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ScienceDirect

Journal of the European Ceramic Society 29 (2009) 1193–1201

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A survey of energy and environmental applications of glass[☆]

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Abstract

Glasses can be engineered with a wide range of properties and in a variety of forms that make them important materials for current and emerging energy and environmental technologies. The increasing worldwide demand for sustainable, environmentally friendly energy supplies, and for access to clean water, will provide glass scientists and manufacturers opportunities to develop new materials for new markets. Glass applications for solar, wind and nuclear power generation are reviewed, and recent research on new glassy materials for super-capacitors and electrochemical devices is discussed, with an emphasis on the needs that will drive glass research through the year 2020.

Keywords: Solar power; Photo-catalysis; Waste vitrification; Glass dielectrics; Glass seals; Glass microspheres

1. Introduction

Through history, glass has been associated with transformative technologies, involved both as a principal component and as an enabling material. For example, the large-scale manufacturing of glass transformed European architecture from the 14th century onward, and Macfarlane and Martin have gone so far as to advance the thesis that the mastery of glass technology, particularly in the realm of optical materials, by Western Europeans paved the way for the Age of Discovery in the 15th and 16th centuries, and was ultimately responsible for the subsequent world-wide expansion of Western economies and cultural influence.[1] More recently, glass and glass–ceramics were identified by the National Academy of Engineering (NAE, Washington, DC, USA) as central to many of the great engineering achievements of the twentieth century, from the transformative development of solid state lasers and optical glass fibers, through many enabling technologies based on biomaterials, glasses for imaging technologies, glass films in microelectronic devices, etc.[2]

In February 2008, the NAE identified the *Grand Challenges for Engineering* for the 21st century.[3] Those challenges are summarized in Table 1 and there are clear opportunities for glass scientists and manufacturers to continue their historical role of improving the human condition. In particular, the development of new and sustainable sources for energy and the development of technologies that enhance the environment offer great opportunities for the glass community as it considers its future through the year 2020.

Two key aspects of glass have made it the singular material to address the engineering concerns of mankind over the millennia. The properties of glass, especially the optical properties, can be tailored over wide ranges through careful compositional control, and glass can be readily manufactured into a wide variety of useful products, from large segments of a 100 m diameter primary telescope mirror[4] to nanometer-scaled fibers for photonic devices.[5] The flexibilities in compositional/property design and in manufacturing processes allow glasses to be considered for many engineering problems that are unsolvable by other materials.

In this paper, we review some of the opportunities for the development and use of glass to address future energy and environmental challenges. Some of these applications will require large-scale manufacturing of glasses that are closely related to current products, and other applications will require materials research to develop new compositions and forms that meet stringent engineering requirements. We will consider here those ‘bulk glass’ applications that require specific optical, thermal, and chemical properties. New, emerging energy and environmental applications that rely on the development of functional coatings for glass substrates are reviewed in a separate paper in these Proceedings.[6] The list of examples reviewed below is by no means complete, but is offered to

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[☆] Presented at the EFONGA Workshop on Advanced Materials and Innovative Melting Technologies in the Year 2020, Brig, Switzerland, March 26–29, 2008.

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doi:10.1016/j.jeurceramsoc.2008.08.011

Table 1
Grand challenges for engineering from the US National Academy of Engineering[3]

- Make solar energy economical
- Provide energy from nuclear fusion
- Provide access to clean water
- 'Reverse engineering' the brain
- Advance personalized learning
- Develop carbon sequestration methods
- Restore and improve urban infrastructure
- Advance health informatics
- Engineer the tools of scientific discovery
- Prevent nuclear terror
- Engineer better medicines
- Manage the nitrogen cycle
- Secure cyberspace
- Enhance virtual reality

illustrate the broad range of opportunities available to the glass community.

2. Energy-related applications

In 2005, the United States Department of Energy estimated that the world's demand for electricity will double by 2050, driven principally by growth in "transitional" and "emerging" economies.[7] The world is presently dependent on electricity generated by fossil-fuel burning sources, but limits on the future availability of petroleum-based fuels and concerns about the environmental impact of the release of carbon from fossil fuels have driven the development of a wide-range of alternative, environmentally sustainable energy technologies. Three technologies offer particular opportunities to glass manufacturers to develop the critical enabling infrastructure. Solar energy power plants will require acres of optically optimized, mechanically robust, and chemically inert glass panels, mirrors, and tubing; wind farms will rely on lightweight and strong glass-fiber reinforced composite materials for the rotors that drive the electricity-generating turbines; and chemically stable glasses (and new melting technologies) will be required to isolate and store the radioactive wastes generated by nuclear power plants. In addition, there are needs for new glass compositions to support many emerging energy-related technologies, including sealing glasses for solid oxide fuel cells, glass electrolytes for super-capacitors and other energy sources, and glass micro-spheres for storing and transporting hydrogen.

