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ADVANCED THERMAL ENERGY STORAGE TECHNOLOGIES

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ENERGY CONVERSION PROCESSES SUPPORTING ADVANCED THERMAL ENERGY STORAGE TECHNOLOGIES*

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ABSTRACT

Research that focuses on fundamental aspects of energy conversion could lead to innovative and improved energy storage technologies. Research progress in two energy conversion processes will be summarized and the associated storage technologies described. These two processes are particle catalyzed solar photodissociation for thermochemical energy conversion and storage, and the controlled emission of thermal radiation using narrow-bandgap semiconductor materials.

The thermochemical energy conversion research at LBL is focused on the study of the endothermic dissociation of SO_3 by direct irradiation by concentrated sunlight. The reaction products, SO_2 and O_2, are recombined to produce high temperatures for driving thermal processes. The specific reaction mechanism involves the use of submicrometer metal oxide particles as solar absorbers and as sites for the decomposition of SO_3. The enthalpy of dissociation, 1.1 eV/molecule, is well within the energy available from the majority of solar photons. Several photocatalytic mechanisms are being considered for direct coupling of the photon energy into the dissociation process. The research program is designed to explore evidence of these mechanisms. The benefit of particle catalyzed photodissociation would be to reduce the dissociation temperature below that required for thermal equilibrium conversion (1150 K to 1200 K). Solar-induced, small-particle-catalyzed photodissociation could be significant in breaking the current economic and technical barriers to the development of viable thermochemical processes.

Research on narrow-bandgap semiconductor materials is being pursued for the development of a solid state radiative heat pump. This work takes a fundamental approach to developing a solid state technology having the potential for exceeding the COP of a vapor compression heat pump while providing, at the same time, unique capabilities for energy storage systems. The goal of the project is to demonstrate the feasibility of making a large-area, efficient solid state device capable of pumping 100 W/m^2 of infrared radiation in the 5 to 20 μm range. This research has focused on proof-of-concept experiments using InSb. The infrared emission spectrum of both intrinsic and p-type material has been measured as has the emission intensity as a function of current density. The measurements for intrinsic InSb are in good agreement with theory.

These two projects represent a technical approach where, by selecting fundamental energy conversion processes and focusing on the atomic and molecular level, the door can be opened to new energy storage technologies capable of achieving improved cost, capacity, efficiency, and reliability factors.

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BACKGROUND

Two projects supported under the Advanced Thermal Energy Storage Technologies program at the Lawrence Berkeley Laboratory have the potential for significantly impacting future energy storage technologies. These projects have characteristics that are important for identifying and selecting advanced thermal storage research. First, they are targeted to energy conversion or supply options where thermal storage is a key element in the overall energy conversion and supply system. Second, the technology that will result from the research is consistent with future energy supply and end use scenarios. This will assure that, if research and development is successful, there will be a driving force for technology transfer. Third, the projects focus on fundamental energy conversion processes that are innovative and have favorable cost to benefit ratios. Projects were judged to be innovative on the basis that they represent new approaches to maximizing the reversibility of energy transfer in the storage process, thereby minimizing the irreversible entropy gains, and that they provide new options for integration of conversion and storage.

THERMOCHEMICAL CONVERSION AND STORAGE USING SMALL PARTICLES AS HEAT EXCHANGER AND CATALYST

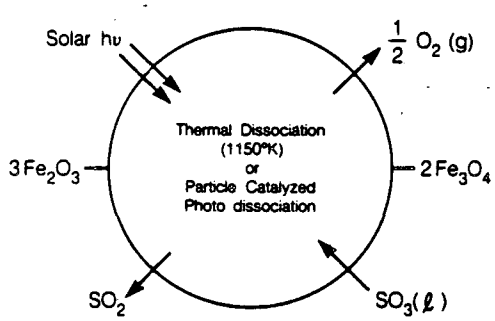
Solar thermal energy conversion is a key renewable energy option for the twenty-first century. When coupled with thermochemical energy conversion, small scale systems (less than 100 MWe) could be built with short lead times to match utility demands. This economic incentive along with increasing environmental pressures will enhance a market for successful, economically competitive solar energy systems. In fact, environmental constraints on power production can be expected to play an increasingly important role in the future. There is increasing concern that the inevitable production of CO_2 from fossil fuel burning and long lived radioactivity from nuclear fuels will have negative global and societal impacts. These two issues may, in the long run, be the strongest incentives for alternative energy sources such as solar thermal electric power.

