Ceramics for Environmental and Energy Applications II

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Preface

This Ceramic Transactions volume represents 25 selected papers based on presentations in eight symposia during the 10th Pacific Rim Conference on Ceramic and Glass Technology, June 2–6, 2013 in Coronado, California. The symposia include:

- Solid Oxide Fuel Cells and Hydrogen Technology
- Direct Thermal to Electrical Energy Conversion Materials and Applications
- Photovoltaic Materials and Technologies
- Ceramics for Next Generation Nuclear Energy
- Advances in Photocatalytic Materials for Energy and Environmental Applications
- Ceramics Enabling Environmental Protection: Clean Air and Water
- Advanced Materials and Technologies for Electrochemical Energy Storage Systems
- Glasses and Ceramics for Nuclear and Hazardous Waste Treatment

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Contents

RECENT RESEARCH ACTIVITIES FOR FUTURE CHALLENGES IN GLOBAL ENERGY AND ENVIRONMENT IN TOYOTA CENTRAL R&D LABS., INC. (TCRDL)

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ABSTRACT

Possible decrease in global supply of conventional oil and greenhouse warming make demands for reduction of oil consumption and diversification of fuels. In association with this, automotive powertrains are also diversifying from conventional internal combustion engine (ICE) into HV, plug-in HV(PHV), EV and fuel-cell HV (FCHV). The main sector is being replaced by HV and PHV, but still stands on ICE. In these hybridized ICE systems, unconventional oils, gaseous-, synthetic- and bio-fuels will be inevitably used more besides conventional fuels. EV as a subsidiary sector for short range use imposes additional demands of electricity from new energy sources. FCHV as another subsidiary sector for route bus and large trucks requests new infrastructures for hydrogen from new energy sources besides industrial by-products. Facing to this situation, it has become important for us to obtain concrete experiences on technologies for future energy sources by conducting R&D by ourselves although the production of energy is out of our business category. R&D for bio-ethanol production from cellulose has been already conducted. This paper describes our other typical recent R&D activities on future energy sources including laser nuclear fusion, solar-pumped lasers, solar cells and artificial photosynthesis, with special attentions to ceramics as key materials.

INTRODUCTION

Possible decrease in global supply of conventional oil and greenhouse warming caused by CO_2 emission make demands for reduction of oil consumption and diversification of fuels. In association with this, automotive powertrains are also diversifying from conventional internal combustion engine (ICE) into hybrid vehicles(HV), plug-in hybrid vehicles(PHV), electric vehicles (EV) and fuel-cell hybrid vehicles (FCHV). The main sector of automobiles is being replaced by HV and PHV, but still stands on ICE. For these hybridized ICE systems, unconventional oils, gaseous fuels, synthetic fuels and bio-fuels will be inevitably used more in addition to the conventional fuels. EV as a subsidiary sector for short range use in imposes additional demands of electricity which must be supplied from new energy sources as well as conventional power plants. FCHV as an another subsidiary sector for route bus and large trucks requests new infrastructures for hydrogen from new energy sources as well as from industrial by-products.

Facing to this situation, it has become important for us to obtain concrete knowledge and experiences on technologies for future energy sources by conducting R&D by ourselves although the production of energy is out of our business category. R&D for bio-ethanol production from cellulose has been conducted in TCRDL. This paper describes our other typical recent research activities on future energy sources including laser nuclear fusion, solar-pumped lasers, solar cells and artificial photosynthesis, with special attentions to ceramics as key materials.

COMPACT AND HIGH REPETITION(10HZ) LASER NUCLEAR FUSION

It is believed that nuclear fusion can meet the global energy demand with much less burdens on the environment than other energy sources as well as solar energy. However it is still at an immature stage with a lot of technical challenges remaining to be solved. These are being tackled by big science projects such as ITER(International Thermonuclear Experimental Reactor) Project for plasma fusion power plants and LIFE(Laser Inertial Fusion Energy) project in National Ignition Facility in US for inertial fusion power plants. Under an idea that we may achieve laser fusion power plants in a different approach using only two counter laser beams with additional one beam for fast-ignition in contrast to the NIF's 192 laser beams from all directions, a compact and high repetition(10Hz) laser nuclear fusion project has been started by The Graduate School for the Creation of New Photonic Industries, Hamamatsu Photonics K.K., TOYOTA Motor Corporation and TCRDL. We have already observed reasonable amount of neutron yield from D-D fusion by implosion of double-deuterated polystyrene foils separated by 100 μm by counter- illumination succeeded by fast heating[1]. Figure 1 shows our present status and future plan displayed as neutron yield versus laser energy. Since it is necessary to develop high- repetition MJ lasers before achieving cost and energy pay- back condition as a power plant beyond the break even condition, some intermediate outputs as neutron sources for analysis, medical and industrial applications are envisaged[2]. At present, Nd- doped phosphate laser glass is a key laser medium whether it is NIF's flashlamp- pumped type or our diode-pumped type[3]. It is said that the efficiency can be improved by employing diode- pumped Yb-doped fluorapatite crystals. Moreover, the laser medium may be further scaled up for higher