3. Glasses for solar energy

The optical transparency, chemical durability and manufacturability of glass make it a critical material for solar energy applications. Solar energy applications include thermal, photovoltaic, and photochemical energy conversion, and the scale of solar systems range from power plants to portable, individual power units. An example of the former is the Solar Electric Generating Systems (SEGS) in the Mojave Desert in Southern California, which have been in full commercial operation for twenty years. Parabolic trough technology is used at SEGS to generate steam at 400 °C to drive turbines to generate 350 MW of electricity[8] for over half a million residents, equivalent to 2 million barrels of oil a year.

Table 2
Critical engineering properties and research opportunities for solar energy applications

Desired properties	Research opportunities
Optical properties	• Compositional control for trace transition metal contents
• Maximum transparency over desired UV/vis/IR ranges	• Nano-composites, glasses and glass–ceramics with engineered transparencies
• Reduced refractive index (to minimize reflection losses)	• New materials for optically active substrates; e.g., luminescent concentrators
• Filter undesirable UV wavelengths	
• No solarization effects	
Mechanical properties	• Stronger, 'less brittle' glasses and glass–ceramics
• Minimize density and maximize strength	• Thermal/chemical treatments to improve strength
• Improve fracture toughness	
• Thermal expansion characteristics of system	
Chemical properties	• Improved resistance to 'acid rain' and to corrosive salt environments
• Maximized weathering resistance	
Manufacturing properties	• New manufacturing techniques for customized designs and compositions
• Viscosities, thermal stabilities that complement specific manufacturing process	

There are many designs for solar power plants, but the general function of the glass component is common: glass transmits desirable solar radiation to an active component (photovoltaic cell, thermal storage unit, etc.) while providing chemical and structural protection of that active component from the ambient conditions. The critical engineering properties for glasses used for solar power generation are summarized in Table 2, along with opportunities for research and development activities for the next decade. Besides optimizing the physical properties of the base glasses, the performance of these solar power units can be improved by improving the design of the glass unit. For example, glass covers for photovoltaic units can be patterned to help concentrate and guide the solar energy to the photovoltaic layer.[9] Reflective layers coated on the patterned, back surface of the cover further guide solar radiation to the photovoltaic cells by means of total internal reflection.

Mirrors are regularly included in solar concentrator designs. One study compared the durability and performance of several solar concentrator materials, including various silvered glass mirrors with a range of thicknesses, silvered polymer film, and polymer coated sheet aluminum.[10] Researchers investigated optical properties and on-site performance, as well as accelerated weathering testing, and the glass mirrors proved to have the best durability and lowest degradation of reflectance over time.

Solar chimney power plants are a newer concept for generating electricity.[11,12] Air currents are created based on heated air rising, and the movement of air is used to drive turbo-generators. Circular glass collector roofs are positioned a certain height off the ground with chimneys located over turbines. Solar radiation transmits through the collector roof and heats the air and ground beneath. As the air is heated, both from the sun and also from the heat being given from the ground, it flows up the chimney tower and powers the turbo-generator to produce electricity while being replaced with cooler air from the edges of the glass ceiling. The shape and dimensions of the solar chimney, optical and thermal properties of the glass, and many other parameters of the chimney design have been studied in attempts to achieve maximum power plant output. For example, a power plant with perimeter diameter of 7000 m, perimeter height of 3.3 m, chimney diameter of 160 m and chimney height of 1500 m can achieve annual power output of over 800 GWh.[11]

