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APPLICATIONS OF PASSIVE THIN FILMS

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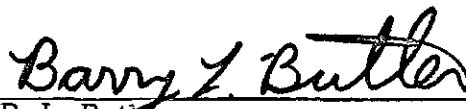
PREFACE

The physical properties of thin films affect the performance and durability of nearly every solar energy conversion device. Familiar examples of thin films for solar applications are optical materials and protective coatings. Optimized optical properties are key to cost-effective photothermal conversion where individual components must have high absorptance, reflectance, or transmittance. The protection of sensitive substrates from corrosion and/or erosion is essential to ensure adequate component and system lifetime. Such substrates range from photovoltaic materials operating near room temperature to turbine blade structural alloys in hostile environments at very high temperatures ($>1000^{\circ}\text{C}$). Although much has been written on particular categories of thin-film materials for solar energy (for example, absorbers for receiver surfaces), to date no one has provided an overview of the spectrum of applications for passive thin films in solar energy. This work is such an overview and also reviews the material state of the art as described in the current literature. Active thin film devices such as photovoltaics and thermoelectrics are not discussed.

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CHAPTER 9

APPLICATIONS OF PASSIVE THIN FILMS

9.1 INTRODUCTION

A remarkable number of applications exist for thin-film technology across the spectrum of solar energy conversion devices. Passive films, defined to exclude those applications such as thermoelectrics and photovoltaics where the film itself is the primary transducer or conversion element, are critical to nearly every solar technology. The category of passive thin films as defined in this chapter includes optical films, protective coatings, high and low energy surfaces, and selective membranes.

Optical films for solar energy conversion systems include absorber, reflector, and enhanced transmitting (antireflection) materials; heat mirrors, and transparent conducting electrodes. Specialty films are also required for particular applications such as switchable optical materials, films that have a high transmittance in the photosynthetic spectral region with a high reflectance or absorptance elsewhere, and ultraviolet (UV) reflecting or absorbing interference films. As important elements of the space program for the control of spacecraft temperature, optical films have received the most attention of scientists and thin-film technologists within the passive category.

Applications for protective coatings are numerous and can be divided into physical (erosion) and chemical (corrosion) protective films. Both erosion and corrosion protection are important concerns for turbine blades, and applications unique to solar energy technologies are determined by a combination of environmental, thermal, and rotational speed conditions. Low velocity/low-temperature applications include leading edge protection of wind turbine blades and very large turbine blades for low-temperature heat engines, such as those proposed for open-cycle ocean thermal gradient energy conversion and ocean current energy conversion devices. High-velocity/high-temperature applications include turbine blade protection for open and closed Brayton cycle heat engines. Corrosion protection is required for low- and high-temperature heat exchanger surfaces and for substrate and superstrate mirrors. Photovoltaic devices require encapsulation for both erosion and corrosion protection.

Surfaces with specific polar and dispersive energies may be useful in enhancing the performance of thermal conversion devices. A high polar energy heat exchanger surface may improve the wetting of heat exchange fluids and thus increase the thermal transfer coefficient. A low surface energy coating on the reflecting surface of a mirror reduces the adhesion of dust particles in the presence of moisture, promising reduced maintenance costs and extended useful mirror lifetime.

Selective membranes are being employed in advanced solar energy conversion devices. Ionic heat engines and batteries require durable high-temperature membranes. Osmotic head hydroelectric systems are proposed to operate at a brine/fresh water interface and will require membranes that can endure high pressures and be cleaned repeatedly.

This chapter provides a closer look at each of the functions of passive thin films outlined here and describes the materials state of the art in each instance. A brief discussion of the taxonomy of solar energy conversion devices is provided in Section 9.2 as background for the thin-film applications (Sections 9.3 through 9.6).

9.2 SOLAR ENERGY CONVERSION DEVICES

The exciting field of solar energy research and development has evolved to include the extraction of energy from a wide range of secondary natural energy systems in addition to the direct conversion of incident sunlight into heat, fuels, and electricity. These secondary natural energy sources include ocean thermal and salinity gradients, waves, tides, ocean currents, hydropower, wind, and processed biomass. Systems may be classified by end-use as indicated in Table 9-1.

Applications requiring a thermal input include hot water, heating and cooling of buildings (to 200°C), and process heat for agricultural and industrial purposes (to greater than 1000°C). Solar energy conversion systems that can provide this heat include solar ponds; flat-plate collectors; evacuated tube collectors; non-imaging, low-concentration ratio collectors; single-axis tracking concentrators (Fresnel, parabolic, and hemispherical); and two-axis tracking concentrators (parabolic dish, spherical dish, and central receiver).

Systems to convert sunlight to electrical (or mechanical) outputs may do so directly (e.g., photovoltaic and photoelectrochemical) or indirectly (e.g., solar thermal input to a heat engine and wind energy conversion). Such devices may be modular and distributed (e.g., parabolic troughs and photovoltaic arrays) or large and centralized (e.g., solar thermal central receiver and ocean thermal gradient closed Rankine cycle heat engine).

Fuels and chemicals from solar energy may be obtained from the processing of biomass residues or energy plantation products, from the synthesis of materials using solar thermal or solar electric energy, and from direct conversion using photochemical or photobiological systems.

Figure 9-1 illustrates some diverse solar energy conversion systems.

9.3 OPTICAL FILMS

Optical films have received considerable materials R&D support during the past 25 years both within and outside the national solar energy program. Indeed, only the study of photovoltaics has had greater emphasis by solid state physicists and material scientists than the development of selectively absorbing films with high solar absorptance and low thermal emittance. In addition to solar absorbers, other optical films are required in photothermal converters. Reflector materials are needed in concentrating collectors. Antireflecting coatings improve the performance of glazings, encapsulants, and photovoltaic devices. Heat mirrors can control the temperature of building spaces and greenhouses, improve heat trapping in solar collectors, and improve furnace performance where thermal processing of materials is required. Transparent conducting materials are essential as front electrodes on Schottky barrier and metal-insulator-semiconductor (MIS) photovoltaic devices. UV reflecting or absorbing interference filters protect plastic glazings and encapsulants from photodegradation. Switchable films are desirable for the protection of plastic solar collectors from high temperatures in the case of stagnation (loss of coolant). Films that transmit in the photosynthetic spectral region and absorb or reflect at all other wavelengths have been suggested for more effective management of greenhouse heating and cooling loads.

The complete optical characterization of thin films requires measurement of the spectral bidirectional reflectance and transmittance from $0.35\mu\text{m}$ to $30\mu\text{m}$ over all angles of incidence and exitance. Such a thorough characterization, however, is unnecessary in all but the most specialized of applications. To discuss low-temperature applications of optical films, the electromagnetic spectrum can be conveniently split into the solar region ($0.35\mu\text{m}$ to $2.5\mu\text{m}$) and the thermal infrared region ($2.5\mu\text{m}$ to $30\mu\text{m}$). Four independent parameters suffice to define optical performance: the solar reflectance (ρ_s) and transmittance (τ_s) and the thermal reflectance (ρ_t) and transmittance (τ_t). These four parameters are determined by weighting the spectral directional hemispherical reflectance and transmittance with the solar (E') and blackbody (I_{bb}) distribution functions over wavelength, λ as follows:

$$X_s = \int X(\lambda; \theta, \phi; 2\pi) E'_\lambda d\lambda / \int E'_\lambda d\lambda \quad [9.1]$$

$$X_t = \int X(\lambda; \theta, \phi; 2\pi) I_{bb\lambda}(T) d\lambda / \int I_{bb\lambda}(T) d\lambda \quad [9.2]$$

(for $X = \rho$ and τ)

where E'_λ is the solar irradiance from Thekaekara [1] corrected to air mass 1.5; $I_{bb\lambda}(T)$ is given by the Planck distribution ($C_1 \lambda^{-5} [e^{C_2/\lambda T} - 1]$ where C_1 and C_2 are constants equal to $3.74 \times 10^{-16} \text{ Wm}^{-2}$ and $1.44 \times 10^{-2} \text{ m}^\circ\text{K}$, respectively) and θ and ϕ are the angles specifying the incident radiation direction with respect to the optical surface assumed to be near normal unless otherwise specified. The solar absorptance (α_s) and the normal thermal emittance (ϵ_t) can then be determined from the equalities

$$\alpha_s + \rho_s + \tau_s = 1 \quad [9.3]$$

and

$$\epsilon_t + \rho_t + \tau_t = 1 \quad [9.4]$$

Thorough discussions of the optical properties and measurements appropriate for solar applications are presented in Touloukian [2] and Masterson et al. [3].

As is apparent from Figure 9-2 the solar and thermal quantities are independent only at low temperatures. At elevated temperatures the spectral overlap between the solar and

blackbody distribution functions necessitates the introduction of a fifth parameter, λ_c , the wavelength at which an ideal step function change in an optical parameter should occur to optimize simultaneously the solar and thermal properties. This parameter is a function of the system operating temperature and concentration ratio [4] and is approximately $2\mu\text{m}$ at room temperature for a concentration ratio of one.

Ideal solar optical materials are achieved when the properties α (ϵ), ρ , and τ approach the extremes of one and zero independently in the solar and infrared spectral regions. Table 9-2 lists the ideal values for the applications described previously. Although the overlap of the blackbody and solar spectra at elevated temperatures introduces some compromises, this tradeoff alone is not severe. As an example, based on this overlap a solar absorptance of 0.95 or greater requires that the thermal emittance be no less than 0.12 at 1000°C . However, the additional effect of thermal broadening of the transition from low to high reflectance at elevated temperatures and the constraints of the Kramer Kronig relationships on the real and imaginary components of the complex index of refraction (n and k) introduce a more modest fundamental limit for ϵ_t . Including these effects, Trotter and Sievers [5] have calculated that for $\alpha_s \geq 0.96$, ϵ_t must be no less than 0.25 at 600°C .

Although considerable work remains to improve the optical properties, cost, and durability of films for particular applications, much of this development will be evolutionary, emphasizing and refining present materials and techniques. A research direction of potential long-range importance is the development of switchable materials (thermally, electrically, or photon activated). A window coating, for example, might be switched from a heat mirror state ($\tau_s \approx 1$) for optimal winter use to a solar shade ($\tau_s \approx 0.3, \rho_s \approx 0.7$) to limit summertime cooling loads. Such materials represent an exciting frontier for materials engineering; however, it is important to note that relatively unexciting criteria such as cost, maintenance, and durability will ultimately determine the marketability of such area-intensive films. Solar devices thrive on simplicity, and well-established if cumbersome alternatives exist in many instances which add to the established market inertia for new materials. For window coatings the competition takes the form of shades, curtains, and awnings.

1. Absorber Surfaces

The optical properties—solar absorptance (α_s) and thermal emittance (ϵ_t)—of the receiver surface are important in a wide range of photothermal conversion devices, from passive solar buildings to sophisticated two-axis tracking concentrators. Primary references to absorber surface research and development number in the thousands and the field has been reviewed extensively [6-10].