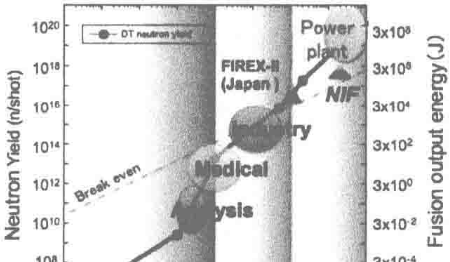

Fig.1. Present status and future plan displayed as neutron yield versus laser energy.

energy output by employing transparent fluorapatite polycrystalline ceramics rather than crystals if micro-domain-control is successful[4,5].

COMPACT SOLAR-PUMPED LASER

High-grade Nd-doped YAG ceramics for laser medium accelerated R&D on solar pumped lasers[6]. Solar pumped lasers usually employ Fresnel lenses or concave mirrors of several meters in diameter to concentrate sunlight into a water-cooled Nd-doped YAG rod of typically 10 mm in diameter and 100mm in length[7]. In contrast, employing an off-axis parabolic mirror of 50mm in diameter and a Nd -doped YAG prismatic rod of 1 x 1 x 5mm in size without water-cooling, we have developed a much more compact solar-pumped laser which can stably emit 1064nm laser light tracking the sun on a commercially available equatorial mounting for amateur astronomers as shown in Fig.2[8]. In the same system, Nd-doped ZBLAN (ZrF_4, BaF_2, LaF_3, AlF_3, NaF) fiber was also successful in laser emission in place of the prismatic rod[9]. The 1064nm laser light or its higher harmonics such as of 532nm is expected to be easily transmitted long distance, to be concentrated into a fine spot to attain high temperature for production of hydrogen from water, and to be converted into electricity using photovoltaic cells with its optical band gap just below the photon energy of the laser light so as to minimize thermal loss.

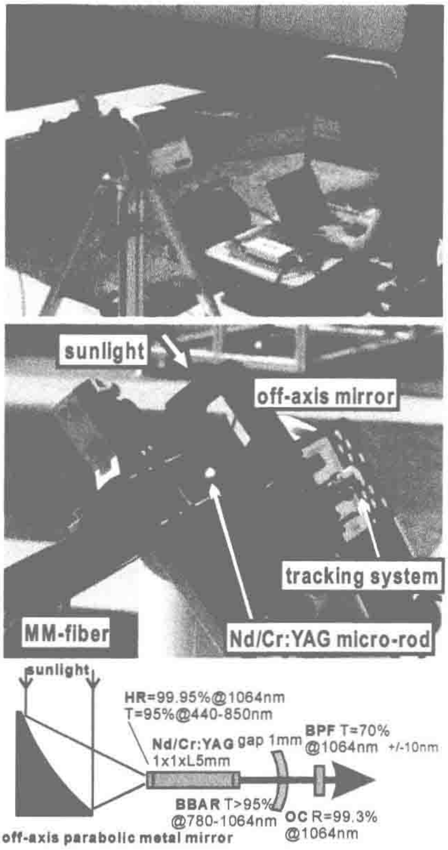

Fig.2 Fabricated compact solar pumped laser mounted on a solar tracker which enables several hours of continuous laser oscillation by tracking the sun.

SOLAR CELLS

Dye-sensitized Solar Cells

R&D on dye-sensitized solar cells(DSSC) comprises of sciences and technologies of ceramics for the optical electrodes typically of sintered nano-porous TiO_2 layers in anatase phase, organic and metal-organic chemistry for sensitizers typically of Ru-complexes and photo-electrochemistry. Conventional solar cell manufacturers working typically on Si p/n junction solar cells have been rather not familiar with such versatile fields but automotive manufacturers are. Taking this advantage, we have been working on DSSC for more than 15 yeaisplayrs with Aisin Seiki Co. Ltd[10,11]. Figure 3 shows outdoor performance test of battery-operated night-lights charged by dye-sensitized solar cells during daylight near the TOYOTA beam line at the synchrotron orbital radiation site "SPring-8" in Japan. Although the top efficiency over 12% has been reported but there remain still tough challenges of outdoor durability mainly because of degradation of organic dyes and liquid electrolytes[12-14]. Although more than 15 years durability was confirmed for small cells, large modules still have different challenges to be durable. In 2012, there came up possible game-changing technologies reported from plural research groups[15,16] in which sensitizers and electrolyte can be replaced by inorganic materials opening the door to all-solid inorganic dye-sensitized solar cells.