Thermal storage for solar thermal systems is a key factor in developing a successful alternative technology by providing for continuous operation in the absence of the sun, and providing for remote stand-alone solar plants. Thermochemical storage as opposed to sensible or latent heat storage has clear advantages in that the output temperature, which can be very high, is independent of the amount of energy remaining in storage. Further, ambient temperature

storage is possible and transport can be economically feasible. The transport feature of the energetic products provides options for moving energy from distributed collectors to central conversion sites, and from sun rich to sun poor areas with low transmission losses.

This project is in support of a technology that is a Solar Thermally Activated Radiant-Receiver (STARR) capable of converting energy from solar radiation into stored energy in chemicals. The radiant-receiver concept is based on the use of small particles suspended in a reactive gas for the direct absorption of solar radiation. The particles catalyze an endothermic reaction leading to the formation of energetic products. The direct absorption and conversion of solar radiation by small particle-gas mixture to produce a high temperature gas has already been demonstrated (1*). One possible energy conversion mechanism and cycle is shown in Figure 1a. The solar radiant-receiver contains hematite (Fe_2O_3) particles. The hematite absorbs the solar radiation to convert radiant energy to thermal energy, and acts as a catalyst for the dissociation reaction. The hematite particles are separated from the product stream and recycled. The energetic product, SO_2 gas, is cooled and stored as a liquid at ambient temperature taking care to recoup as much as possible of its thermal energy. The SO_2 is later reacted with oxygen over a catalyst to produce high temperatures suitable for driving an electric power plant or providing industrial process heat during periods when the stored energy is needed.

(a) Thermochemical Energy Storage Cycle



(b) Particle Catalyzed Photo dissociation Mechanisms

(A)
$$h\upsilon + 3Fe_2O_3 \rightleftharpoons 2Fe_3O_4 + \frac{1}{2}O_2$$
$$SO_3 + 2Fe_3O_4 \rightleftharpoons 3Fe_2O_3 + SO_2$$
$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2 \qquad \Delta H = 23 \text{ kcal/mole}$$

(B)
$$h\upsilon + Fe_2O_3 \rightleftharpoons Fe_2O^{\circ}_3\,(e^- + h^+) \qquad E_b = 2.3 \text{ eV}$$
$$SO_3 + Fe_2O^{\circ}_3(e^- + h^+) \rightleftharpoons Fe_2O_3 + SO_2 + \frac{1}{2}O_2$$
$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2 \qquad \Delta H = 1.0 \text{ eV/molecule}$$

Figure 1. A conceptualization of a storage cycle for a solar thermally activated radiant-receiver using small particles as heat exchanger and catalyst.

A combined experimental and theoretical research program is being carried out to identify the key factors in the use of small particles for chemical conversion for solar thermal-electric power production or solar fuels and chemicals production. The theoretical approach has concentrated on the absorption of solar radiation and on the gas-particle interactions. Variables include the light absorption and scattering properties of the particles, their size distribution, mass loading in the gas, and optical absorption path lengths. The temperature difference between the gas and particles has been shown to be very small and is rapidly established (2). The experimental approach has focused on the SO_3 dissociation reaction. This reaction was selected because it has been extensively studied as a potential storage reaction (3,4,5,) and there has been extensive supporting experimental work on available catalysts (6). The experimental work has two objectives. First to demonstrate that direct absorption and catalysis is possible, and second to research particle catalyzed photodissociation processes. Achieving the first objective would indicate that direct absorption and catalysis may be used with a number of important reactions under consideration, (e.g., methane reforming, water splitting, or ammonia production). Identifying a photodissociation mechanism under the second objective could lead to an economical SO_3 dissociation cycle. In both the theoretical and experimental work particular emphasis is placed on understanding the energy conversion processes at the molecular level.

The thermodynamic equilibrium between SO_3 and SO_2 (Fig. 2) predicts that near complete (> 90%) conversion occurs only above 1150 K. Also note that when using Fe_2O_3 as a catalyst, the reaction does not approach equilibrium along the predicted curve until the temperature is well above 1000 K. This effect can be explained by assuming that thermally reduced sites of iron oxide, e.g., magnetite, must be created on the hematite particles. In Figure 1b, two possible particle catalyzed photodissociation mechanisms are written for the production of SO_2 from SO_3 that do not require temperatures of 1150 K. In the first reaction, a photon directly reduces sites on the hematite liberating oxygen. These reduced sites react with adsorbed SO_3 taking up oxygen and liberating SO_2. In the second mechanism, the semiconductor properties of Fe_2O_3 (indirect band gap = 2.3 eV) are invoked. The intense solar radiation produces electron hole pairs that react with SO_3 adsorbed on the surface of the particles, resulting in reduction of the sulfur and oxidation of the oxygen atom and leading to dissociation.