A partial list of materials in various stages of research, development, and commercialization is included in Table 9-3. The selective materials exploit the physical effects listed in Table 9-4 either singly or in combination, to achieve simultaneously a high solar absorptance and a low thermal emittance. Of the commercial materials, electrodeposited black chrome ($\alpha_s \approx 0.95$, $\epsilon_t \approx 0.10$) dominates the selective absorber market to 200°C and improved control of the Cr^{+3} concentration in the plating bath indicates that thermal stability to 400°C may be achieved [17]. Electrodeposited black nickel with a protective overcoat to impede moisture penetration and electrodeposited black cobalt for applications to 400°C are also being produced. A number of nonselective ($\alpha_s \approx 1$, $\epsilon_t \approx 0.9$) paints are commercially available, including Pyromark, which has undergone extensive tests as the baseline absorber surface for the Barstow, California, 10MW_e solar thermal pilot plant. Issues of concern to absorber surface users are not limited to optical performance and thermal stability, as is emphasized in Table 9-5.

For purposes of comparison, the receiver thermal efficiency (η) of a system can be described by a simplified expression

$$\eta = \alpha_s - \beta \epsilon_t \quad [9.5]$$

where β , a measure of the importance of the receiver thermal emittance to the application, is the radiated heat flux of a blackbody at the system operating temperature, T, divided by the incoming solar flux delivered by the collector to the receiver surface. Table 9-6 lists β for representative applications as a function of operating temperature and system concentration factor (A_c/A_r). It is somewhat paradoxical that, in general, β is highest for current designs of low-temperature systems because the operating temperature of high concentration ratio systems is limited by

other material constraints, such as the interaction of the working fluid and the container walls.

2. Reflecting Films

To exploit the 5800° K thermodynamic potential of the sun using photothermal systems it is necessary to concentrate the sunlight. The degree of concentration is limited ultimately by the finite dimensions of the sun, which impart a 9-milliradian divergence to unscattered incoming rays. In practical cases for solar energy conversion, this limit is not approached because of the optical quality of affordable mirrors and the inability of receiver and containment materials to survive temperatures above approximately 2000° K.

Although the hemispherical reflectance is an important measure of mirror acceptability, as the concentration ratio is increased the specular reflectance (reflectance within a solid angle of exitance equal to a narrow solid angle of incidence at the specular angle) is the appropriate figure-of-merit. Whereas the hemispherical reflectance is determined primarily by the electronic and topographical features of the reflecting surface and its protecting layers, the specular reflectance is also a function of the microstructural and configurational aberrations of the mirror (both short- and long-wavelength variations from the ideal). These aberrations are properties of the entire reflector structure including the substrate or superstrate, bonding layers, protective layers, and structural support elements as illustrated in Figure 9-3 for the two geometries of reflector: superstrate and substrate. (The substrate mirrors include mirrors with thin protective oxides or coatings on the surface of the reflector.)*

For reasons that are clear from Figure 9-4, only two metals, silver and aluminum, are commonly considered for the reflecting layer itself. Freshly deposited bare silver has a high solar reflectance ($\rho_s \approx 0.98$) but does not form a protective oxide layer and thus has poor resistance to environmental attack. Silver that has been protected with a thin overlayer (of refractive index $[n] \sim 1.5$) has $\rho_s \approx 0.97$. The reflectance of aluminum is reduced through most of the visible spectral region (with a pronounced dip at 0.8 μm)

*Historically the two geometries have had the somewhat misleading designation of second surface and front surface mirrors, respectively.

because of interband electronic transitions in the crystalline solid. However, the reflectance at wavelengths shorter than $0.35 \mu\text{m}$ is greater than that of silver and a free electron (Drude model) calculation for aluminum which eliminates interband transitions yields a solar reflectance of 0.99 as compared to a measured value of 0.92, (0.88 with a thin protective layer) [18], prompting discussion that a room temperature stabilized amorphous phase of aluminum might be superior to silver in cost, durability, and performance [19]. Another approach to an improved reflecting material is the alloying of silver and aluminum by coevaporation or cosputtering.* Some system designs employ a secondary concentration scheme where the secondary reflector may experience an incident flux in excess of 1 MW/m^2 and achieve a temperature of 500°C or higher. High-temperature alloys of silver** and thin aluminum films on stainless steel have been proposed for these applications.

High quality commercial silver mirrors are produced by a wet chemistry electroless process and also by evaporation onto glass. Aluminum and silver are both vacuum-deposited onto plastic films and a polished aluminum sheet with an anodized protective film is also available commercially; however, the specularly of such mirrors is a concern. An overview of current solar reflector research and development can be found in Lind and Ault [20] and a thorough review of mirror technology is found in Schweig [21].

The superstrate or substrate to which the reflecting layer is attached is a major factor in the performance and durability of the mirror and may be a glass or a polymeric material. Hampton and Lind [22] review these materials in some detail, and a summary of the appropriate properties is included in Table 9-7. Many of these same materials are being used as transparent glazings for flat-plate collectors, solar ponds, and greenhouses, and as encapsulants for photovoltaic modules. Thus, some of the additional properties appropriate to these applications are included.

*Work being performed under contract to the Solar Energy Research Institute by Rockwell International, Rocky Flats Plant.

**Work being performed under contract to DOE Solar Thermal Test Facility Users Association by Richard Zito, Physics Department, University of Arizona.

3. Antireflection Coatings

The surface reflection of light as it encounters a change in index of refraction at the boundary between two materials can be a critical loss in solar applications such as glazings, photovoltaics, and absorber surfaces. At normal incidence the surface reflectance is given by

$$R = \frac{(n_1 - n_2)^2 + (k_1 - k_2)^2}{(n_1 + n_2)^2 + (k_1 + k_2)^2} \quad [9.6]$$

where n and k are the real and imaginary components of the complex index of refraction $\bar{n} = (n + ik)$ for materials 1 and 2 on either side of the interface. R is approximately 0.04 for a glass/air interface. For high index of refraction materials such as some semiconductors (e.g., silicon), losses in excess of 0.35 can be expected if no attempt is made to reduce the surface reflectance.

Coatings or treatments to reduce the surface reflectance loss are referred to as antireflecting (AR) layers. They are formed by interposing a layer of intermediate index of refraction between the high and low index materials. The simplest technique consists of depositing an antireflecting layer of index of refraction n and thickness d determined by

$$d = \frac{\lambda}{4n} ; \quad n = \sqrt{n_1 n_2} \quad [9.7]$$

where λ is the wavelength of minimum desired surface reflectance. A value of 550 nm, near the peak of the terrestrial solar spectrum, is typically chosen for λ as a value that will minimize solar losses at glazing and nonselective absorber interfaces. However, a more careful analysis of optimum λ may be required for photovoltaics and selective absorbers where the photoresponse is likely to be a more complicated function of wavelength.

A variety of inorganic dielectrics deposited by sputtering, evaporation, glow discharge, chemical vapor deposition (CVD), and thermal oxidation have been explored as potential AR coatings. Si_3N_4 [27], in particular, has received considerable attention as a coating for silicon. Etching the surface of a material reduces the index of refraction in the

etched region; and the effect of the etching process can be modeled through an effective medium approach [28]. The surface reflectance of glass has been reduced in this manner, with the major tradeoff being increased dust adhesion due to the larger surface area, leading to greater cleaning problems.

Researchers [27, 29] have explored theoretically and experimentally the notion of a graded-index, antireflective coating. An experimental graded silicon oxynitride film is illustrated in Figure 9-5. The importance of such graded films is to broaden the wavelength interval over which the reflectance is reduced and to expand the effective aperture for the antireflective coating (i.e., extend the reduction in reflectance to angles of incidence farther from normal).

An abbreviated list of inorganic dielectrics with thin-film values for the real part of the index of refraction (n) is included in Table 9-8.

4. Heat Mirrors

Heat mirrors are films that possess a high infrared reflectance (and thus a low infrared emittance). For solar applications a second constraint is placed on a candidate material: high solar transmittance. Heat mirrors may be incorporated into greenhouse glazings and architectural windows to enhance the thermal gain of the structures. Application to flat-plate, evacuated tube, or solar pond heat collectors allows good optical selectivity without placing stringent thermal stability requirements on the material (in contrast to a system that gains optical selectivity at the absorber surface). This relaxation of the material thermal stability requirement is likely to be even more significant for very high-temperature applications such as Brayton cycle systems, where the receiver wall may be 1400°C but a heat mirror located at the aperture of the cavity receiver could possibly be cooled to 800°C to 900°C . Alternatively, heat mirrors may be applied directly to an absorbing surface to form an inverted tandem stack such as tin oxide doped with fluorine on black enamel [14]. An indirect application of heat mirrors to solar energy technologies occurs in the processing of materials (e.g., semiconductors for photovoltaic devices) in high-temperature furnaces where a heat mirror may greatly enhance the energy efficiency of the processing step without compromising visual access [32].

Heat mirror materials of interest in solar applications are of three principal types: thin metallic films, conducting metallic oxides, and multilayer stacks. Thin metallic films of interest have been Cu, Ag, and Au, all of which have high IR reflectance and a modest transmittance in the solar spectrum. Heavily doped n-type SnO_2 , In_2O_3 (including indium tin oxide) and the metallic oxides ReO_3 , Na_xWO_3 , and Cd_2SnO_4 have been investigated as heat mirrors [33]. Multilayer films that have been studied include TiO_2 -Ag- TiO_2 [34] and ZnS-Ag-ZnS [35]. The dielectric layers in the multilayer systems act as antireflection coatings for the solar spectrum. The inner dielectric layer also plays a critical role in determining the microstructure of the metallic layer. A summary of the optical properties of heat mirrors is included in Table 9-9.

5. Transparent Conducting Electrodes

Since the electronic properties of a material determining the IR reflectance also are involved in defining the electrical conductivity, the set of materials previously considered as heat mirrors also is of interest as transparent conducting electrodes (TCE). In addition to the optical properties, the thin-film electrical sheet resistance and the interface resistance between the underlying electrode and the semiconductor substrate are parameters of interest for TCEs. The boundary resistance is particularly sensitive to the defect density at the interface, and thus the deposition conditions and material compatibility are critical. Vossen [40] has extensively reviewed the material state of the art, concluding that extreme variations in electrical properties (up to ten orders of magnitude for d.c. conductivity) can be reported for nominally similar materials, and careful study of the film microstructure and impurity concentrations is needed to define an electrode material. As an example for a specific material, Fan et al., [41] report the importance of controlling the oxygen pressure during vapor deposition on Sn-doped In_2O_3 .

