**“Oxide materials research for global environment and energy with a
focus on CO₂ fixation into polymers”**

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Abstract

Representing the gas, liquid, and solid phase materials on the earth under the standard conditions, CO₂, H₂O, and SiO₂ attract my interest for their natural abundance, chemical stability, and yet fundamental roles in energy and environmental problems. Chemical consideration is made on the utilization of these stable resources for renewable clean energy materials and processes based on a thermodynamic approximation. A general scheme is presented to compare the utilization of CO₂, H₂O, and SiO₂ for such purposes as CO₂ fixation into

functional polymers, photosynthesis of carbohydrates from CO_2 and H_2O , and solar silicon production from SiO_2 . Focused is CO_2 copolymerization, since it is originated from our discovery of alternating CO_2 -epoxide (oxirane) copolymer in 1968 and it has been revived by the recent industrialization of this unique bio-degradable polymer in China. New ideas of using combinatorial chemical technology and soft plasma processing for fixing CO_2 into polymers are proposed together with some preliminary experimental results.

1. Introduction: Oxide chemistry and electronics

Increasing energy need and global warming are the central issues to be solved by future science and technology. Oxides are key materials in this regard, since they are inevitably formed from almost all types of elements in the periodical table by the exothermic oxidation reactions under terrestrial conditions [1]. Today, the world energy relies primarily on fossil fuels with limited stock in the earth. Rapidly growing consumption of fossil fuels since the mid-20th century is resulting in CO_2 accumulation in the atmosphere at a rate much higher than the rate at which solar energy driven photosynthesis could preserve the CO_2 level constant by reducing it back to carbohydrate [2].

Since CO_2 is a hetero-cummulene with two $\text{C}=\text{O}$ double bonds, it can be used as a raw material of useful chemicals and polymers if one of the $\text{C}=\text{O}$ p-bonds is converted into s-bond by a reaction with another chemical. The development of such an energy minimum CO_2 fixation process can make a

contribution (although not so much) to global CO₂ problem. When I was a graduate student working on ring-opening polymerization of cyclic ethers with organometallic catalysts under the guidance of Professors T. Tsuruta and S. Inoue, an idea to use carbon dioxide as a possible partner of copolymerization came up to result in the discovery of aliphatic polycarbonate from CO₂ and epoxide [3]. There is a possibility that the substitution of this copolymer for pure hydrocarbon polymer would reduce olefin consumption and CO₂ emission in the atmosphere as much as millions of tons, since CO₂ is fixed in 50 % wt. in the CO₂-alt-(ethylene oxide) copolymer.

Alternative ways of CO₂ reduction include the utilization of solar energy and energy saving by efficient energy conversion materials and devices. After working in the polymer chemistry research for more than 15 years (1964-1980), I switched my field to solar energy materials focused on hydrogenated amorphous silicon (a-Si:H) [4] as well as its electrode materials: transparent conductive oxides such as ZnO [5] and SnO₂ [6]. My motivation was to create a new technology for controlling the structure and properties of highly cross-linked polymer network in a-Si:H as well as of electro functional oxides based on the concept of atoms and molecules. From the viewpoint of energy conversion efficiency, solar photovoltaics is much more efficient than photosynthesis and therefore it can be an ultimate solution for the energy and environmental problems. Currently, more than 90 % of solar cell is made from crystal silicon and about 5 % is from a-Si:H based thin film. The Si component in both materials is originated from SiO₂ and the development of efficient

chemical processes is a key to improve the cost and quality of these solar cells.

When the news of the high T_c superconductor reached me around the end of 1986, I got so excited about it that I immediately decided to go into thin film research of this superconducting oxide. Apparently, this was a material which required synthesis control beyond capabilities of physicists and electronic engineers working on conventional superconducting alloys, and our experience in thin films and chemical sense of complex oxides contributed much to our first success in the fabrication of high- T_c superconducting thin film [7]. The subsequent development of laser molecular beam epitaxy [8] and combinatorial solid-state chemical method [9] enabled us to establish nano [10] and parallel integration technology of oxide [1]. This technology is widely applicable to new materials and processes research for screening CO₂ fixation, solar energy materials, and oxide based electronic devices. Summarized in Table 1 are some examples of currently interested oxides from the viewpoint of application to energy, environment, and electronics [1].

