PHYSICAL CHEMISTRY

Materials for Production and Storage of Renewable Energy

The need to revolutionize the way energy is produced, delivered, and utilized is widely recognized. Due to an increasing population and rising living standards around the globe, the need for a reliable, convenient, and adaptable energy supply is increasing. Industry, transportation, lighting, and communication all depend on a continued supply of lowpriced electricity and clean fuels. Our dependence on fossil fuels (coal, petroleum, and natural gas) is largely due to chemical energy being the most convenient and useful form of portable energy. Unfortunately, the extensive use of fossil fuels has had a dramatic negative impact on the environment and peoples' health.

A solution to the clean energy demand can be formulated from simple components, sunlight and water. Sunlight and water are virtually inexhaustible resources and can provide the required diversity of energy supplies. To store energy from sunlight, water can be split to generate hydrogen, a clean and portable energy carrier, which can then be used to supply electricity when needed.¹ High-performance, lightweight batteries can be used to power electric vehicles.² However, such technological advances require systems that have the capability of producing electricity, breaking H₂O bonds, and storing the energy either in batteries or as molecular hydrogen. Currently, such systems pose formidable challenges in terms of the required materials, efficiency, cost, and design of practical devices.

In general, energy conversion and storage systems require a rather complex combination of materials that can selectively promote a desired charge-transfer process with efficiencies close to the thermodynamic limit. Additional criteria for the development of new materials include economically viable components, processability of materials and devices, and long operation life. The four Perspectives in this issue present the scientific advances, recent developments, and challenges in a broad set of energy conversion and storage systems.

Lithium ion batteries, which were successfully incorporated in portable electronics, are now being considered as serious candidates for applications in transportation that entail strict requirements of high gravimetric energy density (rather than the volume energy density that is critical for hand-held applications). In his Perspective, Manthiram³ focuses on the recent advances of lithium ion batteries and the design of new materials. The archetypal LiCoO₂ cathode for portable batteries is too expensive for large storage systems. New materials such as the olivines LiCoPO₄ and LiNiPO₄ with lower electron energy (more positive in the electrochemical scale) have the advantage of delivering high voltages (> 4.5 V with respect to the carbon negative electrode). This higher voltage, however, produces increasing reactivity toward the electrolyte, a problem that must be minimized by postchemical surface modifications. Another route to improving energy storage capability is to use alternative materials such as sulfur or oxygen cathodes that provide enormous capacities. Both types of cathodes, however, present some adverse issues that require further investigation.

Miyasaka⁵ describes practical aspects of low-cost production of dye-sensitized solar cells (DSCs). One key aspect of DSC technology is the choice of substrate for the nanostructured TiO₂ matrix that anchors the photoactive dye molecules. On a glass substrate, the nanoparticles can be sintered and provide a robust and efficient framework for electron transport to the collecting surface. Alternately, a low-cost flexible substrate would allow a fast-speed roll-to-roll production, as in the photographic industry. Because TiO₂ cannot be sintered on a flexible substrate, this introduces a number of challenges concerning the binding of the nanoparticles, the shorter electron diffusion length, $^{\circ}$ and the development of thin metal oxide films. Critical for efficient DSCs on plastic substrates is the finding of high extinction absorbers. There is increasing interest in utilizing inorganic absorbers in the form of ultrathin layers or quantum dots.

Pure hydrogen may be the final destination in the evolution of fuel usage from coal to petroleum to natural gas, which has followed a trail of increasing hydrogen content.⁸ A major bottleneck for the hydrogen vehicle is the problem of hydrogen storage. Hydrogen has the highest energy per unit mass but occupies a large volume. Even in liquid form, the energy density of hydrogen is only 8.4 MJ/L, compared to 31.6 MJ/L for gasoline. In his Perspective, Jena⁹ first describes the fundamental modes in which the H₂ molecule can be attached to a storage material; physisorption provides weak sorption while maintaining molecular integrity; chemisorption dissociates the molecule into individual atoms, which bond strongly to the surface; and finally, in quasi-molecular bonding, the bond between H atoms is weakened but not destroyed. Jena further discusses the stringent requirements of the reversibility of the hydrogen uptake and release using each type of mechanism and emphasizes the use of nanosized configurations to improve the kinetics and thermodynamics of the candidate materials.

Extensive investigations have been launched to exploit the unique properties of graphene in energy applications. Kamat¹⁰ describes a clever use of graphene and graphene oxide films as scaffolds to capture and distribute electrons from a photoactive molecule to catalytic centers. The first step in this strategy is the interaction of graphene-based nano-structures with excited states of molecules and semiconductor nanoparticles. Such interaction may occur via energy transfer, as in the case of individual CdSe/ZnS crystals,¹¹ or by electron transfer from UV-irradiated ZnO nanoparticles.¹⁰ Electrons can be shuttled through the graphene sheet to reach selective catalytic centers. Graphene—semiconductor assemblies can also provide a basis to improve the performance of nano-structured solar cells acting as two-dimensional bridges to assist electron transport.¹² The light absorption in graphene,

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however, does not produce useful electron—hole pairs, and optimization of the graphene concentration in the photoactive assembly will be required.

These four Perspectives illustrate the stringent requirements that materials, nanoassemblies, and devices for clean energy delivery systems must meet in accord with thermodynamic, kinetic, and practical considerations. This field of research is gaining increasing momentum and opens enormous opportunities to exercise scientific imagination in the discovery of processes, materials and systems that ultimately must be robust and demonstrate high performance. Perhaps the most fascinating aspect is that, whatever its sophistication, the creation will be easily observed.

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