Analogous to the situation for absorber materials (where reductions in solar absorptance represent an irretrievable loss to the system but increased thermal emittance can be at least partially compensated for in system design), the solar transmittance of transparent conducting electrodes is the fundamental parameter of concern, and the electrical properties of a film may be at least partially compensated for by device design [42]. An example is the tradeoff between large-area, single cells and multiple parallel Schottky

barrier or MIS photovoltaic cells. Large area cells have simple processing and fewer interconnections but require very low and uniform electrical resistance whereas multiple parallel cells can greatly reduce series resistance losses.

A platinum transparent conducting electrode on amorphous silicon (discussed in Chapter 8), prepared from the glow discharge of silane, has yielded a 5.5% efficient photovoltaic device over limited areas [43]. Metal electrodes on polycrystalline silicon are being investigated with a goal of photovoltaic cells with 12% efficiency [44]. Other applications for TCEs may be found in large area switchable devices; for example, as electrodes for electrochromic or liquid crystal materials in switchable solar shades.

6. Specialized Optical Films

A large number of special applications exist for particular thin optical films in solar technologies. In contrast to most applications described in previous sections, suitable or proven materials do not exist and exploratory research will be required to evaluate the viability of each concept.

For thermal control of buildings and for thermal protection of low-temperature solar collectors, materials whose optical properties can be switched are desirable. To reduce the materials intensity of low-temperature solar collectors, extruded high-strength plastics are being considered. When designed to operate efficiently, such a collector may experience temperatures in excess of 200°C when coolant flow is interrupted under direct sunlight. A straightforward solution to this problem has been proposed in the form of thermally reversible bleaching of organic absorber dyes [45]. The main drawback of this technique is that the solar absorptance and selectivity of such dyes at normal operating temperatures may not allow high efficiencies.

Switchable films at the glazing surface should be considered. Two such techniques might employ electrochromic or liquid crystal technology. Both technologies have been studied extensively from the perspective of visual display devices. For this solar application the electrical requirements for direct switching of large areas may be the limiting factor and power consumption must be reduced to less than 0.1 mW/cm² in the switched state. Field effect liquid crystal devices that operate between crossed polarizers and require

fractions of a microwatt/cm² should be explored, and the discovery of a thermally reentrant nematic liquid crystal phase could provide a truly elegant "passive" solution to this problem. Although development of acceptable optical and electrical properties is a monumental task, any material produced will be required to exist for significant lengths of time (>5 years) in a harsh environment of heat, sunlight, humidity, and pollutants not typical of the hermetically sealed visual display environment.

The protection of plastics used in glazings, bubble domes, and encapsulants from photodegradation by UV absorbing coatings is an important concern. ZnS/ThF₄ and ZnS/Al₂O₃ interference filters have been studied and found promising for the harsh UV space environment [30]. Additives to commercial plastic materials that scavenge UV reaction products in the presence of air and moisture are well established. The cost-effectiveness of coatings for terrestrial use must be judged with respect to both system design modifications that allow easy replacement of plastic components and the performance of available additives.

The photosynthetically active region of the solar spectrum lies at wavelengths below 0.75μm and comprises only 50% of the air mass two insolation. The separation of the photosynthetic and heating portions of the solar spectrum to reduce greenhouse cooling loads and to manipulate independently the delivery of heat to better meet greenhouse heating demand has been proposed using dichroic mirrors in a baffled glazing geometry [46].

9.4 PROTECTIVE COATINGS

Natural and artificial protective layers are essential in many applications to reduce the effects of erosion and corrosion. Depending on the protection needed, the physical (modulus, deformation energy, microstructure, etc.) and/or chemical (adhesion, ionic permeability, etc.) properties of the protective film are important. A surface that is moisture sensitive, for instance, might be protected either by a film that is impermeable to water molecules (e.g., densified SiO₂) or by a film whose interfacial chemistry with the surface excludes water from reacting with that surface (e.g., silicones).

Many reviews of thin-film applications for solar energy ignore the category of protective or passivating layers. This neglect is paradoxical because although the innovative frontier in materials development may appear to be improved performance, in reality some of the biggest questions facing solar technologies are the durability, reliability, and lifetime of materials and components. In deference to the magnitude of the overall subject of protective coatings, this section will attempt to illustrate some critical protective needs unique to solar energy conversion systems.

1. Protection for Turbine Blades

Turbine blades for solar applications span a wide range of rotational velocities, operating temperatures, and environmental conditions. At low velocities (typically 10 rpm to 100 rpm) very large blade structures (up to 100 m in diameter) fabricated from fiberglass or concrete composites are contemplated for advanced wind turbines and for open cycle ocean thermal energy conversion systems. Edge protection from erosion may be required in both wind and low-temperature heat engine environments. Conventional experience with helicopter rotors, propeller blades, and wind turbine blades has turned to thick film technology (e.g., metal alloys and rubber) for incident particle shock absorption. For high efficiency turbine design in solar applications where blade drag and weight may be critical, new applications of dense, adherent, and durable thick-film coatings may appear.

Solar applications for high-temperature turbine blades differ very little from conventional gas turbine applications. However, some system designs that propose purely solar inputs to the turbine would greatly reduce the "hot corrosion" problem experienced at high temperatures in the presence of fuel impurities, especially sulfur. A reduction in "hot corrosion" for these designs would include a tradeoff with regard to unavoidable enhancement of the thermal or mechanical cycling fatigue as the temperature and/or gas flow fluctuates with the solar input.

The materials state of the art for gas turbine coatings was reviewed in a session of the 1978 International Conference on Metallurgical Coatings [47]. Two types of coatings are being explored: (1) metallic alloys that form durable oxides and (2) ceramics for increased corrosion resistance and as thermal barriers. Alloy films of the general type MCrAlY have been found in gas turbine experience to form high-temperature stable

protective oxides that greatly extend the protective life of the alloy coating and protect the substrate turbine blade alloy. CrAlY alloy coatings of nickel, cobalt and iron have been evaluated [48, 49]. Thermal barrier coatings consist of high-temperature stable ceramics (e.g., ZrO_2) with low thermal conductivity. Such coatings increase the permissible turbine inlet temperature for internally cooled blades by providing a temperature differential of up to $200^\circ C$ between the outer protective surface and the surface of the structural blade alloy [50]. The degradation of ceramic coatings due to fracture or spalling is an important concern, and the importance of coating microstructure in the control of these failure modes has been reported [51].

2. Encapsulants for Photovoltaics

Encapsulation of photovoltaic cells appears to be essential to inhibit corrosion of the metallic electrode at the semiconductor interface, to prevent the erosive scouring of the semiconductor surface, and to mitigate the effects of dust and hail. Although most encapsulant candidates are thick polymeric or glass films, antireflection coatings on the semiconductor surface, if suitably dense, can also serve a protective function. In particular, gasless ion plating of Al_2O_3 and SiO has shown considerable promise as a technique to provide an impermeable antireflection coating. Essentially, the first several monolayers of dielectric materials are implanted into the semiconductor surface, thus providing an extremely adherent coating.* The electrostatic bonding of thin glass to photovoltaic cells has received considerable attention [51]. In this technique adhesion is achieved at elevated temperatures by applying a d.c. voltage across the interface to be bonded, thus producing a migration of ions. Integral rf-sputtered borosilicate glass covers ($40\mu m$ to $60\mu m$ thick) have been evaluated and have performed well except for some moisture induced delamination [52].

The UV and erosion stability of the solar transmittance of the encapsulation system (outer cover, adhesives, pottant, antireflection coating) over a 20-year cell life is an important concern. Adhesion of the antireflection coating to the front surface of the photovoltaic cell and the ability of the encapsulant film to disperse the impact energy of incident dust and hail particles are also critical because moisture penetration must be

*Work performed under contract to the Jet Propulsion Laboratory by Endurex, A Division of Illinois Tool Works.

minimized and cracked solar cells may exhibit seriously degraded performance. Reduction of encapsulation cost is also important in producing economical terrestrial devices. The Low Cost Silicon Solar Array Project (LSA) has concentrated significant efforts in this area, and two thorough reviews of the subject are available [51, 52]. Although numerous module configurations and materials combinations exist, leading material candidates for the outer cover are glass, an acrylic (KORAD 201-R produced by XCEL), and a halocarbon (Tedlar UT-BG30 produced by Dupont). The addition of a thin, hard, abrasion-resistant coating to the polymer surface is being investigated.

3. Protective Coatings for Reflectors

Reflectors are unavoidably area-intensive components of solar collectors and represent 25% to 50% of the capital cost. It is imperative that corrosive impurities such as chloride and sulfide ions in the presence of moisture not jeopardize adequate reflector lifetime.

The conventional commercial silvered reflector has a reflective bilayer comprised of 1000 Å of silver and 250 Å of copper covered by a thick protective paint film [21]. This mirror, bonded to a support structure, is the basic consideration for glass heliostats (individual reflecting elements of a Fresnel central receiver solar thermal system). Preliminary evidence suggests that commercial reflectors may not meet the extremely rigorous requirements of reflector performance in current designs for high concentration solar applications because localized corrosion of the silver layer is observed after short-term field exposure. The source of the impurities responsible for the corrosion has not been identified and may be the protective paint, the adhesives, nearby structural elements, or pollutants in the environment. The presence of moisture is an important factor in the degradation, and moisture from frost, dew, and cleaning will be unavoidable even in a desert environment. The solution to this potentially serious problem may require improved quality control of impurities in mirror components or development of an alternate protective scheme, such as improved paints or intermediate impermeable layers.

Innovative second generation mirror structures may be required to solve simultaneously performance, cost, and durability problems, and a large solar concentrator market could

justify the investment in capital intensive equipment with high throughput. Vapor phase techniques such as ion plating will require evaluation, and a laminated mirror structure using thin glass (~1 mm) may provide environmental stability at an acceptable cost.

Advanced aluminum and substrate silver mirrors are also receiving attention with the potential to provide lower cost. The natural oxide on aluminum at an equilibrium thickness of less than 50Å is not sufficient protection for aluminum mirrors, and the oxide is typically augmented by anodization to a thickness of ~500Å. Silazane based varnishes have been explored for protection of substrate silver mirrors [57] and silicone resins are presently being evaluated for this application.*

4. Working Fluid Protective Coatings

Surfaces exposed to working fluids in solar heat engines and receivers must be protected to ensure adequate lifetimes. Titanium and aluminum heat exchangers are being proposed to work between ammonia and sea water in closed Rankine cycle ocean thermal energy conversion systems. Steam at 550°C and 14 MPa (2,000 psig), molten salts, and molten aluminum are working fluids in solar thermal systems. In a different realm, low-cost material approaches to water and space heating must evaluate the impact on system lifetime of the corrosion induced by water and antifreeze solutions. In each case it is important that the protective film not impede the flow of heat and thereby reduce system performance.

A molten aluminum heat transfer medium contained within a stainless steel cavity has been proposed for a point-focusing parabolic dish system. Such a system will require a protective layer at the aluminum/stainless steel interface to prevent the diffusion of aluminum into the stainless steel, with eventual failure of the containment. MoS₂ has been demonstrated to have potential benefit in this application [58]; however, considerable testing will be required to ensure material compatibility in a working environment.

