Inorganic Chemistry

Editorial

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Editorial for the ACS Select Virtual Issue on Inorganic Chemistry Driving the Energy Sciences

Our global energy market is proceeding through a historically significant transition.[1] There are several powerful forces that are driving these changes, including new methods of accessing vast pockets of natural gas,[2,3] geopolitical events, and a rise in meaningful political[4] and financial[5] responses to climate change. Another key factor is the dramatically lower price of electricity produced by photovoltaic (PV) cells and wind turbines, which is enabling significant penetration of renewable electricity into our energy mix.[1] While the deployment of these technologies is closely linked to the financial and energy markets, it is persistent investment into the fundamental research and development of these and complementary technologies that will maintain the trajectory toward a cleaner global energy portfolio.

New discoveries and a deeper understanding of the structural and physicochemical properties of inorganic materials have driven down the cost of solar and electrical energy conversion and storage technologies, and just as inorganic chemistry has been fundamental in so many of these past developments so will it be moving forward. This ACS Select Virtual Issue provides a sample of the inorganic chemistry that has emerged over the past years that is driving the energy sciences forward. While this Virtual Issue is not intended to be comprehensive—the breadth of the energy sciences is too great to cover in such a format—the intent is to give a flavor of the very different chemical approaches to developing and optimizing many disparate applications to meet the terawatt challenge.[6]

One of the most significant recent breakthroughs in the energy sciences was the 2009 report by Prof. Tsutomu Miyasaka and co-workers that alkylammonium lead halide crystals integrated with mesoporous titania in a dye-sensitized solar cell (DSSC) architecture could produce a power conversion efficiency (PCE) of 3.8%.[7] The subsequent improvements in PCE for these so-called perovskite solar cells have advanced at an unprecedented rate, with values approaching 20% at the time of this writing.[8,9] While these rapid advances have been made possible by the efforts of numerous research groups around the world,[9,10] one key finding was provided by Dr. Lioz Etgar and co-workers, who showed that a perovskite/TiO_2 heterojunction solar cell could function without the need for an additional hole-transport layer.[11] The confirmation that this solution-processed, air-stable perovskite material could act as both the light harvester and the hole-transport material was significant and has provided the framework for the many substantial improvements since.

The unexpectedly high PCE derived from perovskite solar cells provides hope for discovering the next breakthrough PV material made up of less toxic components. Iron sulfide is a compelling candidate, but the measured PCEs have been modest for such materials.[12,13] Prof. Amy L. Prieto and Dr. Sarah J. Fredrick have unearthed the possibility that the inclusion of germanium or silicon in this compound may affect the electronic structure to make a viable PV material.[14] By synthesizing pure colloidal platelike Fe_2GeS_4 nanoparticles with exacting conditions, and suppressing the reactivity to air through surface passivation, they were able to measure modest photocurrents under photochemical conditions. These results hint that stabilization of a related composition may reach PCEs commensurate with multicomponent chalcogenide semiconductors that can already reach a PCE of 20%.[15,16] High-performance chalcogenide semiconductors typically contain indium and gallium, however, thus prompting Prof. Yeng Ming Lam and co-workers to explore the soft synthesis of ternary Cu_2SnSe_3 nanocrystals as an alternative to the highly efficient but expensive, quaternary $CuIn_xGa_{1-x}Se_2$.[17] The semiconductor nanocrystals they synthesized using a hot coordination solvent method with hexadecylamine as the capping ligand were measured to have a band gap of 1.3 eV, thus emerging as a promising option for low-cost, solution-processable PV applications.

