and rare earth elements were dissolved. 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 and magnesium were used to stabilize tetragonal ZrO$_2$ type oxide. The nitrates of nickel and calcium or magnesium were dissolved in aqueous zirconia sol. Thermal decomposition was performed to form oxide mixture of NiO and tetragonal ZrO$_2$ stabilized by inclusion of calcium or magnesium. Catalysts were formed by reduction of NiO. Figs. 4 and 5 show the performance of the catalysts and X-ray diffraction patterns before reduction treatment, respectively. The activity of Ni$_{0.5}$(Zr$_{0.41}$Ca$_{0.08}$)O$_{1.917}$ was sufficiently high while that of Ni$_{0.5}$(Zr$_{0.41}$Mg$_{0.08}$)O$_{1.917}$ was not sufficient because of the formation of the mixture of monoclinic and tetragonal ZrO$_2$ type oxide due to insufficient addition of magnesium. Improvement of technology for mass production of catalysts is in progress.

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