*Work performed under contract to the Jet Propulsion Laboratory and the Solar Energy Research Institute by Dow Corning.

The use of chemical conversion treatments on metal surfaces in contact with fluids and other corrosive environments is a well established practice. The degree to which such techniques need be modified for solar applications will be determined by the impurities present and the heat flow characteristics desired. As an example, municipal waste pyrolysis creates reactive environments that can lead to very high rates of attack on conventionally protected steel alloys. New protective systems may be needed as the most cost-effective approach to guaranteeing adequate system lifetime (as opposed to prescreening the incoming waste material).

5. Anti-Biofouling Coatings

Marine surfaces to prevent or at least impede the buildup of organic deposits on ship hulls, moorings, buoys, and cables have been the subject of research for over 40 years. Copper/nickel alloys provide good biofouling resistance due to a concentration of copper ions near the surface in the water. Paints containing heavy metals that can be leached at a controlled rate are also effective in this application. However, increased concern for estuaries and fisheries has forced a closer look at the effects of heavy metals as selective poisons in marine applications, and new coatings may be required.

Closed Rankine cycle ocean thermal energy conversion technology uses vast areas ($\sim 5 \times 10^3 \text{ m}^2/\text{MW}_e$) of heat exchanger surface between the working fluid (ammonia) and ocean water to convert the 20°C temperature difference between the surface and deep ocean water to electricity. Heat transfer coefficients in excess of $5.7 \text{ kW m}^{-2} \text{ }^\circ\text{C}^{-1}$ ($1000 \text{ Btu ft}^{-2} \text{ }^\circ\text{F}^{-1} \text{ h}^{-1}$) are required for commercial viability. The growth on the heat exchanger walls of even thin organic layers ($< 25 \text{ } \mu\text{m}$) from the ocean water begins to reduce the heat transfer coefficient to unacceptable levels. With present shell-and-tube heat exchanger designs the biofouling problem is controlled by brushes or cleaning spheres that scour the surface. Advanced fluted designs may not be so amenable to cleaning, and coatings that protect the surface from rapid buildup are one potential solution to the problem. Since early plants are planned for island and gulf coast sites the solution will probably have to meet strict environmental regulations.

9.5 SPECIAL SURFACE ENERGIES

The energy associated with a free surface is the sum of two terms: the dispersive (Van der Waals) and polar components. Kaelble [59] discusses the physical and chemical origins of the surface energy; however, very little discussion appears in the literature regarding the role of surface energy in solar applications. Such applications include the determination of dust adhesion on reflector and glazing surfaces and the wetting of fluids on heat exchanger walls.

Surface energy may be a very important parameter determining the adhesion of dust. Dust is a significant concern for mirror and glazing performance [60,61], with up to a 0.50 decrease in solar reflectance or transmittance observed in one month. Detailed studies of the adhesion of microscopic dust particles ($0.5\mu\text{m} - 5\mu\text{m}$) have demonstrated that a primary adhesion mechanism is the leaching of inorganic salts from the dust particle by locally condensed moisture. When the water evaporates, an insoluble "glue" that may extend for several dust particle diameters remains. This effect is important for solar mirrors even in dry environments such as desert sites, which are particularly prone to dew and frost. It has been shown that a surface with energy of very low polar component, such as sputtered Teflon and other fluorinated compounds, dramatically reduce the effects of the "glue."^{*} The advantage of reduced dust particle adhesion, however, is partly negated by the tendency of films of such low surface energy to be poorly adherent, easily scratched, and thus difficult to clean. In addition, cleaning solutions do not "wet" the surface well, and thus removal of even poorly adherent dust particles may require specialized treatment. Further basic understanding of the dust/mirror or glazing interface will be required to evaluate the performance of improved coatings or cleaning solutions in removing adhered dust.

Although perhaps more amenable to an engineering solution, turbulent flow at the boundary between a heat exchanger wall and a working fluid may allow a dewetting of the surface for low surface energies and a decrease in heat transfer coefficient. A surface with a very high polar energy component may remain covered over a wider flow regime due to the reduced free energy in this condition. Research is warranted into the stability of the surface energy and the magnitude of the thermal effects to be achieved.

*R. Williams, RCA Corporation, David Sarnoff Research Center, private communication.

9.6 MEMBRANES

Selective membranes are thin films which achieve selective mass transport by a specially engineered microstructure. In a sense membranes are akin to protective films where the constraint of complete impermeability is relaxed to exclude certain molecules or ions. Selectively permeable membranes contain holes sufficiently small to block large molecules while readily transmitting smaller molecules such as water. The pores may average less than 10 nm in diameter. Ion selective membranes transport specific ions (or a set of very similar ions) such as H^+ , Cl^- or Na^+ , by ion exchange transport through the film structure.

Selective membranes have been proposed for use in a number of solar technologies. The most important are the REDOX battery for electrical energy storage in photovoltaic systems, the sodium heat engine (SHE) and sodium sulfur (NaS) battery for high-temperature electrical conversion and storage, the Reverse Electrodialysis (RED) cell for direct electrochemical production of electricity using salt brines, and Pressure Retarded Osmosis (PRO) systems for electrical power production from osmotic head hydroelectric generators which also operate at a salt brine/fresh water interface.

The REDOX battery [62] and the RED cell [63] use cation-selective and anion-selective membranes. In the REDOX battery electrical energy is stored as an electrochemical potential between chloride solutions containing Cr^{+2}/Cr^{+3} and Fe^{+3}/Fe^{+2} couples, as illustrated in Figure 9-6a. The geometry of a RED electrochemical cell is illustrated in Figure 9-6b. The RED cell and REDOX battery systems use ion-selective membranes designed for electrodialysis; these membranes are not well suited for potential solar applications. Ion selective membranes suffer from high cost, high internal (electrical) resistance, and loss of integrity (mostly pinholes). The cost (approximately $\$10/m^2$) and integrity are important because of the very large membrane areas required (typical RED cell power production is projected to be approximately $5 W/m^2$). Thinner, stronger membranes at lower cost per unit area are required. Such membranes could be expected to have higher ionic conductance (lower internal resistance) and greater integrity.

Both the Na/S battery [64] and the sodium heat engine [65] exploit the high conductivity for sodium ions and low electronic conductivity of β'' -alumina. Battery and heat engine processes are carried out at temperatures of $300^\circ C$ and $1000^\circ C$, respectively. Figure 9-7

illustrates the heat engine concept. β "-alumina membranes have been produced at tube wall thicknesses as low as 100 microns [67]. The long-term resistance of the ceramic to cracking is an unresolved important issue.

PRO systems use cast polymer membranes (Loeb-Sourirajan membranes) or composite membranes designed for use in reverse osmosis desalination [68]. Both Loeb-Sourirajan and composite membranes are physical membranes that have an active layer approximately 100 nm thick containing pores about 20 nm in diameter. This thin and fragile layer is supported by a much thicker (\sim 1000 nm) porous layer. Ion concentration in the porous support layer polarizes the PRO membrane and reduces the flux dramatically. The very high pressures (>10 MPa) involved in PRO cause a gradual compression of present polymer membranes and thus a decrease in their permeability (approximately 30% decrease in flux at 10 MPa [1500 psig] over a period of 36 days). A stronger semipermeable membrane with a much thinner support layer could improve the performance of PRO membranes by a factor of at least three. Attempts to use glass have not been successful due to the rapid dissolution of the glass and the consequent widening of the pores in a brine environment.

9.7 CONCLUSION

This chapter illustrates the breadth of thin-film applications across the spectrum of solar technologies. Photovoltaics and selective solar absorbers have attracted and continue to attract considerable attention, but it is important that other critical thin-film problems be addressed in a timely manner.

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Table 9-1 SUMMARY OF SOLAR ENERGY CONVERSION SYSTEMS AND PASSIVE THIN-FILM APPLICATIONS.

END USE	SYSTEM	UNIT SIZE	STATUS	THIN FILM APPLICATIONS
Thermal	Passive Building Design	-----	Commercial	Glazing AR coatings, absorbers, heat mirrors, solar shades
	Solar Pond	to 1 MW _{th}	Commercial	Enhanced transmission covers, evaporation suppression
	Flat Plate	~1 kW _{th} (modular)	Commercial	Selective absorber, glazing AR coatings, heat mirrors
	Augmented Flat Plate	to 5 kW _{th} (modular)	Early	Selective absorbers (to 200°C), glazing enhancement, low concentration reflectors, heat mirrors
	Compound Parabolic Concentrator (CPC)		Commercial	
	V-trough			
	Evacuated tube			
	Parabolic trough	to 25 kW _{th} (modular)	Early	Transparent receiver covers, medium concentration ratio reflectors, selective absorbers
	Cylindrical Trough		Commercial	
	Segmented Linear Array Tracking Systems (SLATS)			
	One and two axis tracking	to 25 kW _{th} (modular)	Early	UV protection of plastic refractors, selective absorbers
	Fresnel lens systems		Commercial	
	Spherical Reflector Tracking Absorber	to 1 MW _e	Developmental	} Selective absorbers (to 700°C) Non selective absorbers (>700°C) High concentration ratio reflectors
	Linear Central Receiver	to 50 MW _e	Research	
	Parabolic Dish	to 50 kW _e (modular)	Early	
Point Focus Central Receiver	10 to 400 MW _e	Commercial		
All Photothermal Convertors	-----	-----		Dust mitigating films working fluid/container interface protection

Table 9-1 SUMMARY OF SOLAR ENERGY CONVERSION SYSTEMS AND PASSIVE THIN-FILM APPLICATIONS. (CONTINUED)

<u>END USE</u>	<u>SYSTEM</u>	<u>UNIT SIZE</u>	<u>STATUS</u>	<u>THIN FILM APPLICATIONS</u>
Electrical/ Mechanical	Wind Energy Conversion Systems	1kW _e to 2MW _e (Modular)	Commercial to Developmental	Turbine blade protection
	Photovoltaics	100W _e (Modular)	Commercial	Encapsulants, AR coatings, transparent conducting electrodes
	Heat Engines (Rankine, Brayton Stirling, Sodium Ion)	10kW _e to 100MW _e	Commercial to Developmental	Heat exchanger augmentation, working fluid/container interaction (steam, molten metal, molten salt), membranes
	Ocean Thermal Energy Conversion (OTEC)	40MW _e to 400MW _e	Research	Heat exchanger augmentation/antibiofouling, large turbine blade protection
	Osmotic Head Hydroelectric (Salinity gradient)	to >100MW _e	Research	Selective physical membranes
	Tidal	to >100MW _e (Modular)	Commercial	} Sea Water Corrosion, biofouling protection
	Wave Energy	1 MW _e (Modular)	Developmental	
	Ocean Currents	to >100MW _e (Modular)	Conceptual	
	Photoelectrochemical	- - - - -	Research	Ion separating membranes
	Fuels & Chemicals	Solar Thermal Heat	Modular	Research
Processed Biomass - Extraction - Digestion - Fermentation and distillation - Gasification - Pyrolysis - Liquefaction - Combustion		Modular (to >50MW _e)		Corrosion protection for containers in reducing atmospheres with wide range of contaminants, membranes

Table 9-2 IDEAL OPTICAL PROPERTIES FOR MATERIALS IN SOLAR APPLICATIONS.