2. Exergy formulation of chemical conversion of CO₂, H₂O, and SiO₂ to polymer, biomass, and solar silicon

As is indicated from large negative values of formation enthalpy (ΔH_f), oxides are thermodynamically more stable in general than the component elements and metals which have $\Delta H_f = 0$ by definition. Instead of ΔH_f which has been traditionally used for evaluating the chemical

energy (activity) of substance, exergy (ΔH_{ex}) can be more conveniently used to measure the effective energy values available for energy and environmental issues [11]. Substantial difference in both parameters exists in the reference values: all single elements are assigned to have zero for ΔH_f while the most stable, i.e. energetically useless, substances under ambient conditions are zero for ΔH_{ex} . Among zero assigned compounds are CO_2 , H_2O , SiO_2 , and Al_2O_3 . All of the active materials from which we can extract chemical energy under ambient conditions have positive ΔH_{ex} values. Using the exergy diagram in Fig. 1, let us discuss basic scheme and efficiency of the following three cases [12].

(a) CO_2 fixation into chemicals

(b) Photosynthesis of CO_2 and H_2O

(c) Silicon and solar cell production from SiO_2

(a) CO_2 fixation into useful chemicals such as polymers

This case can occur when CO_2 is reacted with a highly active chemical to form a product of its exergy lower than the sum of starting chemicals. A typical example is the copolymerization between epoxide (oxirane) and CO_2 to form aliphatic polycarbonate [3]. High strain energy of epoxide is presumed to be responsible for the spontaneous catalytic reaction.

(b) Photosynthesis and related process

The most important CO_2 fixation reaction in nature is the photosynthesis where H_2O and CO_2

are converted into biomass with the aid of photo-excitation of third compounds (R) as summarized by the following elementary equations.

The product biomass (carbohydrate) is an oligomer or a polymer of formaldehyde, CH₂O. Although biomass plays a major role in the CO₂ cycle in nature, it is not such an efficient mass from the viewpoint of energy conversion since its fuel part is only 40 % (12 / 30) by weight and part of the combustion heat should be wasted for evaporation of H₂O. Biomass can further be converted into bio-ethanol by fermentation, but this process is accompanied by energy loss and CO₂ emission as well. Hence, the overall solar-to-chemical energy conversion efficiency of biomass is actually less than 1 %.

(c) Silicon and solar cell production from SiO₂

Oxides employed for solar application include transparent conductive oxides (TCO) for thin film solar cells, TiO₂ for dye-sensitized solar cells and photo-catalysts [13], and in particular SiO₂ for production of low cost solar grade silicon [14]. From the viewpoint of efficiency, a Si solar cell gives solar-to-electric energy conversion efficiency of 20 % or even higher. The energy to fabricate a poly-crystalline Si solar cell from SiO₂ and C is estimated to be paid back in a few years, and therefore we could expect effective conversion efficiency higher than 15 % by using each solar cell

for more than 20 years. Hence, from the viewpoint of energy conversion, solar photovoltaics or silicon farming is far more effective than biomass farming. Despite the inferior cost-competitiveness at present, solar energy conversion is expected to be the best solution which is boosted with the aid of materials research. The current chemical process to produce high purity Si for solar cell and semiconductor devices from SiO₂ is composed of the following three reaction steps.

Research for improving this traditional so-called Siemens process is subjected to the up-grading of step (1) and the increase of yield in step (3). Especially important is presumed to be the latter problem, since undesirable direct pyrolysis ($4 \text{ SiHCl}_3 \rightarrow \text{Si} + 3 \text{ SiCl}_4 + 2 \text{ H}_2$) proceeds in parallel and predominantly to decrease the Si yield of step (3) less than 30 %. Chemistry will be able to play a major roll for improving this step and cost-cutting of high purity Si for solar cell and electronic devices.

As compared with such typical semiconducting electronic materials as Si and GaAs, oxides have much broader spectra of structures and properties applicable to a variety of devices. Not only does an electron have charge, but also its spin and orbital states can be correlated strongly in perovskite and related complex oxides to exert exotic new properties including superconductivity,

colossal magneto resistance [15], and electric-pulse induced resistance. Even a derivative of alumina cement, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$, was tuned up (upgraded) from an insulator to a conductive electride by the oxygen control [16]. Besides these complex oxides, popular oxides such as ZnO and TiO_2 are revived as promising electronic materials by the pursuit of theoretical prediction of exciton based ZnO light emitting devices [17] and by the combinatorial discovery of transparent ferromagnetism in Co-doped TiO_2 [18]. An idea is proposed to transmit solar electricity generated at desert areas to remote urban areas by global high- T_c superconductor networks.