In addition to large-scale power plants, more local solar-power applications will drive glass development and manufacturing. For example, building-integrated photovoltaics (BIPV) have been developed to incorporate energy-efficient structures into building fronts and facades.[13,14] By encapsulating solar cells between glass sheets but alternating the solar cells with transparent resin, it is possible to produce electricity and reduce solar heat gain while still allowing daylight to enter the building.[13] In addition, many of these systems have combined photovoltaics with other solar energy conversion devices. Hybrid photovoltaic/thermal (PV/T) systems produce electricity while heating water or air. When used alone, photovoltaics only convert 5–15% of incoming solar radiation to useful energy.[15] By circulating water or air in thermal contact with the photovoltaic modules, the water and air will act to cool the module and keep it electrically efficient while being heated for other applications, leading to PV/T systems with efficiencies over 60%.[16]

Glasses have also been used in other forms for capturing solar energy. For example, because glass has a large thermal inertia, it can be used to store thermal energy and release it back slowly. This property, when combined with the ability to readily manufacture different glass shapes, has led to the development of new energy-saving technologies; e.g., glass beads for thermal energy storage in building walls.[17] Hollow glass beads are used as a porous medium and are packed into a channel between two walls, one heated by a constant heat flux and the other considered adiabatic. The porosity, heat capacity, density and thermal conductivity of the glass/air system are all parameters which affect the thermal response. Modeling and experimental results confirm the ability of the glass beads to absorb solar energy during times of high solar flux and then store and release that energy slowly when the solar flux is decreased.

Luminescent solar concentrators (LSC) use fluorescent optical materials to absorb sunlight, and the resulting fluorescence is guided to photovoltaic cells by means of total internal reflection[18] or mirrored surfaces.[19,20] Although various designs exist for LSC's, a common design consists of thin films on glass substrates. One recent study[18] added multiple organic dyes between which fluorescence resonance excitation transfer occurs with co-polymer film cast onto a glass substrate. In addition to organic dyes, quantum dots are also used as the fluorescent material, and these could be incorporated directly into the cover glass, simplifying the collector design. Quantum dots are crystalline, semiconductor nanostructures, such as CdSe/ZnS, which absorb light and emit photons of lower frequencies.[19,20] Their size can vary between 10 and 100's of nanometers and they are generally more stable than organic dyes.[21] Quantum dots can be dispersed throughout a transparent matrix, such as glass, which is surrounded by mirrors on all sides except for the top which is exposed to the solar radiation and one edge where a photovoltaic cell is located.[19,20] The photons emitted by the quantum dots are directed through the glass and reflected by mirrors, or by total internal reflection, to the photovoltaic cell, where their energy is converted to electricity. High transparency of the matrix material is essential and high efficiencies require almost complete absorption of the solar radiation within the collector thickness.[19] Quantum dots can also be incorporated into thin films which are deposited on glass substrates[21,22] with similar efficiencies and quantum dot solar collectors can easily be integrated into building facades.[20]

4. Glass for solar-driven water purification

It is estimated that 97.5% of the world's water is salt water, and only a fraction of the remaining 2.5% fresh water is available for use.[23] A human being requires approximately 20–50 l of clean water every day to meet basic needs.[24] However, 1.2 billion people lack safe drinking water and each year there are 250 million cases of water-borne disease resulting in approximately 10 million reported deaths[25] It is estimated that more than 1.7 million deaths could be avoided each year by providing access to safe drinking water, sanitation and hygiene.[24] In 2001, it was reported that the world population consumed 160 billion tons more water than is replenished and that 300 million people were living in areas with severe water shortages.[25]

There are a variety of technologies available to produce clean water, both on local levels and on industrial scales. Solar-driven technologies make use of glass as substrates for photocatalytic decontamination methods, and glass windows and tubes enable the operation of both photocatalytic and desalination systems for producing clean water.

4.1. Photocatalysis using glass substrates

Several recent studies of water purification methods have made use of glass and its properties. Titania photocatalysis are used for the degradation of organic and inorganic water pollutants, including aromatics, polymers, dyes, surfactants and pesticides, into non-toxic compounds, such as CO_2, H_2O and mineral acids.[26–29] When TiO_2 is illuminated by UV light with energy greater than its band gap, electron–hole pairs are created.[28] Highly reactive hydroxyl radicals are generated at the oxide surface and act as powerful oxidizing agents which degrade the adsorbed pollutant compounds.[27,28] Dispersing powdered TiO_2 into the contaminated solution to form a slurry is efficient in that it provides large surface areas for catalytic reactions. However, this suspension method requires time-consuming and expensive post-treatment separation of the titania particles from the liquid in order to recycle the catalyst and obtain clean water.[27–29] Immobilizing the catalyst on a solid