<u>OPTICAL FILM</u>	<u>IDEAL SOLAR(s) and INFRARED(t) PROPERTIES</u>					
	α_s	\hat{c}_s	ρ_s	ϵ_t	\hat{c}_t	ρ_t
Selective Absorber	1.0	0.0	0.0	0.0	0.0	1.0
Reflector	0.0	0.0	1.0	0.0	0.0	1.0
Heat Mirror	0.0	1.0	0.0	0.0	0.0	1.0
AR Coating	0.0	1.0	0.0	0.0	1.0	0.0
Transparent Electrode	0.0	1.0	0.0	0.0	0.0	1.0
Switchable Film						
- cool season (heating)	0.0	1.0	0.0	0.0	0.0	1.0
- hot season (cooling)	0.0	0.0	1.0	0.0	0.0	1.0
Solar Shade	0.0	0.3-0.7	0.7-0.3	0.0	0.0	1.0
Greenhouse Glazing	0.0	0.5	0.5	0.0	0.0	1.0
	(1.0 for $\lambda < 0.75\mu\text{m}$)					

Table 9-3 PROPERTIES OF SELECTED SOLAR ABSORBER SURFACES (from Call [6]).

Material	Technique	Supplier(s)/Developer(s)	Maturity*	α_s	$\epsilon_s(T)$	T Stability** (°C)	Issues	Ref.
Black Chrome	Electro-Deposited	Many	5 3 (low T) 4 (high T)	0.94-0.96	0.05-0.10(100) 0.20-0.25(300)	300		[6]
Pyromark	paint	Tempil	5	0.95	0.85(500)	<750		[6]
S-31 Nonselective	paint	Rockwell International	5	0.8-0.85	0.8-0.85	>550	adhesion, curing process	[6]
SOLARTEX	Electro-Deposited	Dornier (W. Germany)	5	0.93-0.96	0.14-0.18(310)	700		Product Literature
SOLAROX (Proprietary)	Electro-Deposited	Dornier (W. Germany)	5	0.92	0.20	200		Product Literature
Black Epoxy	Paint	Amicon Corp.	5	NA	NA	NA		Product Literature
436-3-8	Paint	Bostik (U.S.M. Corp.)	5	0.90	0.92	NA		Product Literature
Enersorb	Paint	Desoto	5	0.96	0.92	NA		Product Literature
7729	Paint	C. H. Hare	5	0.96	0.90-0.92	NA		Product Literature
R-412	Paint	Rusto-Ieum Co.	5	0.95	0.87	NA		Product Literature
5779	Paint	Rusto-Ieum Co.	5	0.95	0.90	NA		Product Literature
NexTel (nonselective)	Paint	3-M	5	0.97-0.98	>0.90	150		Product Bulletin 206
NOVAMET 150 (proprietary)	Paint	Ergenics	5	0.96	0.84	800 (1 hr)		Product Literature
MAXORB	(proprietary)	Ergenics	5	0.97(±.01)	0.10(±.03)	150 (20 wks) <400 (1 hr)		Product Literature
Tabor black (NiS/ZnS)	electro-deposited & overcoat	Miromit	5	0.91	0.14	--		Product Literature
Proprietary	Vacuum deposited	GE	5	--	--	--		[11]
Al ₂ O ₃ - Mo-Al ₂ O ₃ (AMA)	Sputtering Evaporation	Honeywell	4	0.85-0.95	0.24(100) 0.11-0.4	>550		[10]
Multilayer (proprietary)	proprietary	OCLI	4	0.95	0.05(100)	>300		[6]
NiS/ZnS	2 Layer Electro- plated	Many	3	0.96	0.07	<250	moisture sensitive	[10]
Proprietary inorganic	paint	Martin Marietta	3	0.9-0.95	0.9-0.95	>550	adhesion, curing	[6]
Selective paint	dip coated	Honeywell	3	0.92	0.13 (100)	>150		[12]
Si/Ag bilayer w/AR	CVD	U. of Arizona	3	0.80	0.07(500) 0.05(100)	500 (vacuum)		[12]
CuO/Ag/Rh ₂ O ₃	Fired organo- metallic paint	Engelhard	3	0.9	0.1	<400		[12]
CuO/Au	Fired organo- metallic paint	Engelhard	3	0.8	0.06	>600		[12]
Silicone & silicate	paint	EXXON	3	0.98	0.9	>700		[12]
Au/Al ₂ O ₃ (cermet)	sputtering	U. of Sydney	2	0.95	0.025(20)	<300		[13]
Cu/Al ₂ O ₃ (cermet)	sputtering	U. of Sydney	2	0.91	0.045(20)	<200		[13]
SnO ₂ :F/Black Enamel	Spray	University of Delft (The Netherlands)	2	0.92	0.15	200	Very rugged	[14]
Tungsten stainless steel dendrites	sputtering chemical con- version	IBM	2	0.95	--	>550	angle of incidence	[10]

Table 9-3 PROPERTIES OF SELECTED SOLAR ABSORBER SURFACES (from Call [6]). (CONTINUED)

Material	Technique	Supplier(S)/Developer(D)	Maturity ^a	α_c	$\epsilon_c(T)$	T Stability ^{**} (°C)	Issues	Ref.
Gold smokes	gas evaporation	Many	1	0.99	0.1(100)	100	fragile	[10]
Germanium	gas evaporation	Many	1	0.91	0.2(160) 0.5(250)			[10]
	paint(silicone binder)	Many	1	0.91	0.8(200)			
	etched	Penn State U.	1			<400		[15]
Au/MgO cermet	rf sputtering	MIT Lincoln Labs	1	0.93	0.1	<300		[16]
Cr/Cr ₂ O ₃ cermet	rf sputtering	MIT Lincoln Labs	1	0.92	0.08	<400		[16]
SiO ₂ -Cr-SiO ₂ multilayer	vacuum evaporation		1	0.88	0.1(100)	<450		[10]
Ni/Al ₂ O ₃ cermet	evaporation	Cornell U.	1	0.94	0.16(100) 0.35(500)	500		[12]
Pt/Al ₂ O ₃ cermet	vacuum evaporation	Cornell U.	1	0.94	<0.3(500)	600		[12]
n-Si	plasma discharge	ARL/BNL	1	>0.9 (calc.)	--	>500		[12]
Si/CaF ₂	sputtering	RCA	1	0.7	<0.1			[12]
Ge/CaF ₂ cermets								
Al ₂ O ₃ /ZrC _x N _y /Ag	reactive sputtering	Albany, Or Bureau of Mines	1	0.91	<0.05	175(air) 700(vacuum)		[12]
Aluminum	anodized (organic dye)		1	0.96	0.98(350)	<350		[10]
	anodized (KMnO ₄ dye)		1	0.80	0.35(<100)			
PbS	vacuum deposited		1	0.96	0.05(100) 0.2(240) 0.3(300)	300	UVB ₂ stability	[10]
	paint(silicone binder)		1	0.94	<0.8(200)		binder thickness	
Cu ₂ S	chemical conversion		1	0.79	0.2(200)	--		[10]
WC + Co	plasma spray		1	0.95	0.28(200) 0.4(600)	>600		[10]
Cr ₂ O ₃ + Co	plasma spray		1	0.9(800)	0.5(800)	>800		[10]
Co ₃ O ₄	electroplated		1	0.9	0.3(140)	>1000		[10]
304 stainless steel	chemical conversion		1	0.91				[10]
	thermal oxide (760°C)		1	0.82	0.15(100) 0.2(300)			[10]
Inconel and Incoloy	thermal oxide (1000°C)		1	0.85-0.90	--	1000		[12]
Steel (Fe ₃ O ₄)	chemical conversion		1	0.90	0.07(90) 0.35(200)	--		[10]

^a Maturity: development status of absorber surfaces, 5 commercial, 3 development, 1 research.

^{**} Temperature stability for most absorber surfaces is poorly defined and depends critically on exposure environment, conditions of test, and survival criteria.

Table 9-4 GENERIC TYPES OF SELECTIVE ABSORBER SURFACES. Material examples appear in brackets (from Call [6]).

SINGLE MATERIAL WITH IDEAL INTRINSIC SOLAR ABSORPTANCE/IR
REFLECTANCE {HfC, ReO₃}

BILAYER (IR REFLECTOR/SOLAR ABSORBER TANDEM) {Si/Ag}

MULTILAYER (INTERFERENCE) {Al₂O₃/Mo/Al₂O₃}

SURFACE TOPOGRAPHY (LIGHT TRAPPING MORPHOLOGY WITH PHYSICAL DIMENSION
APPROXIMATELY EQUAL TO THE WAVELENGTH OF THE SOLAR SPECTRUM){W DENDRITE}

SMALL PARTICLE EFFECTS (Mie SCATTERING, RESONANCE AND DIELECTRIC
ANOMALIES) {Pt/Al₂O₃ CERMET}

Table 9-5 ISSUES OF CONCERN FOR ABSORBER SURFACES (from Call [6]).

- OPERATING EFFICIENCY
 - HIGH α_s (T)
 - LOW ϵ_t (T)
 - ANGLE OF INCIDENCE EFFECTS
 - HIGH THERMAL CONDUCTIVITY

- OPERATING LIFE AND DEGRADATION MECHANISMS
 - TEMPERATURE STABILITY (MAXIMUM OPERATING TEMPERATURE, GRADIENT, TRANSIENTS {SHOCK}, AND CYCLING {FATIGUE})
 - EFFECTS OF SOLAR PHOTON FLUX (UV)
 - IMPACT AND ABRASION RESISTANCE (DUST AND HAIL)
 - EFFECT OF ADHERENT DUST ON OPTICAL PROPERTIES
 - CHEMICAL STABILITY (ATMOSPHERIC, WORKING FLUID AND SYSTEM CONTAMINATION, RAIN, HUMIDITY)
 - VACUUM STABILITY

- REPAIRABILITY

- COST/UNIT AREA

- MATERIALS RESOURCE LIMITATION OR VULNERABILITY

- GEOMETRICAL CONSTRAINTS IN APPLICATION OF COATING

- SHAPING OR FORMING AFTER COATING

- LIMITATIONS ON SUBSTRATE CANDIDATES

Table 9-6

IMPORTANCE OF REDUCING RECEIVER THERMAL EMITTANCE TO SOLAR THERMAL SYSTEMS. The parameter β is defined as the radiated heat flux of a blackbody at the system operating temperature, T_1 , divided by the incoming solar flux delivered by the collector to the receiver surface. The parameters are the solar flux (ϕ), the solar transmittance of the system optics (τ), the spillover factor (E), the solar reflectance of the concentrator (ρ), and the geometric concentration ratio (A_c/A_r). For $\beta > 1$ the operating temperature cannot be obtained unless the receiver thermal emittance (ϵ_r) is less than the receiver absorptance (α_s) divided by β . The two classes of receivers are external and cavity geometries. In external geometry the solar radiation is received on the external surface of a body (hemisphere, sphere, tube, etc.). In a cavity geometry the solar radiation is absorbed on the interior surface of the body, incident through an aperture in the body (from Call [6]).

