

Alternative Energy Carriers: Unique Interfaces for Electrochemical Hydrogenic Transformations

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The shift toward renewable energy generation sources, characterized by their non-carbon emitting but variable nature, has spurred significant innovation in energy storage technologies. Advancements in foundational understanding from investments in basic science and clever engineering solutions, coupled with increasing industrial adoption, have resulted in a notable reduction in the cost of storing electricity from variable energy generation sources. These developments have paved the way for the exploration of new and innovative forms of energy storage that deviate from traditional technologies. In this perspective, it is posited that the progress made in energy storage research over recent years has opened the door to the development of energy carriers for technologies that are yet to be realized. To illustrate this concept, examples of alternative energy carriers are provided within the context of unique electrochemical interfaces for electrochemical hydrogenic transformations. The unique properties of these interfaces and electrochemical systems can be leveraged in ways not yet imagined, creating new possibilities for energy storage. A perspective on the progress and challenges for each interface as well as a general outlook for the advancement of energy carrier systems are provided.


and wind—are the primary drivers of this increase coupled with an expected marginal decrease in the cost of electricity (Figure 1). While such a transition bodes well for mitigating the adverse effects of climate change, the variability of these power sources requires solutions for load leveling and frequency regulating electricity production and consumption as well as ensuring electrical reliability. The need to accommodate variable renewable energy has prompted a revolution in energy storage technology research and development. From improvements on mature technologies like pumped hydro,^[1] phase-change materials,^[2] solar-thermal,^[3] and thermochemical^[4] to rapid developments in more modern technologies like rechargeable batteries,^[5–7] fuel cell technology,^[8–11] and even resourcification^[12] of waste products like CO₂,^[13–15] the devotion of resources to find large-scale and general solutions for energy storage has enabled substantial progress to support an increasingly electrified economy.

1. Alternative Energy Carriers

The energy transition from carbon emission-based resources to variable renewable resources is changing the landscape of global energy infrastructure. Global electricity generation is expected to nearly double in the next three decades, but to reduce greenhouse gas emissions, renewable energy resources—specifically solar

Two technologies in particular—batteries and fuel cells—are compelling candidates to bear most of the burden for immediate and intermediate-term new energy storage needs in the stationary and mobility markets. Dedicated research efforts, industrial production, and broad market adoption of rechargeable battery technology, specifically lithium-ion battery (LIB) technology, has driven down the cost of LIBs by

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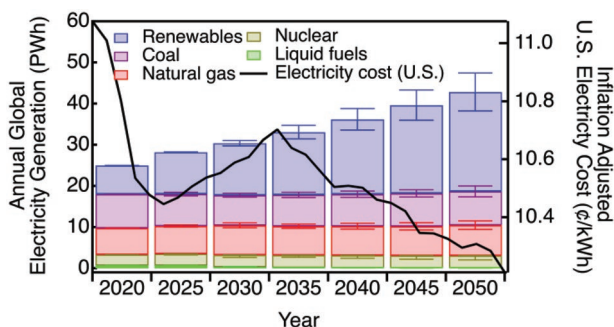


Figure 1. Global projections for the five primary sources of electricity generation (colored bars, left axis), and inflation-adjusted U.S. electricity cost projections (black line, right axis) from 2020 to 2050. The error bars indicate scenarios accounting for high (2.2% and 4.6%) and low (1.2% and 2.6%) economic growth of OECD and non-OECD countries. The renewables category contains contribution from photovoltaic, wind, hydropower, and geothermal generation sources. The data was sourced from the U.S. Energy Information Administration of the U.S. Department of Energy.

>90% from 2010 to 2020,^[16] and is expected to decrease by another 30% through the 2020s with an anticipated cost of <\$100/kWh by 2030.^[16–18] This projection places LIB technology near cost parity with internal combustion engine-based mobility energy systems.^[19] The flexible cell chemistry of LIBs also adds value in the stationary markets. For example, high-voltage lithium–nickel–manganese–cobalt–aluminum oxide-based cathodes are ideal for mobility solutions where gravimetric and volumetric energy density are determining factors, but for stationary storage, lower-voltage but highly stable and domestically sourced iron-based olivine or manganese-based spinel cathodes can be used. Other battery technologies—metal-ion batteries, lead-acid batteries, hydrogen batteries, and reversible redox flow batteries (RFBs)—also offer promising solutions for grid scale storage.^[20–25] Despite major advances in rechargeable battery technology being relatively recent, this energy storage class already occupies a technology readiness level (TRL)^[26] around 9 and is positioned well to meet the immediate mobility and stationary energy storage needs.

Fuel cell technology, particularly H₂-based fuel cells (HFC), also offers an attractive value proposition for both mobility and stationary storage. The gravimetric energy density of H₂ is nearly three times larger than gasoline, and if successful, the U.S. Dept. of Energy’s Hydrogen Shot initiative will achieve H₂ production at a cost of \$1/kg by 2030 which will help to reduce the HFC system cost from \$76/kW to a projected \$30/kW.^[27] While the current capital costs associated with HFC technology and infrastructure (storage, transport, and delivery) lead to a higher levelized cost of energy compared to LIB’s,^[28] the existence of pilot-scale plants and even a few commercially available products place HFCs at a TRL of 7 to 8. With advancements, the potential for cost reduction and broad market adoption of HFCs in the next decade is likely, which cements an intermediate-term energy storage solution.

Basic science research is still needed in both rechargeable battery and HFC technology. For batteries, investigation into

noncritical materials with high energy density and new electrode and cell architectures may help advance the technology. For HFCs, basic science research into catalyst materials, ion-conductive polymers, storage, transport, and other cost reducing/efficiency enhancing factors will greatly aid the development of the technology. However, it is likely that with the continued research investments made to each of these technologies, the combination of HFCs and batteries will meet most of the increasing variable renewable electricity storage needs for the mobility and stationary markets projected from Figure 1.