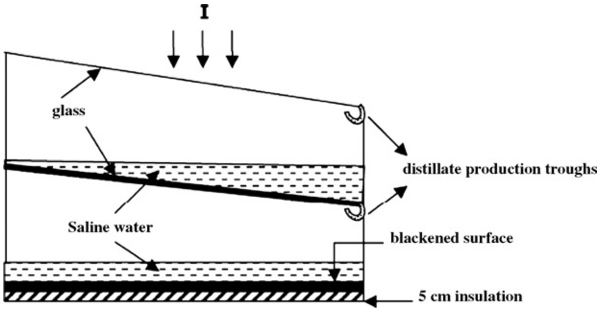

Fig. 1. Double basin solar still design, from reference 34.

support substrate eliminates the difficult post-treatment filtration. Glass is among the materials being investigated for such substrates, including soda-lime glass, borosilicates, and fused quartz.[26,27] In order to manufacture industrial-scale photocatalytic reactors, the electrophoretic coating method was used to deposit titania onto glass substrates which had been coated with indium-doped tin oxide to improve conductivity.[27] The glass substrates were found to have a significant advantage over other options due to their transparency to UV-A light and their chemical stability. This transparency allows for illumination from either side of the coating and increases the surface area available for photocatalysis. Further improvements in efficiency could be realized when glass sheets are replaced by glass beads and fiberglass mesh to increase the active surface areas of the photo-reactors.[28,30–32]

4.2. *Solar stills for desalination*

Glass has also been incorporated into solar stills used for water desalination.[33–35] Transparency to solar radiation is essential for solar collection systems and thus solar stills generally consist of glass covers. The glass covers also act as condensation surfaces and are usually angled to aid in distillate collection. The most basic types of solar stills are single and double basin. Double basin designs (Fig. 1) have the advantage of using the latent heat of condensation from the lower glass surface to provide heat to the upper water basin, and thus have been shown to have higher efficiencies and higher distilled water production than single basin designs.[34] Modeling studies have been performed to predict, among other things, the glass parameters necessary for optimal performance,[35,36] including glass thickness, thermal properties such as steady-state heat flux and temperature distribution, and the spectral dependence of radiation properties, such as specular reflectivity, refractive index, and absorption coefficient.

Another variation to the basic solar still is the separation of the evaporation and condensation sections of the still.[37] The evaporation section consists of evaporation tubes which are transparent to solar radiation that feed the water vapor to condenser tubes which are in a separate, shaded space. Although the evaporation tubes can be made of glass or transparent plastics, glass has been shown to have superior heat resistance and glass can also be used for the condenser tubes. Preliminary results for this system suggest enhanced fresh water productivity compared to solar stills with combined evaporation and condensation compartments.

A new solar still design makes use of glass in yet another form by packing a layer of glass spheres in the bottom of the basin to serve as a thermal storage system and increase water evaporation.[38] Results indicated that the system which incorporated glass spheres stored thermal energy during the sunlight hours and achieved higher water temperatures than the system without the spheres both during sunlight and after sunset. Consequently, using the packed sphere still resulted in higher fresh water productivity.

5. Glass fibers for wind-energy

Wind power provides a safe, renewable, environmentally friendly energy source without the drawbacks of pollution or consumption of natural resources. Wind energy is a rapidly growing market worldwide. The US installed >5.2 GW of wind power capacity in 2007, increasing the total national capacity by 45% to 16.8 GW.[39] This represents enough power to provide electricity for over 4 million average US households with nearly 11 million people and is equivalent to saving over three-quarter billion cubic feet of natural gas per day. In addition, the current US wind energy sector displaces more than 28 million tons of CO_2 each year. The total world-wide wind power capacity installed in 2007 was 20 GW, bringing the total global capacity to over 94.1 GW.[39]

Specialty glass fiber-reinforced composites (GFRC’s) have found wide-spread applications in the wind energy market.[40] E-glass compositions are the most common glass fibers for wind turbine GFRC’s. The fibers provide the necessary stiffness to compliant, easily processed polymers, such as thermosets and thermoplastics. The composites require high strength and durability to withstand both exposure to various environments and high tip speeds generated in wind energy systems, often reaching hundreds of kilometers per hour. Fatigue behavior of the composites is critical for long-term reliability.[41]