System	T_1 (°C)	A_c/A_r	$\beta \equiv \frac{\sigma(T_1^4 - T_2^4)}{\phi\tau E\rho A_c/A_r}$
Passive	25-80	1	0-0.7 ($\rho = 1.0$)
Flat Plate	40-180	1	0.13-3.7 ($\rho = 1.0$)
Evacuated Tube (CPC, V troughs)	100-200	1.5-3	0.5 -3.3
Linear Fresnel and Cylindrical Trough	150-250	6-10	0.3 -1.3
Linear Parabolic & Segmented Linear Array Tracking System (SLATS)	200-350	20-70	0.07-0.77
Two Axis Tracking Fresnel	200-350	50-100	0.05-0.3
Spherical Reflector Tracking Absorber	300-500	100-200	0.06-0.4
Two Axis Tracking Parabolic Dish	500-1100	1000	0.04-3.5
Central Receivers			
Steam Cycle (Ext. Rec.) Barstow 10 MW _e	500	400	0.09
Steam Cycle (Ext. Rec.) 100 MW _e	500	1200	0.03
Adv. Molt. Salt & Metal (Ext. Rec.)	600	1800-2500	0.03-0.04
Adv. Open & Closed Adv. Brayton Cycles (cavity receiver)	1000-1400	2500-4000	0.06-0.3

Assumes $\tau = 0.83$, $E = 1.0$, $\rho = 0.85$, $\phi = 790 \text{ W/m}^2$, $T_2 = 27^\circ\text{C}$

Table 9-7 PROPERTIES OF SELECTED TRANSMITTING MATERIALS FOR ENCAPSULANTS AND GLAZINGS. (Data compiled from Hampton and Lind [22], Ratzel and Bannerot [23], Bouquet [24], Modern Plastics Encyclopedia [25], and Van Krevelen [26]).

Material	Product Example (Manufacturer)	Index of Refraction	n_s	n_r	Typical* Thickness (mm)	Density (g cm ⁻³)
Acrylics	Plexiglas (Rohm and Haas)	1.49	0.90	0.02	3.2	1.20
Halocarbons	FEP Teflon (Dupont)	1.34	0.96	0.26	0.05	2.1
	PVF Tedlar (Dupont)	1.46	0.92	0.21	0.10	1.4
Silicones	RTV's (GE)					
Polyesters	Mylar (Dupont)	1.64	0.87	0.18	0.13	1.4
Polycarbonates	Lexan (GE)	1.59	0.84	0.02	3.2	1.2
Sorosilicate Glass	7806 Fusion (Corning)	1.47	0.88	0.02	1.1	2.1-2.5
Sodalime Glass	Float (Ford)	1.51	0.85	0.02	3.2	2.5

*Value used to obtain optical properties.
 **The UV resistance is a subjective evaluation of material performance based on field weathering experience as well as UV laboratory testing. Additives in materials as well as surface protective UV absorbers may drastically alter material performance.

✓
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Table 9-7 PROPERTIES OF SELECTED TRANSMITTING MATERIALS FOR ENCAPSULANTS AND GLAZINGS. (Data compiled from Hampton and Lind [22], Ratzel and Bannerot [23], Bouquet [24], Modern Plastics Encyclopedia [25], and Van Krevelen [26]). (CONTINUED)

Specific Heat ($J^{\circ}C^{-1}g^{-1}$)	Coefficient of Thermal Expansion ($^{\circ}C^{-1} \times 10^{-5}$)	Service Temp ($^{\circ}C$)	UV Resistance **	Remarks
0.75	6.10	120	Excellent	Thermoplastic and thermoset; flammable; brittle with age or cold long term field tests show good weatherability of optical properties
1.17	10-16	20	Excellent	high cost.
1.26	5	100	Good-Excellent	nonwetttable surface can cause cleaning problems
	0.5-1 (laminates)	150-200	Good	High water permeability; soft surface; not very specular
1.05	1-4	100-150	Poor	May become brittle w/o UV protective coating
1.19	7	120-130	Fair-Good	Specular transmittance, high impact strength, brittle after outdoor aging
0.75	0.9	820 (softening)		
	0.3	700 (softening)	Excellent	

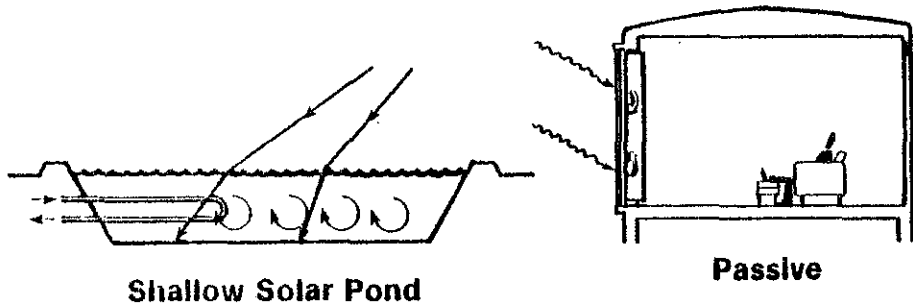
Table 9-8 INDEX OF REFRACTION (n) OF SELECTED THIN INORGANIC FILMS. Values will change depending on deposition conditions, approaching bulk values for the same material as the density is increased (Data from Hussman and Kerner [30] and DiStefano et al., [31]).

<u>Material</u>	<u>n (λ, μm)</u>
Ta ₂ O ₅	2.8 (0.4)
TiO ₂	2.4-2.9 (0.4)
CeO ₂	2.3 (0.4)
WO ₃	2.29 (0.55)
ZrO ₂	2.10 (0.4)
PbF ₂	1.75 (0.4)
Al ₂ O ₃	1.62 (0.4)
SiO _x	1.41-1.48 (0.4)

Table 9-9 Solar Transmittance (τ_s) and Infrared Reflectance (ρ_t) of Selected Heat Mirrors and Solar Shades (Data from Fan and Bachner [34], Koltun and Faiziev [35], Haacke [36], Greenberg [37], Rekant and Borisova [38], and Apfel [39]).

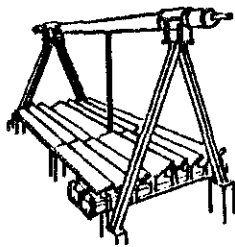
<u>Material</u>	<u>τ_s</u>	<u>ρ_t</u>
ZnS-Ag-ZnS	0.65	0.94
Cd ₂ SnO ₄	0.89-0.78	0.8-0.9
TiO ₂ -Ag-TiO ₂	0.54	0.98
Sn-doped In ₂ O ₃	0.90	0.92
In ₂ O ₃	0.84	0.86
Cu-Ag (electroless)	0.13	0.95 (9.7 μm)
Co ₃ O ₄	0.26-0.67	NA