Greater renewables penetration will require the basic energy science community to create new concepts to store variable renewable electricity beyond conventional batteries and HFCs. Specifically, it will require transformational basic science research on alternative energy carriers that support industries at a TRL of 0–2. Research in this sphere can shape the future of primary and secondary economic sectors in emerging industries like advanced manufacturing, the resourcification of waste, alternative fuel and chemical synthesis, advanced biotechnology, designed material circularity, biomass conversion, and even space-based applications (Figure 2). The energy carriers used in these technologies will be marked by their unique properties that enable unprecedented integration into complex processes, not unlike the cascade of catabolic reactions during cellular respiration. Designing multifunctional carriers that selectively regulate energy flow allows for the possibility of, for example, a systems-level biomimetic industry. Here, multi-step, energy intensive procedures can be consolidated to a highly integrated single step with mitigated energy losses. Reimagining next-generation industry that mimics systems like metabolism can provide integration, efficiency, and resilience that seem unimaginable with current practices.

Naturally, a topic such as “alternative energy carriers” covers an exceptionally broad range of matter. Indeed, through the energy-mass equivalence ($E = mc^2$), all matter in the universe with mass contains tremendous potential energy. Such a broad topic requires considerable efforts to classify and communicate the many possibilities, but for the sake of demonstration (and brevity), we choose to narrow the scope of this perspective to focus on unique interfaces for electrochemical hydrogenic transformations (EHT). Because of the maturity of water electrolysis and HFCs, we focus on hydrogen carrier systems other than H₂. We offer our perspective as well as examples of interesting electrochemical interfaces for EHTs within the context of alternative energy carriers. The intent of this position paper is to encourage researchers to consider how their work fits into future energy carrier technologies, not to provide a comprehensive review of novel electrochemical interfaces.

2. Unique Interfaces for Electrochemical Hydrogenic Transformations

Dating back to 1789,^[29] proton reduction marks one of the earliest accounts of heterogeneous electrochemical charge-transfer and has since been a lynchpin of electrochemistry. From aqueous to organic, gaseous to solid-state, the reduction of protons or oxidation of hydrogen atoms is

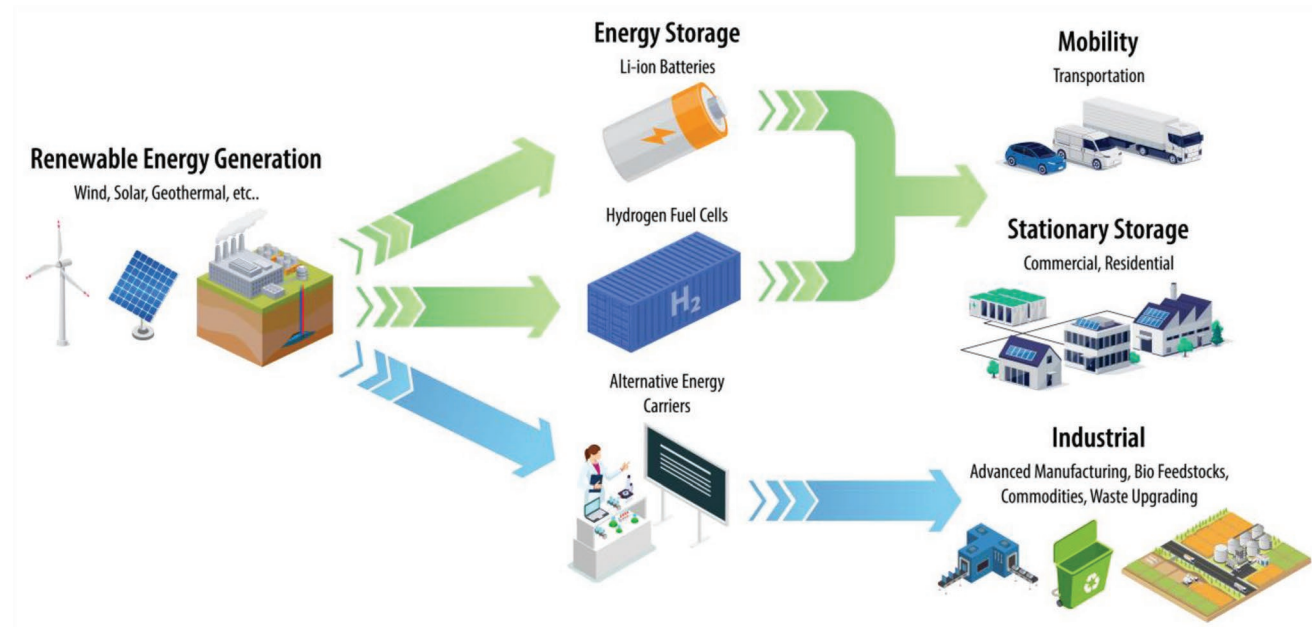


Figure 2. Schematic illustration of energy carriers for renewable electricity generation and the sectors they serve.

ubiquitous and extends to nearly every branch of electrochemistry. In the recent past, electrosynthesis of refined chemicals and fuels, conversion of biomass, and bioelectrocatalysis involving EHTs has emerged as a promising alternative to traditional thermochemical methods.^[30,31] EHTs offer new horizons that combine the foundational knowledge of hydrogen carrier electrochemistry with organic/inorganic/materials synthesis, non-equilibrium energetics, novel mass transport schemes and electrode design, and industrial process integration.^[30–34] The interest in EHTs has accelerated over the last several decades, and when combined with the push toward electrification, will continue to do so.

For electrochemically driven reactions, the interface for charge transfer dictates critical parameters like selectivity, stability, kinetics, Faradaic efficiency, and overpotential. The description of structure, dynamics, and energetics of traditional electrode/electrolyte junctions (rare-earth, planar electrodes in aqueous media) is becoming increasingly sophisticated,^[35] but electrochemical interfaces are becoming increasingly complex and challenge traditional assumptions. The solid/electrolyte interface is typically defined within the first one or two ion/solvent/atomic layers within the electrolyte; however, more complicated interfaces that don't follow the usual description are showing promise for otherwise inaccessible electrochemistry. For example, bioelectrocatalysis is the marriage of enzymatic biocatalysis and electrochemistry and has exceptional potential for selectively driving many difficult chemistries at high rates. However, the active site of an enzyme is surrounded by electrically insulating proteins—which play a critical role in the catalytic microenvironments—and make direct charge transfer from the electrode to the enzyme active site difficult if not impossible without damaging the surrounding protein. Recently, however, works to redesign the electrode interface with bound-functionalities or nanomaterials to couple more

closely to the active site are showing promise to overcome this limitation.^[36,37] This, and many other examples of novel materials, chemical reaction cascades, interfacial coatings, non-innocent electrolytes, catalysts, and more generally our understanding of the fundamental energetics in electrochemical charge transfer require a reexamination of how we think about the electrode/electrolyte junction.