Finland’s Ahlstrom Corporation recently announced plans to double its production of E-glass fibers in the United States to meet the 20% annual growth demands for reinforcements in the wind energy sector.[42] Opportunities exist for developing new, ultra-high strength, high modulus glass compositions for these applications,[43] including environmentally friendly, boron-free glasses. However, the trend towards larger, lighter rotors increase the attractiveness of lower density carbon and polymeric fibers.[40,44]

6. Glasses for nuclear wastes

About 15% of the worldwide electrical power is generated by nuclear power plants,[7] and that fraction will likely increase to meet the growing demands for power without releasing the significant quantities of CO_2 associated with fossil-fuel-fired power plants. Radioactive wastes generated in nuclear power plants (and other nuclear-related industries) must be isolated and safely stored. Glass is the material of choice for high-level waste-forms because it can be designed with good chemical durability, sufficient mechanical properties, and superior radiation and thermal stability than other waste forms.[45] The vast compositional variability of glass makes it possible to incorporate the many different nuclear waste compositions, and glass forming and processing allow for easy, large scale production of waste-forms.

In the United States, the largest-scale vitrification facility for radioactive wastes is on the Department of Energy Savannah River Site (Aiken, SC), where over 4 million kilograms of radioactive waste glass have been produced since early 1996. Radioactive elements are separated from the waste stream, mixed with a borosilicate glass frit, and melted at ∼1200 °C, producing up to 230 pounds of glass waste-form an hour. The molten waste glass is cast into large stainless steel canisters which hold approximately 3700 pounds each. The canisters are decontaminated, welded shut, and stored at the vitrification facility before eventually being moved to a geological repository.[45]

Presently, borosilicate glass is used for high-level waste immobilization. The properties and processing of these glasses are well characterized and many studies have investigated the chemical and mechanical stability of various borosilicate glasses against radiation.[46–48] More recently, other glass compositions have been investigated for improved waste loading and performance, including iron phosphate-based compositions.[49–52] Iron phosphate glasses have excellent chemical durability, and some compositions have corrosion rates one thousand times lower than borosilicate waste glass.[53] Fig. 2 compares the results of a product consistency test (deionized water at 90 °C for seven days) of several iron phosphate glasses (IP) and a standard borosilicate glass (EA).[54] The cumulative mass loss from the iron phosphate glass IP40WG is about 35 times less than the EA glass. Iron phosphate glasses also have lower melting temperatures than borosilicate glasses, usually between 950 and 1150 °C.[55] In addition, many wastes for which borosilicate glasses are not well-suited are very soluble in phosphate glasses, such as nuclear wastes with high contents of phosphorus, iron oxide, fluorine, and heavy metal oxides such as Bi_2O_3, UO_2 and Cs_2O.[50,51] Iron phosphate glasses have been shown to have waste loading as high as 40% for certain simulated wastes,[55] which would greatly decrease the volume and cost of the final waste product.

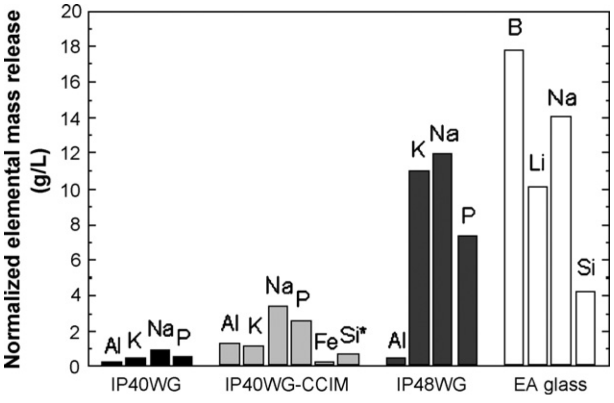

Fig. 2. Normalized elemental mass release (g/L) from three sodium waste-loaded iron phosphate glasses (IP) and a standard borosilicate glass (EA); from Kim et al.[54]

7. Glasses for other power sources

Glasses play important roles in smaller-scale (and individual) power supplies, including dielectrics for super-capacitors, electrolytes for electrochemical devices, and sealants for high temperature solid oxide fuel cells (SOFC's). In each case, the ability to engineer a material with a particular set of thermal, electrical, and chemical properties, and then fabricate that material into a desired geometry, make glass a crucial material to enable these emerging technologies.