Thermal

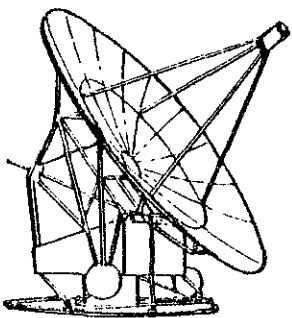


Shallow Solar Pond

Passive



Single Axis Tracking Concentrator

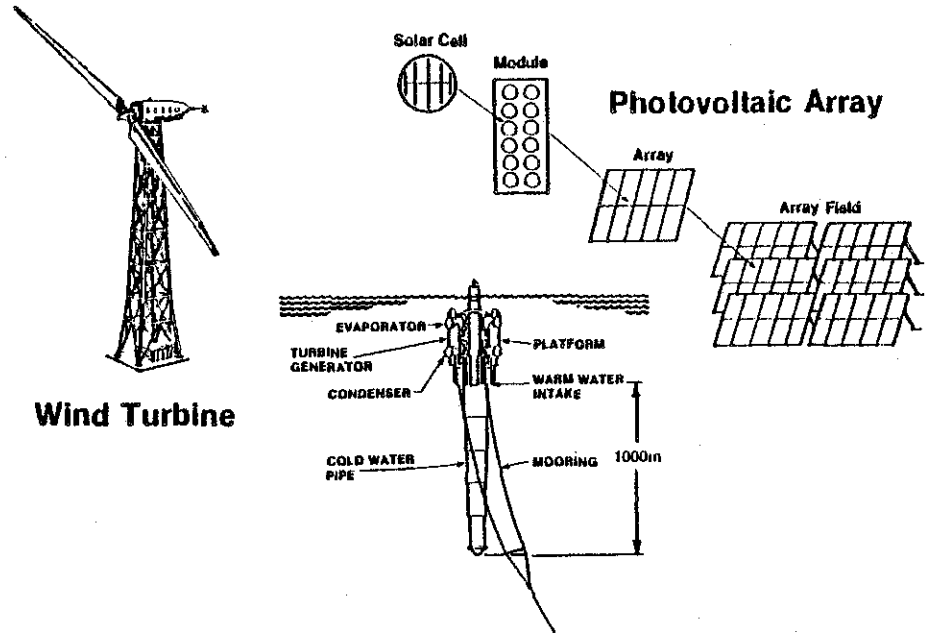


Parabolic Dish



External Central Receiver

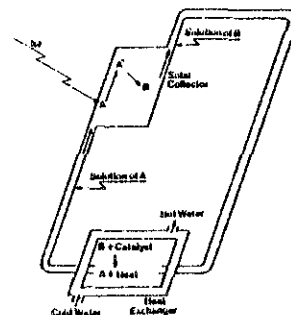
Electrical



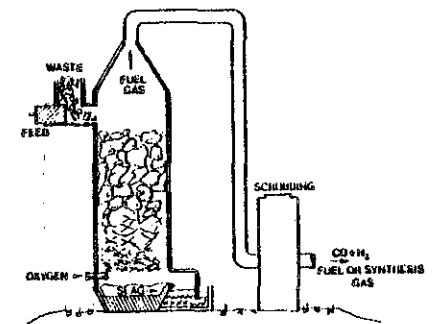
Wind Turbine

Ocean Thermal

Fuels/Chemicals



Photochemistry



Pyrolysis

Figure 9-1 SELECTED SOLAR ENERGY CONVERSION SYSTEMS

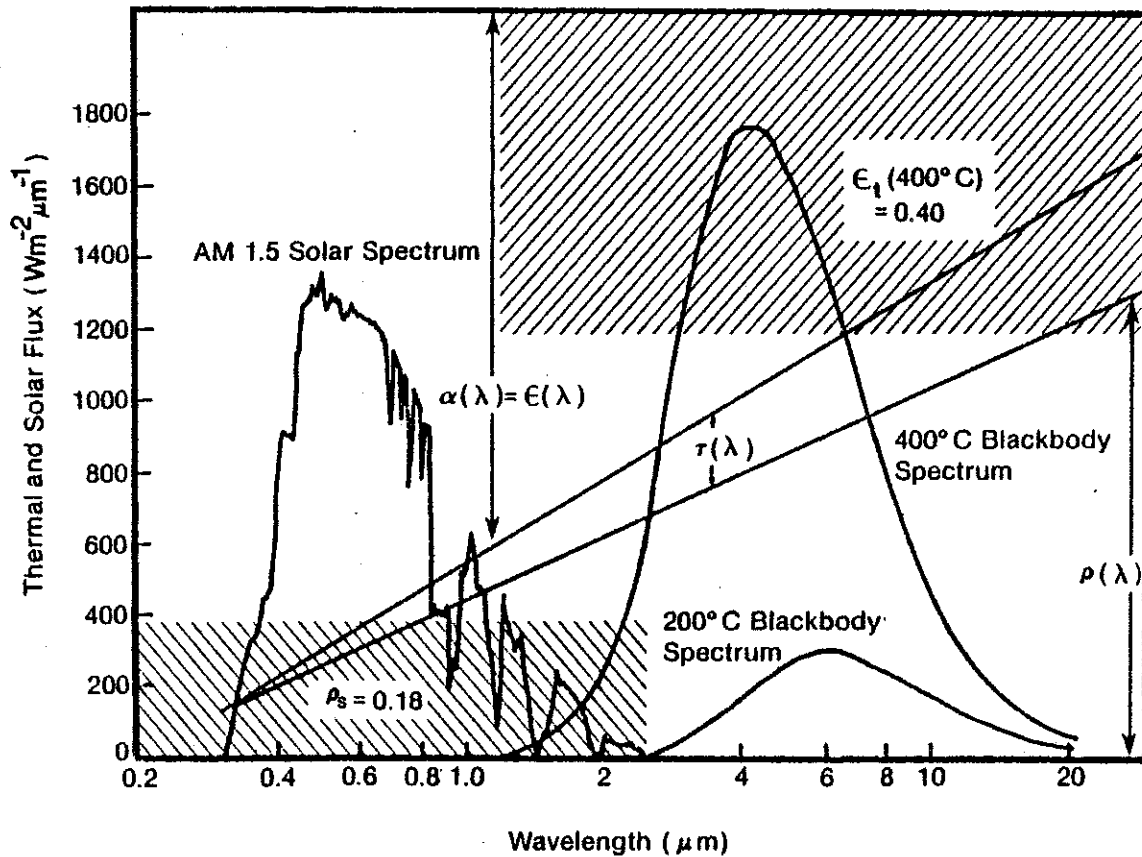


Figure 9-2 SOLAR AND INFRARED OPTICAL PROPERTIES. The solar (s) and infrared (t) optical properties of a material are determined by weighting the spectral hemispherical reflectance [$\rho(\lambda)$], transmittance [$\tau(\lambda)$], and absorptance [$\alpha(\lambda)$] (or emittance [ϵ]) over the solar and infrared radiation distribution functions (E_λ^s and $I_{bb\lambda}^t$, respectively). The smoothly varying optical properties of a hypothetical material are illustrated with $\alpha(\lambda) + \tau(\lambda) + \rho(\lambda) = 1$. In addition to ρ_s and ϵ_t values shown, solar and blackbody weighting yields $\alpha_s = 0.77$, $\tau_s = 0.05$, $\tau_t(400^\circ\text{C}) = 0.13$, and $\rho_t(400^\circ\text{C}) = 0.47$.

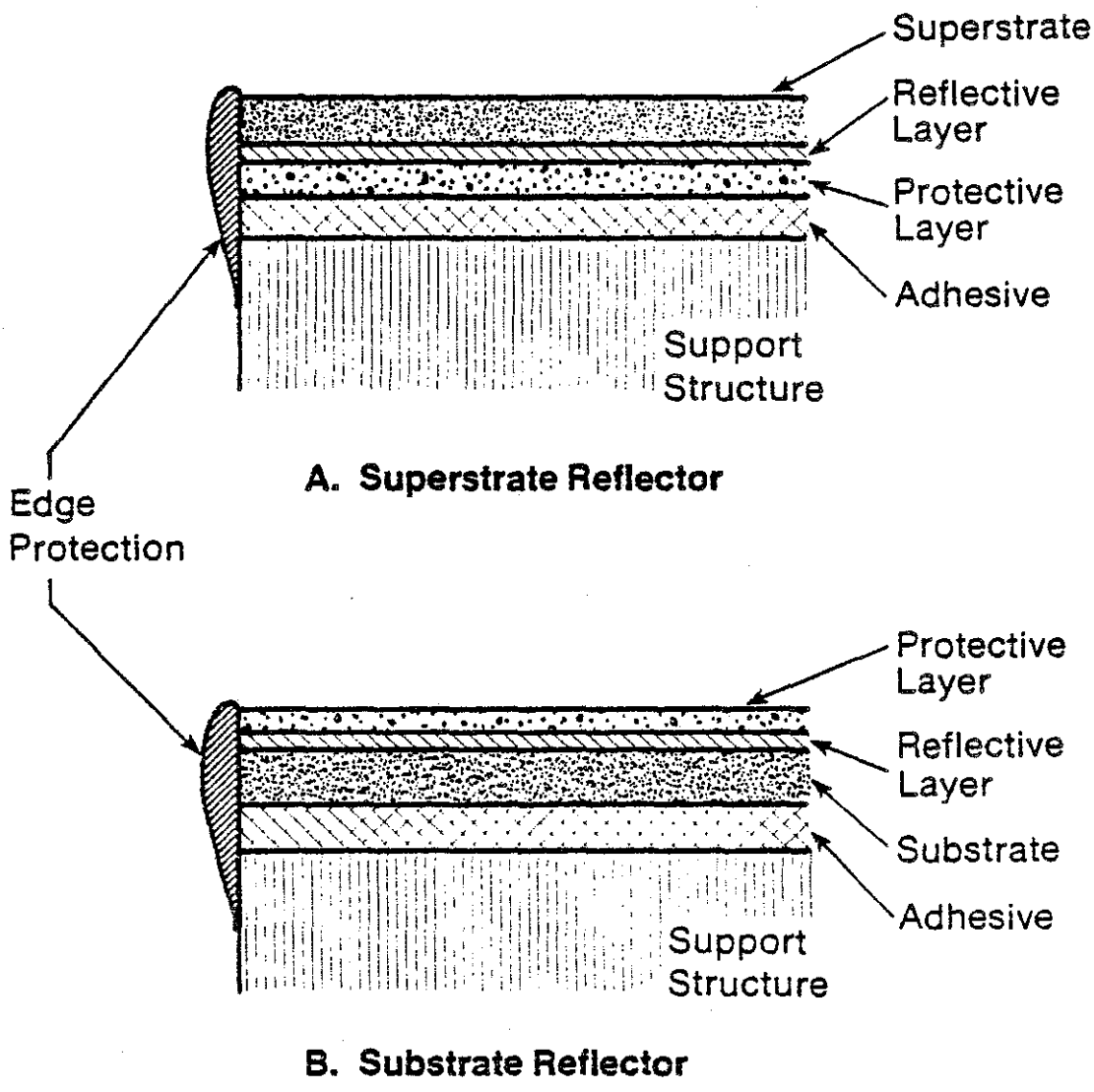


Figure 9-3 SCHEMATIC DIAGRAM OF SUPERSTRATE AND SUBSTRATE REFLECTORS (from Masterson [3]).

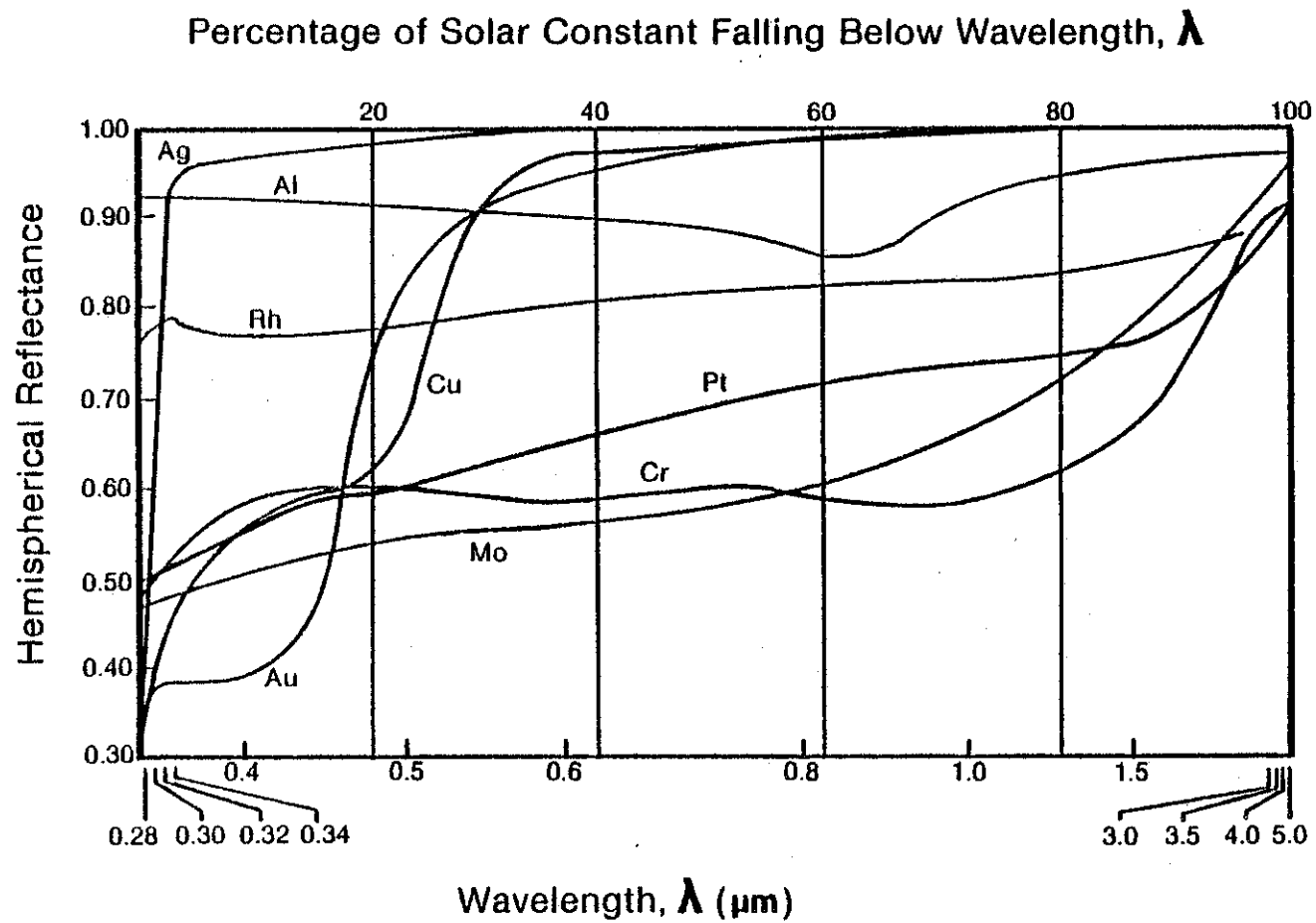


Figure 9-4 HEMISPHERICAL REFLECTANCE OF SELECTED CANDIDATE MIRROR METALS (adapted from Touloukian [2]).