Here, we broaden our consideration of the electrochemical interface to include high-complexity junctions that are not well described by classic models. We profile four non-traditional interfaces that provide advantages over classical electrode interfaces like improving reaction selectivity for the CO₂ and N₂ reduction reactions, accessing new scaling relationships that reduce electrochemical overpotentials, and combine useful properties like suspensions with heterogeneous catalysis and capacitive energy storage. We discuss the properties that make them interesting for EHTs, and their scientific challenges and opportunities.

2.1. Unexpected Deviations from the Classical Electric Double Layer

Charged surfaces exert Coulombic forces on ions, solvent, and other species in electrolytes, causing regions close to charged surfaces to become enriched in counter ions and depleted in co-ions to screen, or compensate, surface potentials. Coulombic forces also influence distributions of solvent or other dissolved species, with a general trend toward enhancing the concentration of highly polar species, like water, close to polarized surfaces, relative to the bulk phase. For example, charged surfaces can locally increase water concentrations to much higher levels than are present in the bulk of organic electrolytes,^[38] with large implications for proton-mediated reactions.

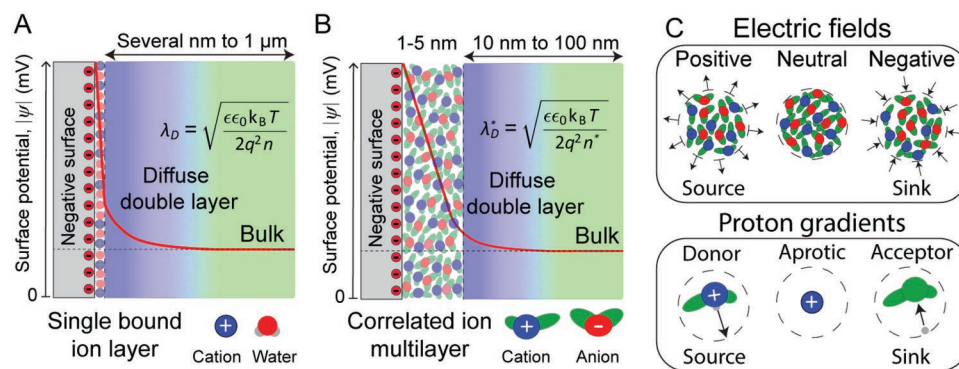


Figure 3. A) Classical electric double layers consist of a bound ion layer in series with a diffuse layer. Within this framework, most of the potential is screened within less than 1 nm away from charged surfaces, implying that local potential gradients are extremely high. The thickness of the diffuse layer is determined by the Debye length, λ_D (nm), which is inversely dependent on the total concentration of ions in the electrolyte, n (C m^{-3}). B) Experiments show bound double layers often extend several nanometers away from surfaces, especially in concentrated electrolytes, such as ionic liquids. In concentrated electrolytes, bound layers are composed of both counter ions and co-ions, substantially lowering local potential gradients, relative to classical predictions. The diffuse layer often extends tens of nanometers away from charged surfaces in concentrated electrolytes, with a characteristic rescaled Debye length, λ_D^* (nm), where the rescaled charge density, n^* (C m^{-3}) is much lower than the total ion concentration. C) In correlated electrolytes, clusters with charge imbalances take on the role of electric field sources and sinks that determine screening lengths and potential gradients. Formation of ionic aggregates causes screening to be much less effective than classical predictions. Further, organic ions can also serve as proton sources or sinks, which couples local charge densities and pH in a complex manner. Determination of how these effects intersect to sculpt both proton and electric field gradients promises to open new avenues for influencing electrochemical reactivity.

The region over which ion, solvent, and redox mediator concentrations differ from that of the bulk phase is often referred to as the electric double layer and can extend from molecular distances to many nanometers.^[39,40] These distances are defined by a balance of electrostatic interactions, which favors thinner double layers via ion condensation, and entropy, which favors thicker double layers. This length scale of screening is often a critical determinant of electron transfer (ET) kinetics, as energetics are governed by local potential gradients,^[41] and thinner double layers enhance local potential gradients. Hence, there is great interest in understanding fundamentals of double layer formation in complex multicomponent electrolytes, especially with high concentrations of ions, reactants, or redox mediator species.

The classical electric double layer model of electrode–electrolyte interfaces was developed for dilute electrolytes comprised of idealized point charges. In Gouy–Chapman–Stern theory and other classical models,^[39] electrolytes are predicted to respond to surface potentials by de-mixing into distinct bound and diffuse double layers (Figure 3A). The bound portion, known as the Stern layer, was envisioned as a single condensed ion layer of counter ions that compensates most of the surface potential.^[42] The diffuse layer then extends between the Stern layer and the bulk solution,^[43,44] where the surface potential is fully screened.

The Debye screening length is the characteristic of length scale of ionic screening within a classical electrolyte^[39] and depends inversely on the bulk ion concentration. Increases in ion concentration decrease the Debye length, indicating more efficient screening and steeper potential gradients in the diffuse layer. The Debye length also depends on the temperature, ion valence, dielectric permittivity, and is fundamentally a property of the bulk electrolyte (Figure 3). For context, the Debye length is 10 nm for a 1 mM solution of NaCl in water at 295 K, drops to 1 nm for a 100 mM solution of NaCl in water at 295 K, and is around 1 μm for neat water at 295 K.