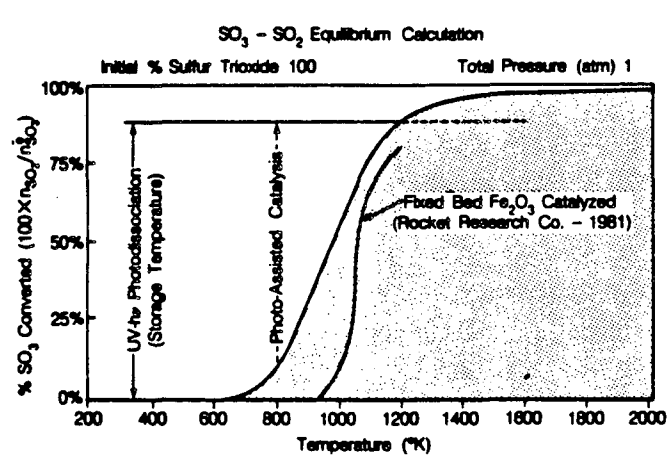


Figure 2. Equilibrium percent of sulfur trioxide dissociated as a function of temperature.

* Numbers in parentheses designate References at end of paper.

A series of experiments are planned that will determine the SO_2/SO_3 ratio as function of temperature in the presence of concentrated sunlight and with isothermal conditions. The first experiments utilize a batch reactor to assure that the equilibrium ratio is reached. Submicrometer particles of Fe_2O_3 will be used as the catalyst. Concentrated sunlight will be simulated using a focused 2.2 KW xenon arc lamp with UV filtering. The simulator is capable of providing a peak light intensity of 4000 KW/m^2. A heated vacuum transfer system was designed and built inside a laboratory hood to transfer SO_3 vapor from a 100 g vial of liquid SO_3 to the reactor vessel.

The reactor vessel was designed to meet a number of criteria. The vessel was made only of quartz and teflon to avoid unwanted side reactions. The geometry of the vessel allows the reaction zone to be heated up to 1200 K while being irradiated by the solar simulator. Accurate measurements of the maximum temperature in the reaction zone are required in both isothermal and irradiated conditions. A reactor vessel with these features has been designed and testing is underway.

Future directions will include work on particle-gas separation, or alternatively, on combined particle-gas storage and radiant-receiver design options before technology transfer could be considered. There is great economic incentive for lowering the dissociation temperature of the SO_3 to avoid new or potentially expensive technology for transferring heat from outgoing products to incoming reactants (3,7). For this reason, the experimental program not only seeks to demonstrate the feasibility of the small particle absorber concept, but searches for particle catalyzed photodissociation processes to provide lower temperature reaction pathways.

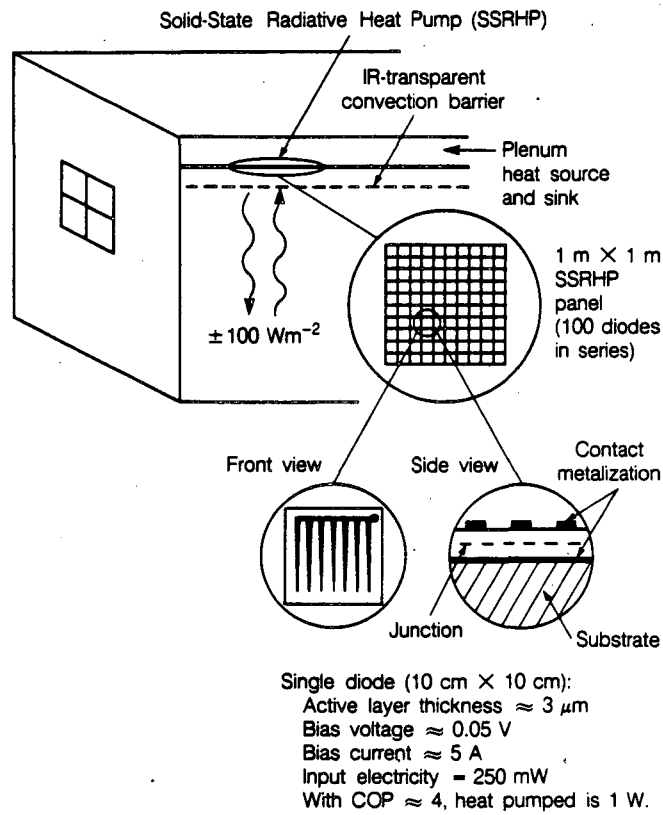


Figure 3. Characteristics of a working solid state radiative heat pump.