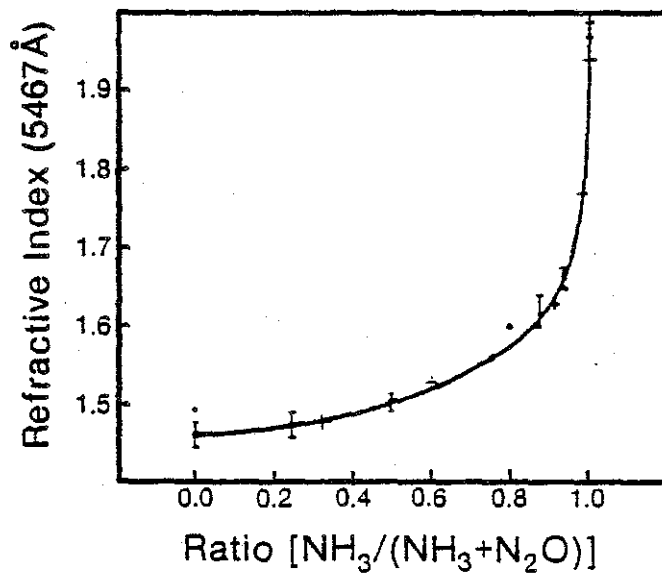
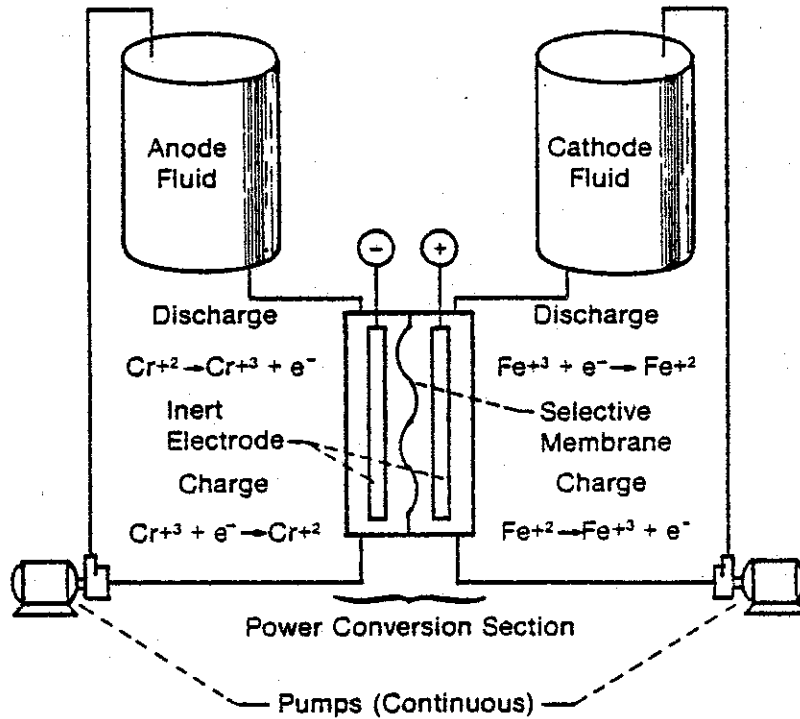


Figure 9-5 REFRACTIVE INDEX VARIATIONS OF SiO_xN_y. The O/N ratio in a SiO_xN_y film can be continuously varied by changing the ratio of inflowing gases (NH₃/N₂O) in a chemical vapor deposition process with He, N₂ and SiH₄ constituents at 700°C to 885°C. Thus, the index of refraction, n, can be varied between the expected values for SiO₂ and Si₃N₄ (from Seraphin [27]).

A.



B.

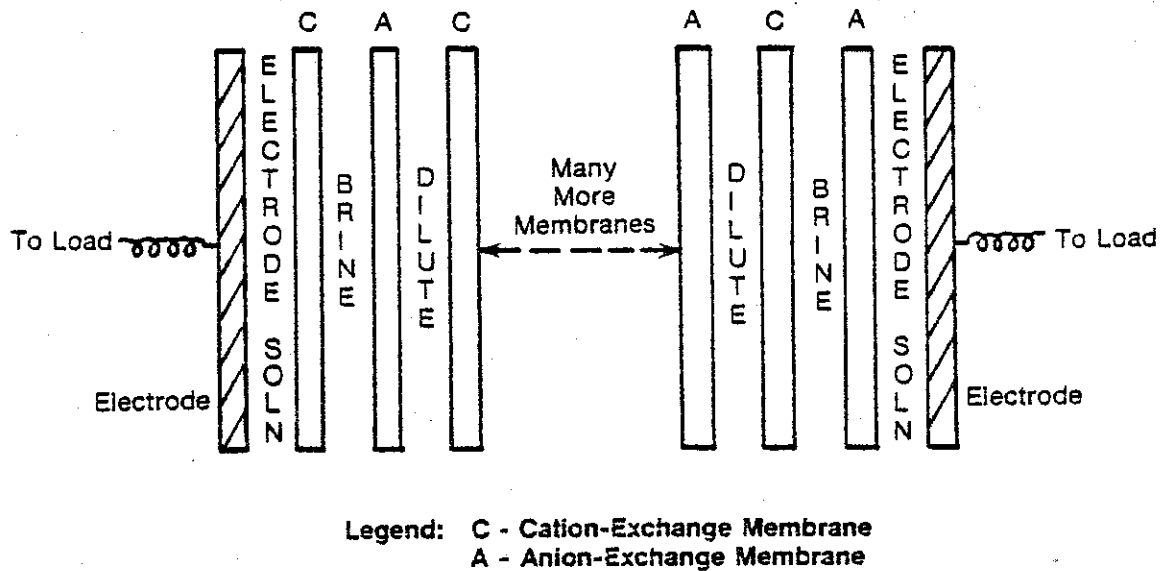


Figure 9-6 (A) A SCHEMATIC DIAGRAM OF A Fe/Cr TWO-TANK ELECTRICALLY RECHARGEABLE REDOX FLOW CELL (from Thaller [68]). (B) SCHEMATIC DIAGRAM OF A REVERSE ELECTRODIALYSIS STACK (RED CELL) (from Lacey [63]).

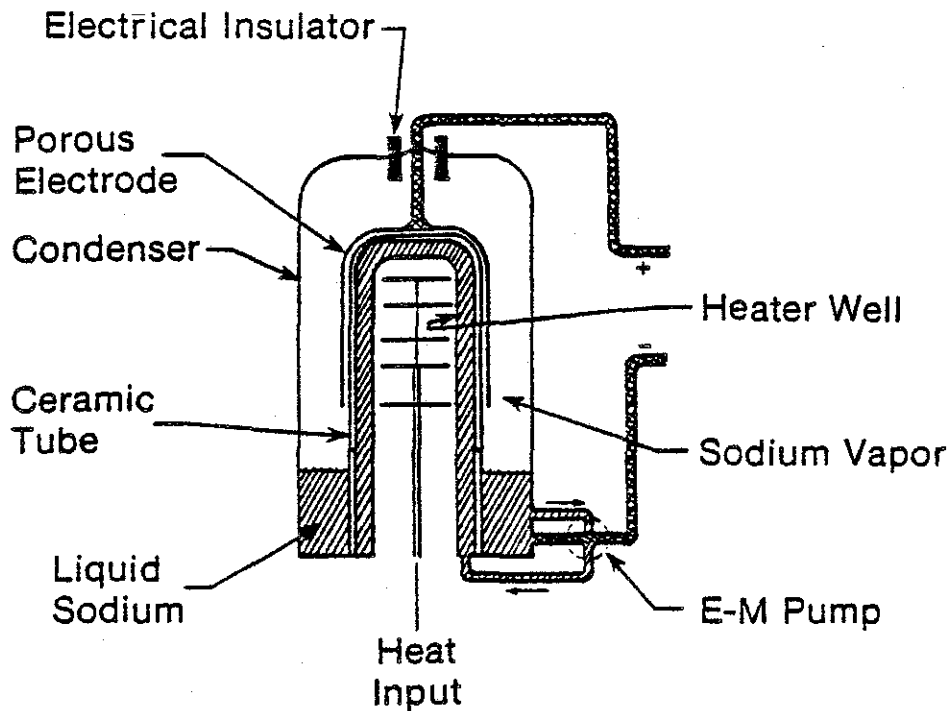


Figure 9-7

SCHEMATIC DESIGN OF SODIUM HEAT ENGINE. A closed container is partially filled with liquid sodium working fluid and is physically divided into high and low pressure regions by a pump and a tubular membrane of solid electrolyte which bears a porous metal electrode. The inner section of the device is maintained at a temperature T_2 by a heat source while the outer section is maintained at temperature T_1 ($T_2 > T_1$) by a heat sink. The temperature differential between the two regions gives rise to a sodium vapor pressure differential across the solid electrolyte membrane.

During operation sodium travels a closed cycle through the device. Starting in the high temperature (high pressure) region, the heat source raises the incoming liquid sodium to temperature T_2 . Since β'' -alumina has high conductivity for sodium ions and negligible electronic conductivity, a mole of electrons must exit the high temperature zone for each mole of sodium ions entering the β'' -alumina. Sodium ions then migrate through the β'' -alumina membrane in response to the pressure differential (gradient of Gibbs free energy). After passing through the external load, the electrons are recombined with sodium ions at the porous electrolyte interface. Neutral sodium then evaporates from the porous electrode at pressure P_1 and temperature T_2 passing through the vapor space to the condenser at temperature T_1 . The condensed liquid sodium is then returned to the high-temperature zone by an electromagnetic pump completing the cycle. (From Hunt et al., [65]).

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