While the Gouy–Chapman–Stern model remains in frequent use in many areas of energy and electrochemical science, recent paradigm shifts emerging from the surface forces community^[38,45–47] are advancing qualitatively new models for double layer formation in correlated electrolytes. In particular, surface forces measurements revealed that double layers formed by neat ionic liquids routinely extended beyond 10 nm,^[46] which is one to two orders of magnitude thicker than expected from classical theory. This work on long range screening in ionic liquids was quickly generalized to show that screening lengths are non-monotonic with ion concentration for many combinations of salts and solvents.^[46–48] This is a key departure from classical theory, which suggests that increasing ion concentration always leads to enhanced screening and more strongly confined electric fields.

While many details of double layers in ionic liquids remain under discussion, consensus has formed around the idea that ionic assembly or aggregation into effectively neutral clusters likely plays a key role in long range double layers in ionic liquids and other concentrated electrolytes.^[46] One promising way to conceptualize double layer formation in ionic liquids is to reimagine Stern layers as a surface-templated charge-ordered ionic domain of between 1 and 5 nm in thickness that is in series with a longer range diffuse double layer extending 5–50 nm into the bulk electrolyte (Figure 3B). As in classical models, the length scale of double layers is a fundamental property of electrolytes and indicates effective ion strengths or “free ion densities” within the fluid.

The surprisingly inefficient screening exhibited by ionic liquids and other concentrated electrolytes indicates that electric field gradients and other electrochemical properties, like capacitance, are suppressed due to the formation of excessive neutral clusters. This is consistent with the fact that ionic liquids exhibit only modest double layer capacitances^[38] and often need to be blended with higher permittivity solvents, like acetonitrile or water, to facilitate catalysis (Figure 4).^[49–51]

Enhanced potential gradient at intermediate ion concentration

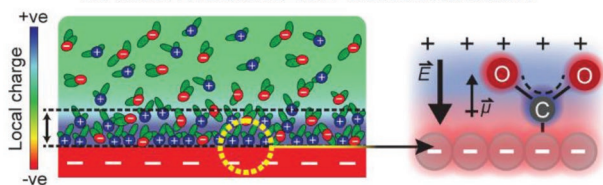


Figure 4. Electrostatic screening is most efficient at intermediate ion concentration of between 0.5 and 1 M in ionic liquid-acetonitrile electrolytes. At these “strong screening” conditions, applied potentials are screened within molecular distances from surfaces, leading to enhancement in local potential gradients, relative to the dilute and neat ionic liquid limits. Since CO_2 is quadrupolar and reduction involves a dipolar transition state, larger potential gradients correspondingly lower the reactant-transition state energy barrier, leading to enhanced reaction rates. Further control over product selectivity is also obtained by sourcing protons from imidazolium cations, instead of water molecules. Together, these approaches can be leveraged to enhance selective CO_2 reduction to CO by fivefold, compared to electrolytes with a more typical ion concentration of 0.1 M. Reproduced with permission.^[51] Copyright 2022, American Chemical Society.

Hence, the understanding that excessive ionic clustering leads to unexpectedly long-range double layers has provided important insights into how to target enhanced screening to accelerate electrochemical reactivity. For example, a common practice in the study of CO_2 electrochemical reduction in ionic liquids has been to perform structure-reactivity studies in acetonitrile solution with electrolyte ion concentrations held at 100 mM supporting electrolyte doped with around 10 mM of ionic liquids as additives.^[50]

Yet, recent work shows that CO_2 reduction rates, selectivity, and structure-reactivity relationships can be disrupted by investigating previously overlooked concentration regimes where ionic correlations emerge.^[51] Notably, reaction rates were seen to be accelerated by up to fivefold at intermediate concentration of 0.5–1 M for ionic liquids dissolved in acetonitrile, as compared to prior regimes of study focusing on lower ion concentrations and neat ionic liquids. Surprisingly, non-proton active, inert ionic liquid cations that were found to be the most effective electrolyte additives at low concentrations exhibited the lowest steady state reaction at intermediate concentration. This poor performance was found to be due to formation of organic carbonate precipitates under steady state electrolysis, as sourcing protons from water results in formation of bicarbonate anions and most organic bicarbonate salts are sparingly soluble in acetonitrile.

This case study highlights how understanding ionic screening and double layer formation at complex interfaces opens distinct opportunities for controlling reactivity as well as unexpected basic science questions. Within the emerging area of non-classical double layer formation, we find two especially interesting underexplored concepts: 1) investigating how changes in charge state associated with proton donating or accepting events can be used to tune ionic screening, double layer formation, and interfacial concentrations of active species (Figure 3C), and 2) understanding how redox-active surfaces, such as semiconductors, influence double layer formation by

serving as a source or sink of ions, protons, or other species via defect formation.

As one example, the most efficient ionic liquid co-catalyst identified to date is the di-alkyl-imidazolium cation,^[49] which can serve as a proton source via de-protonation. Upon de-protonation, the conjugate base is a neutral carbene that can form coordination complexes with CO_2 . Hence, imidazolium cations participate in screening as well as donating protons to CO_2 reduction, which is a process that should impact local electric field gradients, interfacial dynamics, and ionic correlations.

We posit that rational development of “dual-function” cations that serve as both double layer modulators as well as proton sources and sinks provide promising new avenues for unlocking additional control over electrochemical reactivity. Future avenues for research in this emerging area could focus on generalizing the concept of sourcing protons from cations to other electrochemical reactions, such as nitrate reduction.^[52] Studying the implications of having cation-derived neutral conjugate bases, as compared to the strongly coordinating OH^- anion would also be an area ripe for investigation. Additionally, we anticipate that there may be synergistic ratios of water to proton-active cations to maximize the rate and selectivity of different reactions, and that these ratios may depend on the solvent used in non-aqueous electrochemistry.

Nevertheless, development of electrolytes with high concentrations of redox active ions may face several challenges and potential drawbacks which must be balanced with gains to control over reactivity. For example, many redox active cations which can serve as proton sources can undergo additional proton-activated reactions, such as carbene-mediated dimerization or electrocatalysis upon de-protonation of di-alkyl imidazolium cations to N-heterocyclic carbenes.^[51] Hence, careful control over proton activity and balancing more general chemical reactivity will be important for developing high performance electrolytes.