Coordination chemistry is fundamental to the requisite light absorption and charge separation within the DSSC, which remains one of the most prominent energy conversion technologies in the academic literature a quarter century after its discovery.[18] The community has gained a much clearer picture of the myriad of kinetic processes that occur in the DSSC,[19] particularly at the dye−semiconductor interface, where facilitating rapid charge injection into the nanoparticle and suppression of back electron transfer remains paramount.[20] One team of researchers looking to optimize these interfacial processes through the discovery of new linker moieties is led by Profs. Robert H. Crabtree, Victor S. Batista, Charles A. Schmuttenmaer, and Steven K. Konezny.[21,22] They developed a novel synthesis of hydroxamate anchors for the purpose of tethering pyridine- and imidazole-based linker ligands to the TiO_2 semiconductor surface in a DSSC. They show that the anchoring moiety has negligible effects on the ground- and excited-state energies of ruthenium polypyridyl dyes, yet the water-stable hydroxamate anchors gave the greatest overall efficiencies, presumably because of suppressed back electron transfer and more efficient electron injection.[22] The improved performance of hydroxamate-anchored dyes suggests that they could be promising candidates for artificial photosynthesis technologies because they provide stable attachment to the semiconductor surface in aqueous environments.

While the preceding work described materials designed to convert sunlight into electricity, many researchers are looking to store sunlight directly as a clean fuel through the conversion of water to hydrogen. The seminal work of Fujishima and Honda in 1972 demonstrated that this could be done by shining UV light on titania photoelectrodes immersed in water.[23] There has been a significant effort to extend the absorption of semiconducting materials into the visible region, with one very promising approach shown only recently by Prof. Bart M. Bartlett and co-workers at the University of Michigan.

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They prepared the anatase form of $Ti_{1-(5x/4)}Nb_xO_{2-y-\delta}N_y$ (x = 0.25 and y = 0.02) by a sol−gel/ammonia nitridation method that significantly enhanced the absorption of visible light.[24] Deposition of a cocatalyst (RuO_2) onto this light-absorbing material yielded a system that was found to be effective at photocatalytic water oxidation.

A common molecular approach for converting sunlight directly into fuels is to couple a chromophore with a catalyst in the presence of a terminal donor/acceptor while paying respect to the relative ground- and excited-state reduction potentials of each of the components. A departure from the usual line of inquiry was recently provided by Prof. Franco Scandola, Prof. Sebastiano Campagna, Marie-Pierre Santoni, and co-workers, who communicated the first molecular oxygen evolution reaction (OER) catalyst containing only vanadium atoms as metal centers, namely, the mixed-valence methoxopolyoxovanadium compound $[Bu_4N][(V^{IV}{}_5V^{V})O_7(OCH_3)_{12}]$.[25] They found that, in the presence of $[Ru(bpy)_3]^{2+}$ (bpy = 2,2′-bipyridine) and a sacrificial electron acceptor, the anionic cluster catalyzes photoinduced oxygen evolution in acetonitrile/aqueous phosphate buffer with a quantum yield of 0.20. This work should stimulate further studies in the search for synthetic OER catalysts made with earth-abundant metals that can be used in photocatalytic schemes.

A major driver of fundamental research in the solar energy field is the use of cheaper transition metals as catalysts, but the work of Prof. Dwight S. Seferos and co-workers from the University of Toronto raises the possibility of not even needing transition metals to photocatalytically produce hydrogen.[26] Transition-metal complexes designed to catalyze hydrogen formation from water (or HX) are hampered by the slow kinetics associated with M−X bond cleavage, and thus Seferos has been testing organotellurium compounds for these reactions because of their ability to reversibly bind dihalides. Building on their findings that tellurophene compounds can absorb visible light when substituted at the 2 and 5 positions with 5-(*N*,*N*′-dihexylisoindigo) groups, they find that this compound can also cleanly bind and exchange Br_2 and Cl_2 at the tellurium center. Furthermore, they show that this binding is reversible either by heat or visible light, which represents one of the few examples of thermoreductive elimination from an organotellurium compound and the first report of photoreductive elimination from such a material. This work offers promising alternative to transition-metal catalysts for hydrogen production.