Super-capacitors are energy storage systems with extremely high charge storage capacities which can provide high power densities and specific capacitances. Recent interest in super-capacitors has been fueled by applications in hybrid electric vehicles.[56] Materials with high dielectric constant and high breakdown strength are required, and these materials must be synthesized by a process that can produce thick, defect-free layers to withstand high voltage. Both high dielectric constant and high breakdown voltage are possible in glass–ceramic materials in which a ferroelectric phase is crystallized by the devitrification of a glass matrix.[57] Glass–ceramics also offer advantages of controlled crystallite sizes and fully dense (porosity free) materials to improve the dielectric breakdown strength. Glass–ceramics with ferroelectric phases like barium titanate and strontium–barium niobate have been investigated and the dielectric properties have been correlated with composition and microstructure.[58–60] Glass–ceramic materials with superior energy densities (6–8 J/cm^3) to commercial ceramic dielectrics have been reported,[61] making them competitive materials for high energy-density applications.

Glasses are also being investigated for applications as solid electrolytes in lithium batteries.[62–64] Lithium ion conducting glasses, such as fast ionic conducting (FIC) LiI-doped sulfide glasses, have great potential as solid electrolytes due to their high room temperature conductivities ($\sim 10^{-3}$ S/cm).[64,65] Lithium batteries using these LiI-doped glasses have been produced but are often unstable when in contact with the lithium anode.[64,66] Different oxysulfide glass compositions have been considered to optimize both stability and conductivity. The Li_2S–GeS_2–GeO_2 glass system has a large, melt-quench glass forming region.[65] The highest conductivity (4.36×10^{-4} S/cm) in this system was exhibited by bulk $0.7Li_2S$–$0.18GeS_2$–$0.12GeO_2$, which was also determined to be the highest conductivity of any GeS_2-based glass investigated.[64] Fig. 3,[67] summarizes the room temperature conductivities of several different Li-oxysulfide glasses, along with the respective ($T_c - T_g$) data, where T_c and T_g are crystallization and glass transition temperatures, respectively. While the addition of different oxides improves the chemical stability of the electroyte, the deleterious effects on room temperature conductivity and stability against crystallization (decreasing ($T_c - T_g$)) shown in Fig. 3 remain a principal challenge for materials scientists. Although lithium oxysulfide glasses remain a viable option for solid electrolytes in lithium batteries, current research has not yet produced a

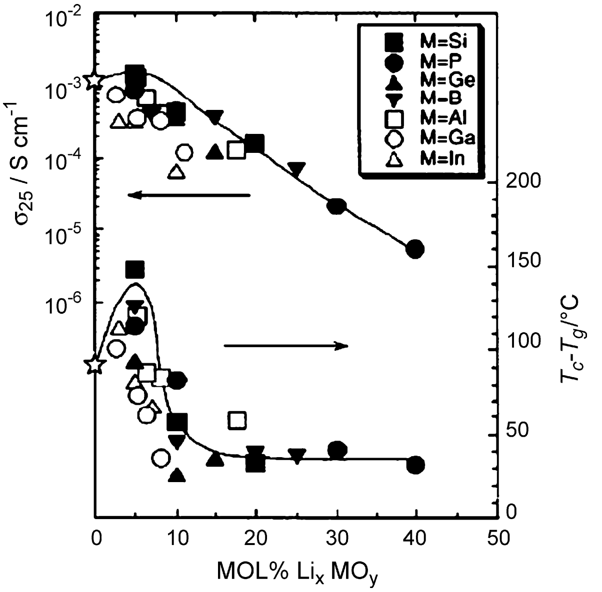

Fig. 3. Room temperature conductivities (top) and ($T_c - T_g$) (bottom) reported for a variety of Li-oxysulfide glasses; from Minami et al.[67]

stable glass with ionic conductivities higher than 10^{-4} S/cm. Li-conducting oxide glasses and glass–ceramics have superior chemical stabilities,[68] but do not yet have the greater conductivities of the Li-conducting chalcogenide glasses.