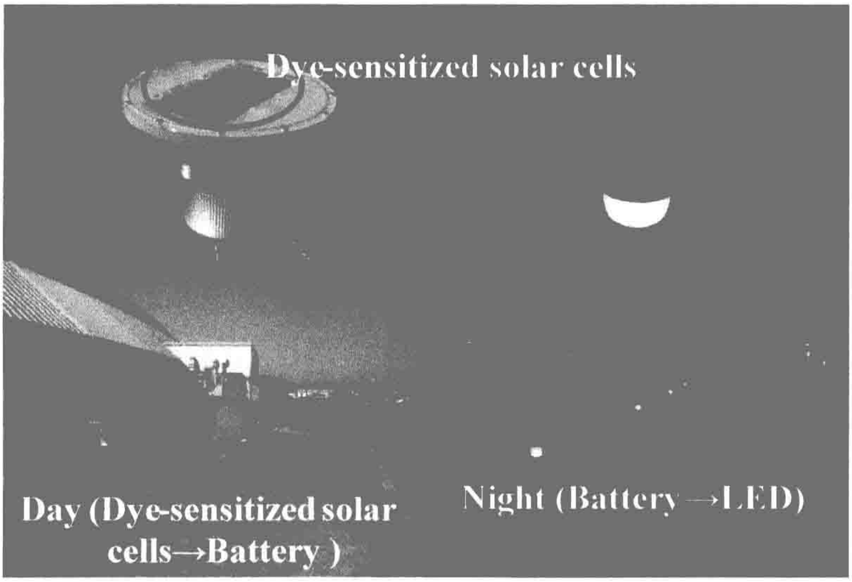

Fig.3 Outdoor performance test of battery-operated LED night-lights charged by monolithic dye-sensitized solar cells in day time (since April, 2009).

Cu_2ZnSnS_4 Thin Film Solar Cells

Inorganic semiconductor solar cells have evolved starting from single-elemental Si, through binary GaAs and CdTe to essentially ternary $Cu(In_{1-x}Ga_x)Se_2$. We have been working on quaternary Cu_2ZnSnS_4 system of kesterite crystal structure since 2006[17-22], because (1) Cu_2ZnSnS_4 is composed of earth-abundant and nontoxic elements, (2) thin-film technologies can reduce both the material cost and the fabrication cost, and (3) the bandgap energy of Cu_2ZnSnS_4 about 1.4eV is optimal for single-junction solar cells leading to the detailed balance limiting efficiency of about 31%[23]. In reactive sintering process, a precursor layer formed on a Mo-coated glass substrate changes into a polycrystalline Cu_2ZnSnS_4 thin film where grain boundaries take important effect on photovoltaic properties. Although this quaternary system can cause difficulties in stable production, the number of R&D reports is increasing rapidly now as shown in Fig.4 since it uses neither rare elements nor environmental pollutants, and since there is an estimation that only this system can make the electricity generation cost lower than that of Si solar cells. More recently, solution-processed kesterite with an additional element of Se has been successful attaining an energy conversion efficiency beyond 11%[24,25]. On the other hand, a quaternary system without Zn but with Ge: $Cu_2Sn_{0.83}Ge_{0.17}S_3$ was found to have a bandgap of 1.0eV and attained energy conversion efficiency of 6%[26]. This also shows a possibility of higher efficiency constructing a multi-junction type solar cell using this $Cu_2Sn_{0.83}Ge_{0.17}S_3$ for a bottom cell[26].