3. CO_2 copolymerization into polymers

CO_2 is generated from the combustion of fossil fuels not only for transportation but also for many industries such as steel, cement, electric power, and brewery. An immediate option to reduce the CO_2 level in the atmosphere is to capture and store it deep in the sea or under ground by using extra energy, but this is not such a smart option as compared to using CO_2 as a chemical resource. Two topics are presented from our research for this purpose.

3-1. Catalytic alternating copolymerization of CO_2 with epoxide

During my Ph.D. research, I found that CO_2 could be copolymerized alternatingly with epoxides.

This first observation of CO₂ fixation into high polymers came when IR spectrum was measured on a trace of greasy extract from a CO₂ bubbled mixture of propylene oxide (PO) with a small amount of ZnEt₂ / EtOH (1/2 molar ratio) in benzene solution. It turned out, however, that this catalyst, despite its high activity for homo-polymerization of PO, was not active for the copolymerization. Active catalyst was presumed to have been made by contaminated H₂O, because it was revealed that molecules with two or more active hydrogens were needed as cocatalyst to activate ZnEt₂ [19]. The alternating copolymerization is understood to be composed of the following elementary steps.

From the viewpoint of bond rearrangement, this copolymerization is described in net as a π -bond conversion to a σ -bond:

From NMR spectra, almost perfect alternating sequence was verified to indicate exclusive insertion

reaction of CO_2 into $-\text{Zn-OR}$ propagating site and copolymerization rate determination by the resulting $-\text{Zn-OCO}_2\text{-R}$ reaction with epoxide to reproduce $-\text{Zn-OR}$ site. The aliphatic polycarbonates obtained by this process not only contained CO_2 in 50 molar % but also had the following characteristic properties; 1) injection molded, 2) low glass transition temperatures, 3) thermal decomposition at a temperature as low as 200°C , and 4) bio-degradable [20]. Our patents licensed to two companies in Japan and US expired without industrial production due mainly to the low efficiency of catalysts made from an expensive organozinc compound. However, recent revival of research interest in this copolymer apparently made some progress to reach a level of industrial production in China [21]. As was expected from the fact that equimolar $\text{ZnEt}_2\text{-H}_2\text{O}$ mixture should result in the formation of inorganic ZnO , commercially available ZnO powder also exhibited catalyst activity by mixing with glutalic acid. Some examples of catalysts reported to be active are summarized below [22]. Oxetane, a four membered cyclic ether, was also copolymerized with CO_2 [23].

1) Organozinc base:

ZnR_2 / dihydroxy, dicarboxy, amine, Al_2O_3 , MgO , Zn(OH)_2 , ZnCO_3 , Rare earth compound

2) Inorganic zinc base: ZnO / glutaric acid, Zn(OAC) , etc

3) Organo-Al base: AlR_3 / PPh_3 , acac, poly-hydroxy

4) Metal complex: Co(OAC)_2 , Co(Salen) , Cr(OAC)_2

For high throughput screening of new catalysts, combinatorial chemical technology was employed for parallel copolymerization in 3×4 autoclave arrays using catalyst composition and concentration, and time as variable parameters [24]. There will be a chance we could make a little contribution to global warming problem by fixing CO_2 as much as millions of tons in the form of solid copolymers if we could find a catalyst to produce more than 1kg of polymers with a cheap 1g of catalyst. Because of its unprecedented structure and properties, CO_2 copolymerized aliphatic polycarbonate can be very important in future from both viewpoints of basic polymer science and technology.

3-2. CO_2 fixation into polymer films by a soft plasma process

Artificial photosynthesis is attractive research target and photo catalysis of water splitting into H_2 and 0.5 O_2 can be regarded as such a case, since the essential part of photosynthesis is the oxidation of water to give O_2 in combination with hydrogenation of photo-excited species. As far as we use a wide-gap semiconductor for photo catalysis, however, the conversion efficiency of solar-to-chemical energy will not exceed the efficiency of water splitting by the electrolysis coupled with photovoltaic electricity.