Combined solar-power-harvesting and fuel-producing systems, such as dye-sensitized photoelectrosynthesis cells (DSPECs),[27] are attractive targets in the pursuit of renewable energy sources to replace fossil fuels. The incorporation of both functionalities in a single device, however, requires attention to many design principles. Prof. Thomas J. Meyer and his research group are interested in the development of effective photosensitizers for use in DSPECs. They have focused on the functionalization of ruthenium polypyridyl complexes with surface-anchoring groups, such as phosphonates, capable of surviving the harsh conditions necessary for water oxidation. While the synthesis of such ligands is challenging, Meyer and co-workers have recently reported a streamlined synthesis of two such ligands with no need for chromatographic purification.[28] 4,4′-Bis(diethylphosphonomethyl)-2,2′-bipyridine was produced in five steps in 68% overall yield, while 4,4′-bis(diethylphosphonate)-2,2′-bipyridine was obtained in 41% overall yield. The ability to access these compounds is significant given that phosphonate has such a high binding affinity for titania, particularly in aqueous media.

The storage of sunlight into fuels can also be accomplished by converting solar electricity to hydrogen in an electrolyzer, a mature technology for producing hydrogen at a cost that is closely linked to the efficiency of the OER electrocatalyst. A huge challenge in the very active area of OER catalyst design, however, is comparing the performances of catalysts that are measured under disparate conditions. This shortcoming provided the impetus for Dr. Charles C. L. McCrory, Suho Jung, Prof. Jonas C. Peters, and Prof. Thomas F. Jaramillo to document paper a protocol for testing OER catalysts under standardized conditions.[29] This manuscript outlined a basic set of electrochemical experiments to follow for reporting OER activities. The paper encourages the disclosure of catalyst activities at meaningful current densities over a sustained period while normalizing for the number of active sites. The authors advocate, with my full support, that the vast amount of data appearing in the literature be presented following their guidelines so that electrocatalysts prepared in different settings can be compared in a meaningful and straightforward fashion.

Another recent breakthrough was the recent discovery that a single transition metal was capable of mediating water oxidation, something that was long thought to be impossible. While Prof. Randolph P. Thummel claimed that a single ruthenium site could act as an OER catalyst in 2005,[30] it was not until his more comprehensive follow-up paper in 2008,[31] Prof. Stefan Bernhard's demonstration of the photocatalytic activity by iridium complexes,[32] and a keen mechanistic paper by Prof. Thomas J. Meyer elucidating the critical O−O bond formation step[33] that it became apparent that "one site is enough".[33] Other groups[34−36] have been at the leading edge of these developments, including the research program led by Prof. Licheng Sun that has continued to systematically improve on the efficiencies of their distinctive ruthenium platform.[37] Previous work by these authors has shown that the axial 2,2′-bipyridine-6,6′-dicarboxylic acid ligand (H2bda) is essential in yielding high OER activities,[38] while the paper featured in this issue explores the structures and activities of a series of complexes $[Ru(bda)L_2]$, where L = $(HNEt_3)$[3-SO_3-pyridine], 4-(EtOOC)-pyridine, 4-bromopyridine, pyridine, 4-methoxypyridine, 4-(Me_2N)-pyridine, and 4-[$Ph(CH_2)_3$]-pyridine, and nicely correlates the activity of these compounds to the donating ability of the axial ligands.[39]

Contemporary molecular OER catalyst studies are looking to better understand the behavior of complexes based on earth-abundant metals,[40−42] but determining whether catalysis is mediated by a molecular species or a decomposition product is a persistent issue.[43] The team led by Prof. Wonwoo Nam, Prof. Antoni Llobet, and Prof. Shunichi Fukuzumi recently addressed this concern for iron-based OER catalysts by testing two water-soluble mononuclear iron complexes, $Fe(BQEN)(OTf)_2$ and $Fe(BQCN)(OTf)_2$ [BQEN = *N*,*N*′-dimethyl-*N*,*N*′-bis(8-quinolyl)-ethane-1,2-diamine; BQCN = *N*,*N*′-dimethyl-*N*,*N*′-bis-(8-quinolyl)cyclohexanediamine; OTf = $CF_3SO_3^-$] under variable conditions.[44] A homogeneous species was observed in acidic conditions during cerium(IV)-driven oxidation, while a heterogeneous pathway involving iron oxide nanoparticles derived from the catalyst was elucidated in basic photooxidative conditions. These results highlight the complexity of the issue and the need to fully understand the sensitivity of the catalyst to each specific set of experimental conditions during these types of studies.