Further, organic ions are often much more costly than neutral organic solvents. Hence, care will be needed to mitigate decomposition pathways, as high ionic strength electrolytes will need to have lifetimes vastly exceeding that of lower concentration electrolytes to offset cost increases. Notably, high electrochemical stability is a property that is common to many highly concentrated correlated electrolytes, as ion-ion interactions act to stabilize these species against oxidation and reduction.^[46] Indeed, this is one of the key strengths of ionic liquid-based electrolytes, although detailed techno-economic analysis will likely be important for evaluating exactly when and how tradeoffs in cost, lifetime, and performance can be balanced to justify the use of complex electrolytes with redox active ions.

We envision that further study of ionic clustering and collective assembly of ions, redox mediators, and other components of electrolytes will continue to reveal new mechanisms for influencing hydrogenic reactions. In parallel with continued development of multifunctional solid surfaces, we anticipate that distinct types of chemical reactivity can be harnessed to produce, store, and use hydrogenic species to support the growth of alternative energy carriers.

2.2. Redox Mediators as Soluble Interfaces

Molecular redox mediators can serve as energy carriers equipped to use renewable electricity to drive diverse redox processes for energy storage and conversion. Energy conversion includes chemical synthesis of products not readily integrated within conventional electrochemical systems. Molecular mediators under consideration here undergo liquid-phase oxidation or reduction at the electrode interface (Figure 5). They are then transported (e.g., by convection and diffusion) into the bulk solution where they undergo follow-up chemical reaction with a substrate molecule or with a catalyst that subsequently reacts with the substrate of interest. In this process, the mediator effectively serves as a “soluble electrode,” capturing the energy supplied by the solid electrode and delivering it elsewhere within the system.

Various types of mediated redox reactions are possible, but they most commonly feature ET or proton–electron transfer (PET) reactions. ET and PET mediators are widely encountered in biology. For example, photosynthesis involves the use of quinones (PET mediators) and other molecular species to shuttle electrons between enzymes in reaction pathways such as the reverse Krebs cycle and the Calvin cycle. Similarly, mitochondrial respiration leverages quinones, cytochrome c (ET mediator), and other diffusible ET and PET mediators to support NADH oxidation by O_2 . This net reaction releases energy, akin to H_2 oxidation by O_2 in a fuel cell, and this energy provides the driving force to pump protons across a membrane to promote ATP synthesis.^[53] For more direct energy storage schemes, molecular mediators serve as the energy storage reservoir in RFBs. RFBs pair high-potential and low-potential molecular mediator species in a liquid-phase electrochemical cell via reversible ET or PET redox reactions of the mediators at the electrode without follow-up charge transfer. These biological and RFB examples validate the utility of dissolved mediators as energy carriers for energy transduction and storage, and they provide a foundation for development of mediated EHT applications, ranging from fuel cells to chemical synthesis.

Mediated EHT has been the focus of historical attention for power generation, using both conventional and non-conventional fuels.^[8,54] Polymer electrolyte membrane fuel cells (PEMFCs) typically work by coupling anodic reaction of

a fuel such as H_2 and cathodic reaction of an oxidant such as O_2 to form a galvanic cell, with charge balance and reaction stoichiometry maintained by migration of protons through a hydrated polymeric separator. Desirable alternative fuels such as alcohols or biomass feedstocks can be challenging to use in typical PEMFC configurations due to their low aqueous solubility and/or poor catalytic kinetics at the electrode interface. Development of fuel cells that employ mediators in liquid-phase electrolytes can address several limitations that have been encountered, including electrode “flooding” with liquid fuels, mass transport limitations of complex substrates to the electrode surface, and challenges with solid or sparingly soluble fuels in aqueous electrolyte.

Both inorganic and molecular mediators have been used to good effect, enabling fuel cell concepts to be demonstrated with a wide variety of fuels. Inorganic mediators, including Fe^{2+}/Fe^{3+} complexes or salts and polyoxometalates (POMs), have been used in fuel cells that oxidize alcohols,^[55,56] sugars,^[57] biomass,^[58–60] and even coal.^[61] The iron systems are notable for often achieving relatively high power densities of 50–100 $mW\ cm^{-2}$ while operating with challenging fuels such as glucose, wheat, or grasses. POM systems frequently operate at lower current densities, and often require the integration of separate chemical and electrochemical processes; however, these materials interface well with heterogeneous or polymeric feedstocks and resist poisoning. Substituted quinones are among the most commonly used organic energy carriers for EHT in fuel cells and have been demonstrated for oxidation of alcohols, sugars, and lignin.^[62–64] Quinone systems can be tuned by the addition of various substituents to the central ring to promote solubility and to adjust the redox potential, making them well-suited as tunable energy carriers and have been incorporated in mediated fuel cells for both cathodes^[65] and anodes.^[66]

These same mediator concepts have been leveraged for electrochemical synthesis, where the end goal of the EHT is generation of a value-added product rather than electricity. Mediated electrolysis frequently leads to advantages in chemoselectivity.^[67] Inorganic and organic mediators have been used to support chemical reactions with biomass feedstocks and facilitate the synthesis of industrially relevant chemicals.^[68–71] Additional value can be found by harnessing mediated systems to improve product purity via phase-transfer technology.^[72]

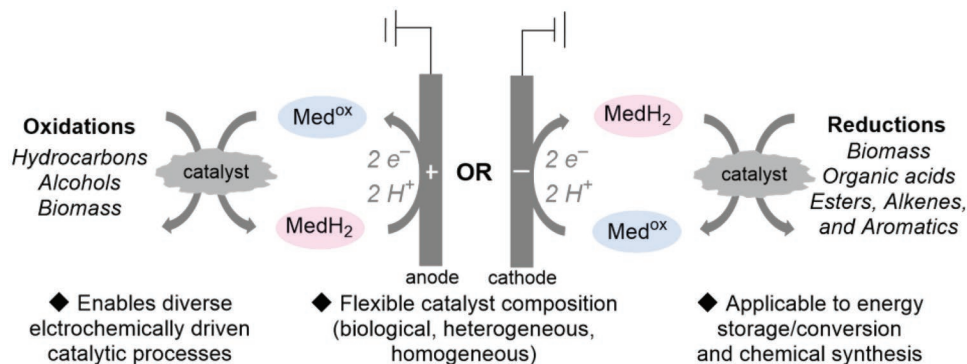


Figure 5. Mediated electrochemistry provides a means to enable diverse electricity-driven redox processes that may be challenging via direct electrolysis.