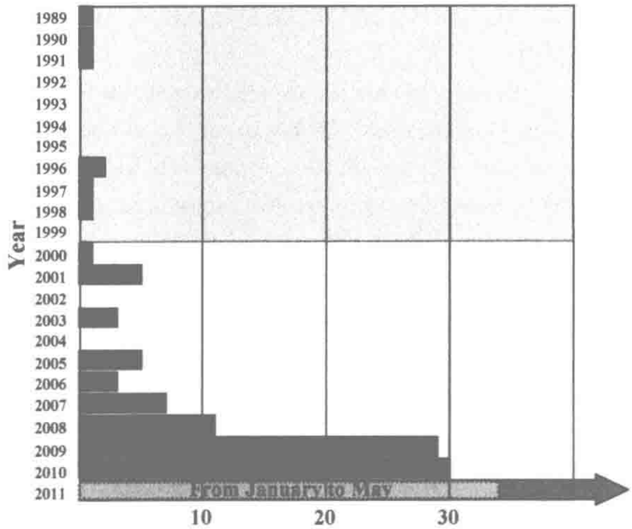

Fig.4 Number of published papers on the topics related to Cu_2ZnSnS_4

The Third Generation Solar Cells

The best strategy to decrease thermal loss of photon energy larger than the bandgap and transmission loss of photon energy less than the bandgap in such a widespread solar spectrum is to construct multi-junction solar cells comprising of plural active materials of different optical absorption edges. To compensate the increase in the fabrication cost to form multi-junction structures, concentration of solar-light onto a solar cell of small area is usually employed. However, since more than half of the sky is shadowed by cloud in average and the percentage of direct sunlight which can be concentrated is lower than 80% even in a typical clear day because of moisture in Japan, the area in which the combination of the solar concentrator and the multi-junction solar cells of small area is applied advantageously is quite limited. The third generation solar cells such as (1) hot-carrier type, (2) multi-exciton generation type, and (3) intermediate-band type have been proposed to decrease the loss mentioned above without using solar concentrators. We have also studied these solar cells both theoretically[27-32] and experimentally [33,34]. Spontaneous formation and arrangement of quantum dots is a key factor in these solar cells. At the present time of writing, however, we are not successful to get any promising perspective for these third generation solar cells.

ARTIFICIAL PHOTOSYNTHESIS OF FORMIC ACID FROM CO_2 AND H_2O ONLY USING SUNLIGHT

Hydrogen production by photo-electrochemical water splitting has been extensively studied all over the world. Hydrogen can be also produced from water electrolysis combined with solar cells. In this situation, syntheses of hydrocarbons using solar energy are much more challenging rather than hydrogen. We had an experience of R&D on visible-light photo-catalysis in nitrogen-doped TiO_2 for photolysis of organic contaminants which has been commercialized as a series of environmental catalysts under the name of VCAT [35]. Based on this experience of photolysis, we have begun R&D on photosynthesis of methanol from CO_2 and H_2O only using sunlight. At present, photo- synthesis of formic acid has been attained[36,37]. Figure 5 schematically shows the process. Here, H_2O molecules are oxidized to yield oxygen using holes formed by photo-excitation in the left electrode and residual electrons are transmitted via conducting wire to the right electrode and reduce CO_2 to form formic acid. To increase selectivity of CO_2 reduction in comparison with hydrogen formation, a Ru-complex layer was formed on the surface of the right electrode. By choosing an appropriate materials combination of the two electrodes, solar-energy conversion efficiency of 0.04% was attained which is 20% of solar-energy conversion efficiency of natural photosynthesis in switchgrass. This was the first achievement of complete artificial photosynthesis from CO_2 and H_2O only using sunlight without applying any bias voltage or additional chemicals in the water. We are continuing effort on further improvement of conversion efficiency and development of electrode materials of lower cost[38].

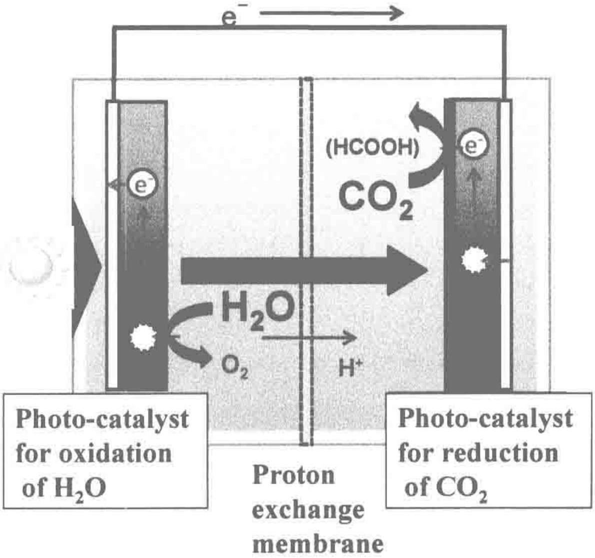

Fig.5 Schematic diagram of artificial photosynhesis of formic acid from CO_2 and H_2O only using sunlight.

SUMMARY

Typical recent research activities on future energy sources including laser nuclear fusion, solar-pumped lasers, solar cells and artificial photosynthesis in TCRDL are reviewed with special attentions to ceramics as key materials. Although every activity introduced here has