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A study at the interface of heterogeneous and homogeneous catalysis by Prof. G. Charles Dismukes and his team on a suite of cobalt clusters casts light on the requisite nuclearity for water oxidation chemistry.[45] By comparing the rates of water oxidation for six cobalt−oxygen clusters of different nuclearities in (near-)neutral solutions, the group found that only the cubic clusters were catalytically active. The results should help researchers to better tailor their search for ideal water oxidation catalysts, and adds to the significant body of literature seeking to better understand the underlying activity of amorphous cobalt oxide since the 2008 report by Prof. Daniel G. Nocera and Matt Kanan.[46]

Electrolysis of water in acidic conditions has historically been confined to precious metal OER electrocatalysis, thus providing the imperative to discover the conditions necessary to stabilize OER catalyst films using earth-abundant elements at low pH. The groups of Prof. Mark D. Symes and Prof. Leroy Cronin show that this goal can be achieved with first-row transition metals under a positive applied bias.[47] They disclose that self-assembled, metastable cobalt-based catalysts under a constant positive bias produced water-splitting activity for over 24 h and that gas evolution continues from the deposited films as they redissolve into the acidic medium, long after electrolysis has ceased. The system is able to cycle and produce gas at full Faradaic efficiency because both catalysts are inherently unstable with respect to dissolution at the relevant pH values probed. This illuminating work offers hope for using electrocatalysts based on abundant elements that have previously been discounted because of their instability in acid.

Another OER catalyst featured here is the natural system. Prof. Erwin Reisner and co-workers examined the photocurrent derived from electrostatically and covalently attaching photosystem II isolated from a thermophilic cyanobacterium to a mesoporous conducting glass substrate bearing a monolayer of functionalized phosphonic acids.[48] The acids functionalized with either carboxylate or amine moieties enabled the role of the electrode surface charge to be modulated, while coupling agents enabled the covalent attachment of photosystem II to the surface to engender greater stability. They found that a negatively charged surface preorganized photosystem II, benefiting interfacial charge transfer and, in turn, enabling visible-light-driven OER catalysis.

The reduction of protons to balance the water-splitting equation is also a very active area of research, with a common theme being the study of nickel thiolate catalysts that bear a structural and electronic resemblance to the active site of [Ni−Fe] hydrogenase.[49] The research group of Prof. Stefan Bernhard has diverged from these more common themes of investigation by interrogating the untested hexametallic nickel(II) phenylethylthiolate cluster, $Ni_6(SC_2H_4Ph)_{12}$, as a molecular catalyst for the hydrogen evolution reaction (HER).[50] The cluster was shown to be an excellent HER catalyst when reduction was driven at an electrode or by a photoreductant. A particularly intriguing aspect of this study was the sensitivity of the structure to the ligand, thus affording a direct handle for tuning the structure and reactivity moving forward.

The study of molecular species for water-splitting chemistry often requires nonaqueous systems, which can complicate conceptually simple tasks such as choosing a proton source. An interest in molecular HER catalysts led Prof. Jillian L. Dempsey and co-workers to study the electrochemical behavior of a series of 20 weak Brönsted acids in an acetonitrile solution.[51] Although it was found that the potential required to drive the HER correlated linearly with the pK_a for the majority of the acids, many of the acids were determined not to be suitable as proton sources for such electrochemical studies, including pyridinium and trifluoromethanesulfonic acid. The use of the pyridinium produced significant electrode fouling during electrochemical reduction, while the trifluoromethanesulfonic acid was found to chemically react with the acetonitrile solvent to produce a cocktail of degradation products. This paper conveniently indicates the Brönsted acids that offer suitable stability and reproducibility over a pK_a range from 1.57 to >30 and a hydrogen evolution potential of −0.65 to −2.60 V versus Fc/Fc^+. Her findings extends to many proton-coupled electron-transfer (PCET) reactions in nonaqueous systems and highlights the importance of carefully choosing and examining all components of an electrocatalytic system.