The mediator is a crucial enabling technology for this application, avoiding gas diffusion kinetics which might hinder a solid electrode and allowing for interfacial reaction between species in different liquid streams, which is frequently impractical for direct electrochemical systems. As emphases on atom economy and green chemistry continue to foster the growth of industrial electrochemistry, approaches to maximize product purity and minimize cross-contamination during mediated electrolysis are expected to become more important.

Key basic science challenges remain as this field evolves. The multiple requirements for an appropriate mediator—stability, solubility, redox potential, electrochemical, and thermal kinetics—sometimes make it challenging to identify candidates for a given system. The design of new mediators and chemical modification of existing ones to optimize properties of interest represent key molecular/materials synthesis challenges.^[73,74] Enhancing mediator stability is a particularly important challenge, as this property contributes to long-term efficiency and performance metrics, in addition to avoiding side products that could complicate product isolation in electrosynthetic applications. High-potential organic mediators merit special attention given the common instability of highly oxidizing organic molecules.^[75] In the field of energy storage, research efforts have demonstrated that modifications to mediators like fluorenone or *N*-oxyl species can enhance stability and tune redox potentials to improve cell voltages.^[76,77] Synthetically modulating a mediator's potential is especially impactful because energy carriers can be used to escape the limits of traditional electrochemical Tafel slopes, enabling higher catalytic rates at lower overpotentials. **Figure 6** provides an example of this phenomenon when comparing rates of a quinone-mediated oxygen reduction reaction (ORR) to that of the direct electrocatalytic ORR.^[78] The shallower slope for the mediated process suggests that access to a higher-potential quinone would support higher rates relative to the direct electrocatalytic ORR at high potentials.

As new mediated systems are identified, it will also become increasingly important to determine the mechanisms by which they operate. Reactions that pair mediators with thermal heterogeneous catalysts (i.e., not physically integrated with the electrode) can potentially operate by different pathways. One possibility involves direct chemical reaction between the substrate and mediator on the catalyst surface, while another involves formal electrochemical half-reactions that take place at different sites on a conductive catalyst surface. Studies to elucidate these catalytic mechanisms in mediated and non-mediated systems are an area of active study.^[78–83] Further efforts to probe these questions will be crucial to improve performance of mediated systems and extend mediator accessibility to new applications.

Mediated electrochemistry is a strategic area for further research. Fundamental science advances are needed to engineer stable mediators across a wide potential range, to undertake investigation into their mechanisms of action, and to integrate them with new catalytic systems. Potential applications are diverse, as mediators are well-suited to leverage electrochemical energy to drive chemical transformations with off-electrode catalyst systems, including molecular, heterogeneous, enzymatic, and microbial catalysts.

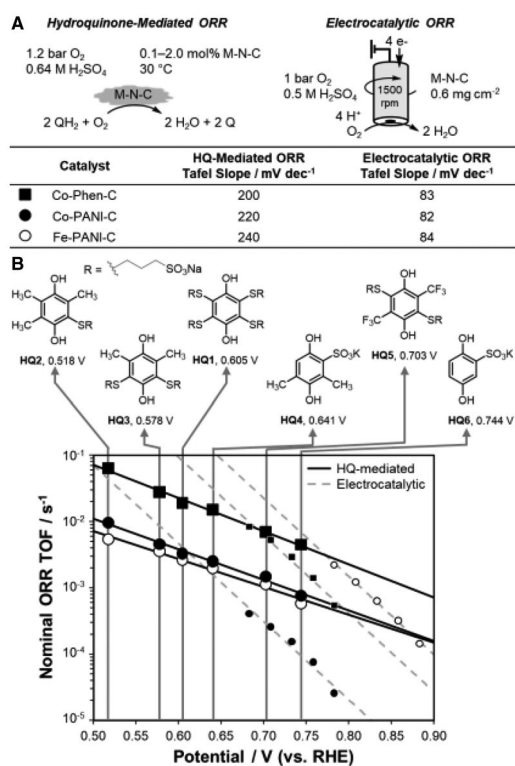


Figure 6. A) A comparison of direct electrocatalytic oxygen reduction and quinone-mediated oxygen reduction. B) Different thermodynamic-kinetic scaling relationships are among the potential opportunities that may be realized via mediated electrolysis. Reproduced with permission.^[78] Copyright 2022, American Chemical Society.

2.3. Suspended Catalytic Capacitors

0D colloidal semiconductor nanocrystals (SCNCs) are isolated single crystal semiconductors with sizes at the single to tens of nanometer scale. Between the synthetic control over redox potentials, size, shape, surface chemistry, and composition,^[84–87] and their ultra-high surface-area-to-volume ratio, they are an ideal platform to drive EHT chemistries. Moreover, SCNCs are optically active, which creates opportunity for alternative energy delivery schemes. Where most reports of electrocatalytic and photocatalytic chemistries on 0D nanoparticles describe configurations where NCs are supported and immobilized on an electrode,^[88–96] here we focus on the possibilities of SCNCs suspended in a liquid matrix as this configuration overcomes diffusion-limited reaction rates and enables storage in a similar way to RFBs.