Instead of photo-excitation, we can also use plasma excitation for practical CO_2 conversion to

functional chemicals and polymers. Reported here is a case of pulsed plasma copolymerization of CO₂ and hydrocarbons to form polyester films. To avoid the wasting of plasma energy by the random decomposition of monomers into many fragments, we developed a combinatorial plasma reaction system schematically illustrated in Fig. 2 [25]. The system generates rf (13.56 MHz radio frequency) plasma in continuous and pulsed modes under atmospheric pressure He or Ar, which is flowing out through a slit of rf electrode (cathode) towards the parallel aligned anode (grounded) whose surface is covered with an insulator. The gas temperature can be regulated as low as 100°C by using aluminum cathode and controlling rf power and pulse sequence. CO₂ gas is fed either by mixing with R (volatile monomer) or separately from R so that R could be activated exclusively prior to its contact with CO₂ on a substrate surface.

Both unsaturated and saturated organic compounds can be used as co-monomers to form cross-linked thin films. Due to the low gas temperature, substrate (and materials to be treated with the plasma) can be plastic films and paper to enable a roll-to-roll process. By varying process parameters such as gas flow rate and ratio, rf power, and pulse sequence during the roll-to-roll operation we can get combinatorial sample library.

Figure 3 shows the FT-IR spectra of the products copolymerized by applying a cw and pulsed rf power of 20 W. The C=O and C-H stretching modes can be clearly seen around 1710 – 1725 cm⁻¹ and 2950 cm⁻¹, respectively. The mixing of CO₂ causes the carbonyl absorption to shift from 1713 to 1725 cm⁻¹, which is assignable to the ester carbonyl, and also increases its intensity relative to the 2950 cm⁻¹ absorbance. These results indicate that CO₂ was fixed into polymer in the form of an ester linkage. Pulsing of the plasma can be useful to save the energy consumption of the extra decomposition of CO₂. As judged from the strong IR absorption assignable to ester bonds in the plasma polymerized film, primary chemical bond rearrangement for the reaction may be described as follows:

This CO₂ fixation by plasma excited copolymerization is not catalytic, but it can be regarded as an energy minimum process, since only one of the two C=O π -bonds in CO₂ and another π -bond in ethylene were converted to σ -bonds without cleavage of any C-O or C-C covalent bond.

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Table Captions

Table 1, Some topics of oxides for environment, energy and electronics.

Figure Captions

Figure 1, Exergy profile of CO₂ fixation, biomass, and Si-photovoltaics

Figure 2, Combinatorial atmospheric pressure cold plasma processor applied to plasma
copolymerization of CO₂ and volatile organic compounds.

Source gases : A: Inert gas (He or Ar), B: A volatile organic compound, C, D: CO₂

Figure 3, FT-IR spectra of plasma copolymers of CO₂ and ethylene obtained from the
combinatorial soft (atmospheric pressure plasma with a gas temperature as low as 100°C)
plasma processor.

Table

Table1

Environment			Energy		Electronics		
H ₂ O	→	Water pollution	SiO ₂	→	Solar grade Si	ZnO	{ Transparent FET UV-blue LED, LD Co-doped Transparent magnet
CO ₂	→	Green house effect	ZnO SnO ₂	→	TCO for thin film solar cells	TiO ₂	
O ₃	→	Ozone hole	TiO ₂ SiTiO ₃	→	Dye-sensitized solar cell	12CaO · 7Al ₂ O ₃ : Perovskite (ABO ₃)	{ Electride and derivatives Ferroelectric
TiO ₂	→	Photocatalysis	LiCoO ₂ NaCoO ₂	→	Li battery Thermoelectric	BaTiO ₃	
			O ² ion conductors	→	SOFC	SrTiO ₃	{ Dielectric Quantum paraelectricity Transistor Spintronics Superconductor New memory
						LSMO	
						YBCO	
						PCMO	

SOFC: Solid oxide fuel cell, LED: Light emitting device, LD: Laser Diode.

LSMO: (La, Sr)MnO₃, YBCO: YBa₂Cu₃O_{7-δ}, PCMO: (Pr,Ca)MnO₃.

Figure1

Figure2

Controllable parameters

- Substrate temperature
- Moving stage speed
- Rf power
- Gas flow rate × 4

Figure3

FT-IR spectra of the products from $\text{CO}_2/\text{C}_2\text{H}_4$ system