Proton-conducting glasses have been investigated as electrolytes for proton exchange membrane (PEM) fuel cells. Proton conducting phosphate glasses have been studied for some time; e.g., see references,[69,70] but they generally do not possess the requisite conductivities for efficient fuel cell applications.[71] More recent ‘super-protonic conducting’ compositions have greater conductivities and appear to be stable at temperatures above 100 °C, an advantage over other proton conducting materials that do not operate above 100 °C and that require humid conditions.[72] These glasses are variants of the proton-conducting salts that hold great promise for producing solid-state ‘anhydrous’ PEM cells that might compete with the lower temperature polymeric systems.[71]

Solid oxide fuel cells (SOFC’s) are electrochemical devices that derive electrical power from the diffusion of oxygen ions through ceramic electrolytes like Y-stabilized zirconia. Planar fuel cell designs are relatively simple and efficient, but require hermetic seals to separate the fuel and oxygen sources.[73] The sealing materials must possess thermal expansion characteristics that are compatible with other SOFC materials, must be thermo-chemically stable in both wet reducing (anode-side) and dry oxidizing (cathode-side) conditions, and must be processed in ways that are compatible with the SOFC design parameters. The US Department of Energy has indicated that the development of a robust, reliable sealing technology is one of the principal technological barriers to the wide-spread commercialization of SOFC’s.[74] Glasses and glass–ceramics are viable candidates for SOFC sealing applications and a significant amount of research has been done to develop glass–ceramic systems for this application. Many of these systems are based on alkaline earth silicate and aluminosilicate materials with expansion coefficients in the range 10–12 × 10^{-6} °C^{-1}. Recent publications have reviewed the properties and performance of many of these systems; e.g., see references,[75–77] and the references therein.

Because an SOFC operates at relatively high temperatures (600–900 °C), the key materials challenges that must be overcome are often related to the thermo-mechanical and thermo-chemical stabilities of the sealing glass. For example, the potential volatility of glass components in SOFC operational conditions must be considered. B_2O_3 will volatilize under wet, reducing conditions[78] and this limits some compositional designs. Changes in the phase distributions of glass–ceramic seals, or at the interfaces with other SOFC components, over hundreds of hours of operation can lead to thermal stresses on cooling that cause seals to fail.[79] One intriguing approach to overcome problems associated with ‘rigid seals’ is the use of non-crystallizing glass compositions that perform as a ‘viscous gasket’ under the operational conditions.[80]

8. Glass microspheres for hydrogen storage

The use of hydrogen as a combustion fuel or use in fuel cells is considered a safer and more environmentally friendly alternative to the use of gasoline and fossil fuels. However, the hydrogen economy has been hindered by difficulties associated with safe and economical storage and transportation. To be of practical use, hydrogen must be concentrated to high energy densities. Thus, it currently is either stored at low temperatures as a liquid, requiring high costs to maintain the low temperatures, or at high pressures as a gas, necessitating heavy storage cylinders and resulting in high transportation costs and risk of explosion. Metal hydrides and hydrogen-loaded carbon nanotubes offer ‘solid state’ options for storing hydrogen, although issues about reversibility and desorption/absorption kinetics for these different systems must be resolved.[81] Hollow glass microspheres (HGMS) have been shown recently to be another viable alternative as a hydrogen storage vessel.

There are several advantages to using HGMS as hydrogen storage and transportation containers.[82,83] The materials are cheap and most of the batch can consist of recycled cullet. The microspheres are non-explosive and each individual sphere contains too small a volume of hydrogen to be hazardous should the sphere break. HGMS are relatively strong due to their small size and are able to contain hydrogen at pressures up to 100 MPa.[83] No additional transportation vessel is needed, so they serve as lightweight containers for relatively high hydrogen mass density. In addition, HGMS are reusable and recyclable.

HGMS can be produced several different ways, perhaps the most common method of which is flame spray pyrolysis of glass frit.[84,85] In general, glass frit is dropped directly into an oxy-fuel flame such that the viscosity of the glass is low enough for the particles to take on a spherical form due to surface tension. The particles cool quickly upon leaving the flame and retain the spherical shape. Another common method involves dropping glass frit or liquid-based precursors into a vertical drop tower with carefully controlled temperature zones designed for very precise heat treatment and viscosity control of the