The spatial confinement of SCNCs provides an avenue for high energy density energy storage and catalysis that cannot be met by their bulk counterparts. The Fermi level (E_F) of SCNC's can be moved outside of their equilibrium position into the conduction or valence bands through redox processes which add or subtract one or several electrons (exceeding carrier densities of $6 \times 10^{20} \text{ cm}^{-3}$)^[97] (**Figure 7**). Without a continuous path for charge flow (i.e., open-circuit conditions), these electrons can be stored in the nanoparticle indefinitely. Depending on the electronic structure, the dopant density, and the nature of the dopants (intrinsic vs extrinsic), these excess carriers are

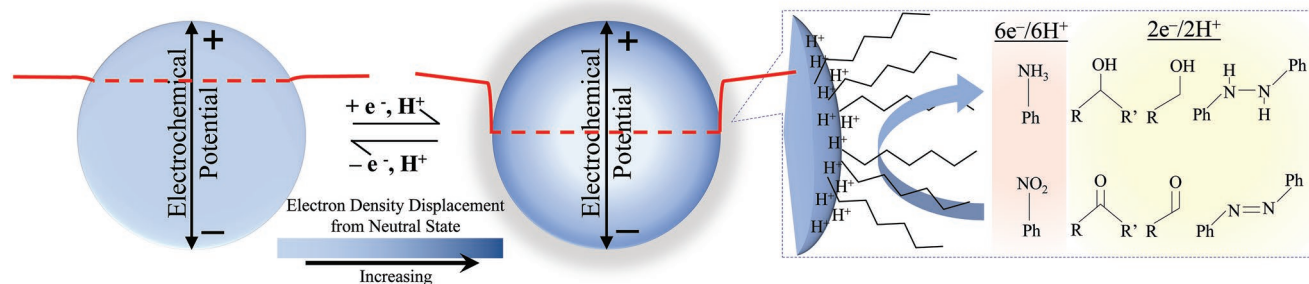


Figure 7. Schematic illustration of uncharged (left) and electronically charged (right) semiconductor nanocrystals. The SCNC electron density is uniformly distributed, and the Fermi-level (red, dashed line) and the solution potential (red solid lines) do not deviate in a significant way (for convenience, the bulk solution potential and SCNC Fermi-level are assumed to be nearly equivalent). The Fermi-level of the charged NC (right) deviates from the solution potential significantly. The electron density is localized near the SCNC surface and solution phase protons accumulate to screen the increased charge density resulting in a large energy displacement from the bulk solution potential.^[100] The color gradient of the charged SCNC indicates differences in the radical distribution of electron density and the shaded area outside of the NC indicates accumulation of protons in the double layer. The inset shows a simplified representation of the molecular structure at the SCNC/liquid junction. Both surface ligands and solution protons are present. The reaction diagram to the right displays documented hydrogenation reactions.

asymmetrically distributed across the nanoparticle volume with charge localization at or near the SCNC surface. When a SCNC is charged, a solution-phase ion closely associates with the NC surface to compensate the SCNC charge and minimize the particles' energetic displacement from the surrounding phase. The energetic structure that develops at the SCNC interface, therefore, conforms to the same physical picture as an electrochemical capacitor (Figure 7) with an electric double layer at the surface.^[98–101] Since the excess charge is stored in SC bands, the band edge potentials and energy-level spacing dictate the SCNC's redox potentials. These band edge potentials can be synthetically controlled through NC size variation,^[102,103] interfacial dipoles,^[104–107] aliovalent or isovalent doping,^[99,107–111] electric double-layer engineering,^[112] as well as other methods.^[113] Moreover, the energy profile of stored charge at the SCNC surface is nearly flat with increasing electron density which enables multiple electron–proton chemistries with a single particle. Coupling their charge storage character with their redox potential tunability, these materials can be envisioned as dual functional suspended capacitor-catalysts.

Where any solution-phase ion can, in principle, populate the Stern layer at the SCNC surface, protons are the most common and arguably, the most useful for catalysis (Figure 7).^[113] This proton- and electron-dense SCNC interface readily transfers these reducing equivalents to molecular species through simple electron reduction or catalytic hydrogenation via PET,^[114] and enables heterogeneous catalysis that would otherwise be diffusion-limited from a planar electrode surface to occur quickly and selectively. Catalytic hydrogenation chemistries from reduced colloidal SCNCs have been demonstrated for dozens of transformations and range in complexity. One electron/one proton ($1e^-/1H^+$) reductions on nitrosyl and phenoxy radical species were used to demonstrate concerted PET (CPET) chemistry on ZnO and TiO₂ NCs.^[114] $2e^-/2H^+$ hydrogenations are far more common and have been demonstrated on aldehydes,^[115,116] quinones,^[117] azines,^[117] arylhalides,^[118] enamines,^[117] epoxides,^[119] and more.^[113] Indeed, up to $6e^-/6H^+$ reductions have been demonstrated taking nitroarenes to aromatic amines.^[120,121] In addition, the surface of SCNCs can be modified with a number of co-catalysts to further broaden the possible reaction

scope.^[122] Finally, piggy-backing off of research enabling SCNC-biocompatibility,^[112,113] the tantalizing prospect of integrating these chemistries into more complex interconnected systems which involve biological transformations arises. These highly charged nanostructures are an exceptionally promising class of materials for both storing and transforming energy via electrochemical hydrogenation chemistry.

Despite the progress in catalytic chemistry with suspended nanoparticles, however, SCNCs have yet to truly realize their potential as suspended heterogeneous catalysts. Standing in the way of such a scheme is their surface, the same aspect which makes them suitable soluble hydrogenic catalysts. SCNC colloidal stabilization is the sum Van der Waals forces—achieved in SCNCs from molecular surface functionalization with aliphatic or oligomeric molecules—and surface potentials and is described by Derjaguin–Landau–Verwey–Overbeek (DLVO) theory.^[123–125] If the particle–particle interaction energy overcomes the stabilization energies, particles will spontaneously aggregate and precipitate. Where SCNCs are stable as a suspended colloid, introducing direct ET from a highly polarized electrode surface with a large potential gradient often overcomes the stabilization energy of the SCNC or performs electroreduction of surface ligands instead of the SCNC itself. As a result, large overpotentials are required to drive quasi-reversible or irreversible redox chemistry (Figure 8) that leads to electrochemical plating of SCNCs on the electrode surface. In fact, “electrogelation” is a method of controlled colloidal destabilization through the application of an electrochemical bias and subsequent ligand exchange.^[127,128] Such instability is clearly not satisfactory for a technology that would be continuously cycled between charged and discharged states thousands of times.^[126] Therefore, nearly all the demonstrations of SCNC-driven catalysis on suspended colloids were derived from either photochemically or chemically reducing SCNCs via a sacrificial small molecule instead of direct electrochemical reduction. The challenges of direct electroreduction on suspended colloids have been known for several decades and have yet to find a suitable solution.