The theme of Brönsted acids continues with the creative approach taken by Xiaojiang Xie and Prof. Eric Bakker to generate a photocurrent.[52] Photocurrents are typically derived from semiconducting materials, but this study draws a photocurrent from a solution containing a photoisomerizable molecular species capable of PCET chemistry that generates a pH gradient across an electrochemical cell. Irradiation by UV light produces a ring-opening isomerization of spiropyran, while the ring-opened product spontaneously reverts to the cyclic spiropyran when the UV light source is removed. Because the two molecules have significantly different pK_a values, a constant pH gradient was successfully generated across the cell simply by tuning the cell thickness. The introduction of a single redox couple (quinone/hydroquinone) capable of undergoing PCET (i.e., the equilibrium voltage is pH-dependent) induced a photovoltage across the cell. This first iteration provides an intriguing new conceptual approach to solar energy harvesting.

Storing hydrogen at scale is another challenge that continues to improve through creative research.[53,54] One approach to increasing the energy density, safety, and practicality of storing hydrogen is by managing the facile reversible chemical transformations involving ammonia borane, which is 19.6% hydrogen by weight.[55] This Virtual Issue features the work of Prof. Theodor Agapie and co-workers at Caltech, who have been optimizing molybdenum catalysts to enable the rapid release of up to 2.5 equiv of hydrogen from ammonia borane.[56] The higher stability of this catalyst is derived from the hemilabile pendant arene that can accommodate variable coordination modes during redox changes at the metal. This work leaves open many new possibilities through further optimization of the coordination chemistry for this class of materials.

Advances in electrochemical energy-storage materials are also required for storing renewable energy from variable solar and wind power. While lithium-ion batteries are pervasive in society, the notion of using sodium-based batteries is an attractive alternative owing to the abundant supply of sodium. Exploring some of the fundamental aspects of these materials, Prof. Masashi Okubo and co-workers prepared a cyanide-bridged coordination polymer, $Eu[Fe(CN)_6]\cdot 4H_2O$, to study the phase separation that occurs during electrochemical sodium insertion/extraction in materials.[57] They found that the mechanism of phase separation arises from a long-range interaction as opposed to elastic strain between nearest neighbors, thus suppressing the activation energy required for phase boundary migration compared to conventional electrode materials such as $Li_{1-x}FePO_4$.

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Peroxide (O_2^{2-}) is a key discharge product of lithium−air batteries used for energy storage, yet very little is known about the electron-transfer kinetics due to the instability of O_2^{2-} under nonaqueous conditions and the inherent reactivity toward protons and metals. A collaborative effort led by Prof. Christopher C. Cummins and Prof. Daniel G. Nocera devised a scheme for encapsulating O_2^{2-} within an hexacarboxamide cryptand that enabled the electron-transfer chemistry to be defined.[58,59] The peroxide/cryptand complex was dissolved and reacted with a series of substituted quinones to be rapidly oxidized and tracked by stopped-flow methods.[59] Modeling by Marcus theory yields data consistent with both homogeneous and heterogeneous electron kinetics observed experimentally, offering a better understanding of the underlying chemistry that will lead to performance improvements in lithium−air batteries.