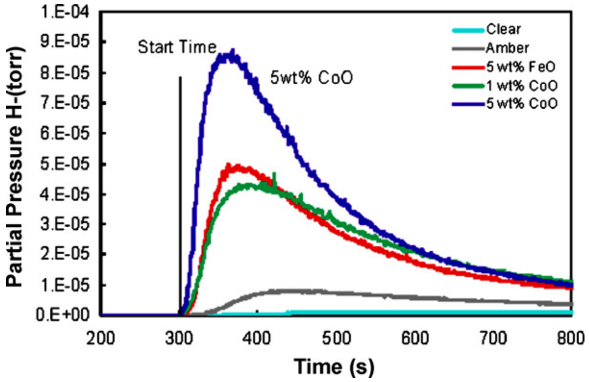

Fig. 4. Hydrogen release profiles from soda-lime glass microspheres doped with different transition metal oxides; from Hall and Shelby.[91]

spheres.[84,86] This method often results in extremely uniform sphere diameters and wall thicknesses. For either method, the hollow cavity formation within the microspheres is achieved via the addition of a blowing agent, such as sulfates, to the glass frit or liquid precursors. The blowing agents will decompose and expand upon heating, creating an internal cavity[87,88] which will be “frozen” in place with rapid cooling of the glass sphere.

For hydrogen loading, the HGMS are placed in a high pressure hydrogen environment and heated to a temperature sufficient for diffusion of hydrogen into the spheres. Once filled, the spheres are then cooled back to ambient temperature and are removed from the hydrogen atmosphere.[89] The gas contained within the hollow micro-sphere cavity will be retained due to the low diffusivity and permeability of hydrogen at room temperature. Recent studies by Shelby and co-workers have suggested the occurrence of photo-induced outgassing of hydrogen from HGMS that may provide the key for a viable hydrogen transportation technology.[89–91] When silicate glass microspheres doped with iron, cobalt or nickel are exposed to light in the near-IR region, the diffusion of hydrogen is greatly enhanced and occurs at a rate much faster than with heating alone. Fig. 4 shows the hydrogen release rates from soda-lime glass microspheres doped with different transition metal oxides after exposure to a 250 W infrared light source.[91] No photo-induced effect is observed for undoped glasses and the amount of gas released increases with increasing dopant concentration. The photo-induced hydrogen release is immediate and does not show evidence of a lag time as observed when heating. In addition, the release rate can be controlled by varying the light intensity.[89] Studies are also being conducted to evaluate the hydrogen storage efficiency of HGMS with different radii and wall thicknesses.[92] Although the mechanism of the photo-induced outgassing has not yet been determined, the existence of this phenomenon allows for the practical use of HGMS as hydrogen storage vessels for energy applications.

9. Summary and outlook

The increasing world-wide demand for sustainable sources of energy and clean water offer great opportunities to the glass scientific and technological communities. To realize the full potential of these opportunities, however, advances in our understanding of the properties of glass and our ability to manufacture complex shapes must be made.

The summary of the critical glass properties and research opportunities for solar energy applications in Table 2 offers one means for considering the challenges facing the glass research community. Consider these examples of glass properties that, if improved significantly, will lead to expand the use of glass in energy and environmental applications through the year 2020:

- *Glass strength*—The development of stronger or ‘less brittle’ glasses,[93] or manufacturing techniques that eliminate the creation of strength-limiting flaws will lead to new structural applications for glasses in large-scale solar-plants or water-purification facilities needing larger, lighter weight, less expensive solar windows and mirrors. Stronger glass fibers will compete with low-density carbon and polymeric fibers for reinforcing composites in wind-power generating turbine blades.
- *Glass weathering and corrosion*—Improved compositions and coatings will enhance the transmission characteristics of solar components, reduce fatigue effects in fiber-reinforced composites, and ensure the long-term stability of vitrified nuclear wastes.
- *Transport-related properties*—Glasses can play significant roles in active energy storage and generation technologies if limitations on ion or proton diffusion kinetics can be resolved for chemically stable, solid-state materials. Research on ion-transport mechanisms will guide the materials-development research.
- *Optical properties*—Passive and active optical systems, including solar windows with specific transmission characteristics and luminescent systems that enhance solar efficiencies, with enhanced optical properties will be required, and the ability to control optical properties in thinner glasses with new compositions will be needed. The ability to grow or pattern semi-conducting quantum dots in specific glass matrices will lead to new energy-related applications.

It seems apparent that glass will play an important role in these emerging technologies, but the competition with other materials approaches will determine how significant a role that will be.

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