SOLID STATE RADIATIVE HEAT PUMP

The purpose of this research is to establish the basis through research for the development of a new class of heat pump. The new heat pump would be a solid-state device that accepts input energy in the form of electricity and pumps infrared (heat) radiation across a thermally insulating gap. An illustration of this concept is shown in Figure 3. This configuration (which does not show thermal storage) shows that radiant heat in the form of infrared radiation is "pumped" into, or out of, a conditioned space by the Solid-State Radiative Heat Pump (SSRHP). Direct current electricity is the motive force which causes the heat pumping action. In this example the plenum serves as the heat sink which provides or absorbs the required heat. Since the SSRHP device would be at the plenum temperature rather than at room temperature, an IR-transparent convection barrier (e.g., a polyethylene film) is provided to inhibit convection.

One research goal is to provide 100 W/m^2 of available heat pumping capacity. Another goal is the achievement of this heat pumping action with high thermodynamic efficiency, approaching the Carnot limit. For purposes of illustration a COP of 4 is indicated, but even higher values of COP are possible if temperature differences are not too large. While the SSRHP could be used in a conventional manner with, for example, chilled water storage, it is intrinsically a large-area device, therefore, it would be natural to integrate the heat pump into the building structure, to charge or discharge heat from distributed thermal mass provided by structural concrete or phase-change tiles. Furthermore, the availability of a new type of quiet, reliable chiller which is efficient in small sizes will offer new design flexibility for engineers concerned with heating and cooling systems.

Cooling of buildings in conjunction with thermal storage is a particularly important potential application. Chilled water or ice storage in buildings is cost effective in regions of the country where utility pricing structures encourage shifting from peak demand hours (8).

Semiconductor materials with direct narrow bandgaps in the range of 0.03–0.25 eV emit equilibrium thermal radiation which is in large part due to electron-hole recombination. An excess or deficit of infrared radiation, compared to the thermal equilibrium value, can be produced when the concentrations of electrons and holes are varied from their thermal equilibrium values by electrical means. Two techniques for varying the concentrations of electrons and holes are being investigated: 1) electrical bias of a p-n junction to produce carrier injection or, for reverse bias, carrier extraction; 2) the magneto-concentration effect in which orthogonal electric and magnetic fields are used to enhance (or deplete) the concentrations of electrons and holes near the semiconductor's surface. The p-n junction technique is particularly promising for the development of technologically mature devices, while the magneto-concentration effect offers the opportunity to study the key recombination phenomena in a simpler and easier to realize experimental system.

The research approach being pursued is based in large part on measurements of Galvano-Magnetic Luminescence (GML). A narrow-bandgap semiconductor material is selected that is a candidate for eventual use in a p-n junction diode (with no magnetic field). A thin crystal of the material is placed on a heat

sink in orthogonal electric and magnetic fields, each parallel to the crystal surface. This combination of fields produces either an excess or deficit of electrons and holes near the free surface of the crystal. This condition in turn produces a corresponding excess or deficit of infrared radiation, compared to the equilibrium thermal emission. If carrier mobilities are known the rate at which the carriers approach the free surface may be calculated. If the (equilibrium) optical absorptivity is known, a measurement of the emitted infrared intensity can then be used to infer the probability η_q that an excess electron-hole pair will produce an infrared photon. This same quantum efficiency η_q gives the probability that the absence of an electron-hole pair will result in the net absorption of one photon. Thus, η_q is the most important figure-of-merit for SSRHP materials, and it can be measured with a GML experiment. Experimental results (9) for intrinsic (pure) InSb show that at room temperature the quantum efficiency is 2%. This value is too low to permit the development of an efficient SSRHP using intrinsic InSb, but it is high enough to permit the construction of experimental cooling devices, discussed below. The same experiment (9) shows an alternating (2 kHz) heating and cooling effect of about 4 W/m^2. According to the theory (10) and from approximate measurements in our laboratory, this value can be raised by a factor of 10, by increasing the electric and magnetic fields. Still higher heat pumping capacity, to approach the 100 W/m^2 goal, will require a material with a narrower bandgap or doping to introduce impurity states near the band edges.