Methods for utilizing these clean fuels are, of course, necessary, and the hydrogen peroxide (H_2O_2) fuel cell is a promising candidate because selective electrodes for the reduction and oxidation of H_2O_2 are available and therefore membranes are not required to separate the cathode and anode. Prof. Shunichi Fukuzumi's group has led a significant effort toward optimizing the H_2O_2 fuel cell, with the study highlighted here demonstrating a version with a nickel mesh anode and carbon-based cathode containing three-dimensional pyrazine-bridged complexes of $Fe[M(CN)_4]$ (M = Pt^{2+} and Pd^{2+}).[60] The power density of a H_2O_2 fuel cell with this configuration reached 4.2 mW cm^{-2}, which is claimed to be the highest value reported for the one-compartment H_2O_2 fuel cells. Cells with cathodes containing pyrazine-bridged $M[Pt(CN)_4]$ (M = Co^{2+} and Mn^{2+}) exhibited power densities lower than 0.01 mW cm^{-2}, indicating an important role for iron ions in achieving the high power density. While stability issues need to be addressed for both the anode and cathode under highly acidic conditions, this work provides clues for making more efficient one-compartment H_2O_2 fuel cells.

The last few articles of this Virtual Issue feature some important work related to reducing CO_2 into alternative and more usable forms of carbon. The reduction of CO_2 to CO, for example, is a key step for the formation of hydrocarbon fuels; however, the most efficient electrocatalysts for this reaction are often based on precious metals, such as gold and silver. Prof. Joel Rosenthal and his team recently discovered that electrodeposited bismuth displays catalytic behavior that rivals the performance of gold and silver surfaces.[61] Indeed, the bismuth-based electrocatalyst selectively catalyzed the conversion of CO_2 to CO in the presence of imidazolium-based ionic liquid promoters at current densities as high as ∼30 mA/cm^2 with efficiencies of 80%. This exciting discovery provides a cheap pathway for the electrochemical conversion of CO_2 to fuel. Another more fundamental approach to demonstrating cheap CO_2 reduction electrocatalysis was reported by Prof. Clifford P. Kubiak and his co-workers. Borrowing design elements from established rhenium-based molecular catalysts, they isolated the manganese analogues $Mn(bpy\text{-}^tBu)(CO)_3Br$ and $[Mn(bpy\text{-}^tBu)(CO)_3(MeCN)](OTf)$ and tested their catalytic activities.[62] They found that the manganese derivatives required the addition of Brönsted acid to achieve catalytic turnover, but they did act as catalysts for the reduction of CO_2 to CO, operating at a lower overpotential in the presence of water, methanol, and 2,2,2-trifluoroethanol.

The team led by Prof. Christopher J. Chang reported the synthesis and characterization of a distinctive family of nickel complexes supported by N-heterocyclic carbene−amine ligands that exhibit high selectivity and activity for the electrocatalytic and photocatalytic conversion of CO_2 to CO.[63] Using the most active catalyst in their series in tandem with an iridium-based photosensitizer and electron donor, visible-light-driven photocatalysis of CO_2 to CO was measured with high stability (TON = 98000) and activity (TOF = 3.9 s^{-1}); concomitant hydrogen formation was not detected, thus offering guidance for bypassing undesirable byproducts during the reductive process. Balancing these advances in electrocatalysis, Prof. Osamu Ishitani and co-workers have explored alternative photosensitizers with bathochromically shifted absorption profiles in order to drive up the efficiency limits imposed by common photosensitizers. By utilizing the lower-energy metal-to-ligand charge-transfer band of an osmium(II)-based photosensitizer in combination with a rhenium(I)-based electrocatalyst, the team was able to photochemically reduce CO_2 to CO using red light.[64] While they also showed that the phosphine ligands on the rhenium center play an important role in the photocatalytic activity, the chief advance provided by this study was the successful reduction of CO_2 to CO using longer wavelengths, expanding the portion of the visible spectrum that can be utilized to drive this process.

These examples from the recent literature make it abundantly clear that inorganic chemistry is at the core of discoveries in the energy sciences that are amounting to better solar cells, (photo)electrocatalysts for fuel production and CO_2 utilization, batteries, and fuel cells. These results not only are providing clues to improve established technologies but also include unorthodox approaches for extracting and converting energy. I am excited to see how inorganic chemists are able to influence energy consumption for the years and decades to come.

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Notes

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