An experiment has been designed to explicitly produce a continuous cooling effect, using magneto-concentration effects with intrinsic InSb (Fig. 4). The active InSb layer is made rather thin to reduce ohmic heating; it is only a few times the thickness of the carrier diffusion length (about 3 micrometers). The carriers are pushed away from the free surface of the active chip by the magneto-concentration effect (Lorentz force), and the depleted layer near the free surface can thus absorb IR radiation emitted by the passive chip without emitting the counterbalancing radiant flow which would occur under conditions of thermal equilibrium. Thus, the passive emitter chip can be radiantly cooled. Observation of a cooling effect is complicated by edge effects and the release of ohmic heat in the active layer. Procedures for observing a cooling effect will be discussed in a subsequent publication. The demonstration of this cooling effect will show that the alternating heat pumping action observed at 2 kHz in the GML experiment extends to zero frequency and, therefore, that continuous cooling is not prevented by any parasitic mechanism.

The status of the Solid-State Radiative Heat Pump research can be summarized as follows. It has been clearly established that heat pumping effects can be produced. The GML technique has been developed to assess candidate materials, and intrinsic InSb has been evaluated. Projected device efficiencies are still too low for the InSb investigated to date, so the near-term research will focus on finding materials with higher quantum efficiencies. P-type InSb and the alloy system $Pb_{(1-x)}Sn_xTe$ will be investigated. In general, it is necessary either to find a material with adequate quantum efficiency (>50%), or to understand the physics of the parasitic mechanisms which reduce the efficiency so that a material can be designed in which these competing mechanisms are weak. Once quantum efficiencies reach the 20% range, an order of magnitude improvement over present levels, design of p-n junction structures should begin. Given a suitable material, the engineering to fabricate large-area p-n junctions devices will be the major technical task. Key issues will be: (1) efficient transmission of IR radiation into and out of the device, complicated by total internal reflection, (2) minimization of resistive losses while distributing electrical current, and (3) construction of an IR-transparent contact to carry electrical current. Complicating these tasks will be the requirement to manufacture the devices for only a few dollars per square meter. However, recent advances in materials and developments in manufacturing of amorphous silicon photovoltaic cells, for example, suggest that the devices can be manufactured.

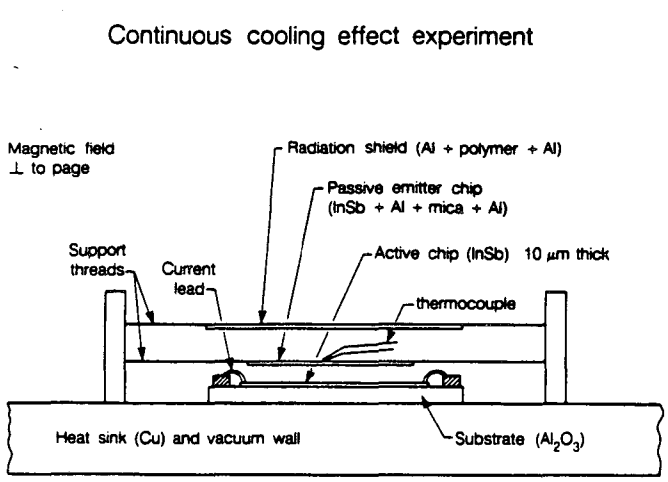


Figure 4. Diagram of the continuous cooling experiment components.

SUMMARY

Advanced thermal energy storage technologies will require new scientific developments. Research and development that focuses on the molecular and microscopic energy conversion processes that have potential for low irreversible entropy production, have the greatest potential for making significant gains. Furthermore, research that is targeted both to the key conservation and renewable energy options and emphasizes recognized areas of opportunity in basic research should be encouraged. Two projects have been described that offer the potential for significant improvement and innovative design possibilities in thermal storage systems. The solid state radiative heat pump concept seeks to develop a narrow bandgap semiconductor panel capable of pumping 100 W/m^2 of radiant energy targeted at cooling and cool storage in buildings. The research emphasis is on development and/or identification of narrow bandgap semiconductor material with a large quantum efficiency. The small particle radiant-receiver for heat exchange and catalysis seeks to provide a combined solar energy conversion and storage option for solar thermal electric power and solar fuels and chemical production. The research emphasis is on demonstrating radiantly heated particle catalysis and identifying particle catalyzed photodissociation mechanisms. These projects represent new research and development paths to improved thermal storage systems.

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