Overcoming the limitations of direct electrochemical charge injection into suspended SCNCs will require foundational

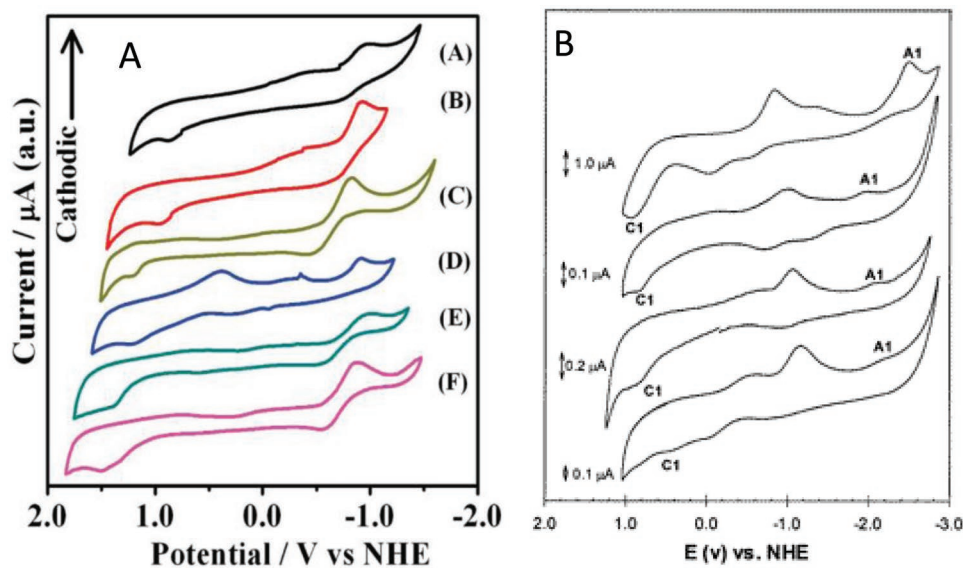


Figure 8. Cyclic voltammograms (CVs) of colloidal suspended A) cadmium telluride and B) cadmium sulfide nanocrystals of varied sizes below 10 nm in diameter. These data show quasi-reversible or irreversible redox waves for both the reduction (addition of electrons to the conduction band) and oxidation (removal of electrons from the valence band) of the nanocrystals. A,B) Reproduced with permission.^[129,130] Copyright 2011 and 2001, American Chemical Society.

research to better understand these interfaces, as well as creative solutions to redesign the interfaces themselves. Several strategies are currently being explored. A recent report by Homer et al. utilizes a panel of redox mediators with varied reduction potentials to measure and predict photochemical NC charge transfer rate constants.^[131] Applied to a charging scheme, this approach can mimic a redox mediator which removes the necessity for direct NC|electrode contact. Designing the ligand shell to imbue electrochemical functionality is also an interesting approach. For example, covalent molecular surface functionalization of group 4 semiconductors has been an active field of research for decades,^[132] and using assemblies with redox active molecules tethered to one end creates a charge-transport pathway to the semiconductor.^[133] Applied to suspended colloidal SCNCs, these assemblies can potentially act as charge conduits between an electrode and a SCNC therefore mitigating electric double layer overlap with the electrode. Finally, modifying the SCNC surface itself with dopant atoms can alleviate the need for stabilizing ligands altogether. Wheeler et al. demonstrated that boron atoms at the surface of silicon nanoparticles create highly Lewis acidic surface sites. When paired with a solvent mixture or electrolyte with sufficient Lewis basicity, single nanometer particles spontaneously form stable colloidal suspensions without the need for surface ligands.^[134] Reducing the necessary Van der Waals interactions from molecular surface ligands may enable a greater stability against electroplating and surface reduction.

Spatiotemporal models to describe structurally evolving non-equilibrium double layers at the SCNC|liquid junction are also needed. Under DLVO theory, electrode–nanoparticle interactions are treated as an asymmetric geometry (two nonequivalent materials with interacting double layers). Where DLVO theory can predict colloidal stabilization for simple, well-controlled, symmetric interacting surfaces, it is very difficult to apply

DLVO to asymmetric surfaces with complex molecular or ionic configurations that are not well-described or well-controlled. Compounding this problem, the SCNC surface potential is dynamic with charging and discharging which introduces non-equilibria to the interacting surfaces. Systematic and careful studies to better describe asymmetric geometry under DLVO theory are needed.

While promising for energy storage and catalysis, research of SCNCs in this context is still in its infancy, and foundational science is needed to describe the nuances of the SCNC|electrode interface as well as the interplay between protons, ligands, solvated small molecules, and the microevent around the interface. We anticipate that as control of the chemical environments at the SCNC interface becomes more precise and well-defined, these materials will be applied broadly to a variety of energy storage and conversion technologies.

2.4. Electrocatalysis through a Solid–Electrolyte Interphase

Solutions that decarbonize fuel technologies while using existing infrastructure will have a decreased barrier for adoption and lower implementation costs. Ammonia, which has a unique advantage as a carbon-free energy carrier option,^[135] is produced through the Haber–Bosch process at 150 MT/year,^[136] has a high energy density, and is transportable through present infrastructure for liquid fuels.^[137,138] Ammonia is used on a global scale as a fertilizer, cleaning agent, and precursor to nitrogenous compounds, among other applications. As a fuel, ammonia can be utilized in fuel cells, thermal engines, and as a hydrogen source through cracking reactions. While ammonia has potential as a zero-carbon fuel, its current production method—the Haber–Bosch process—is inefficient; accounting for >1% of global energy usage. To decrease the

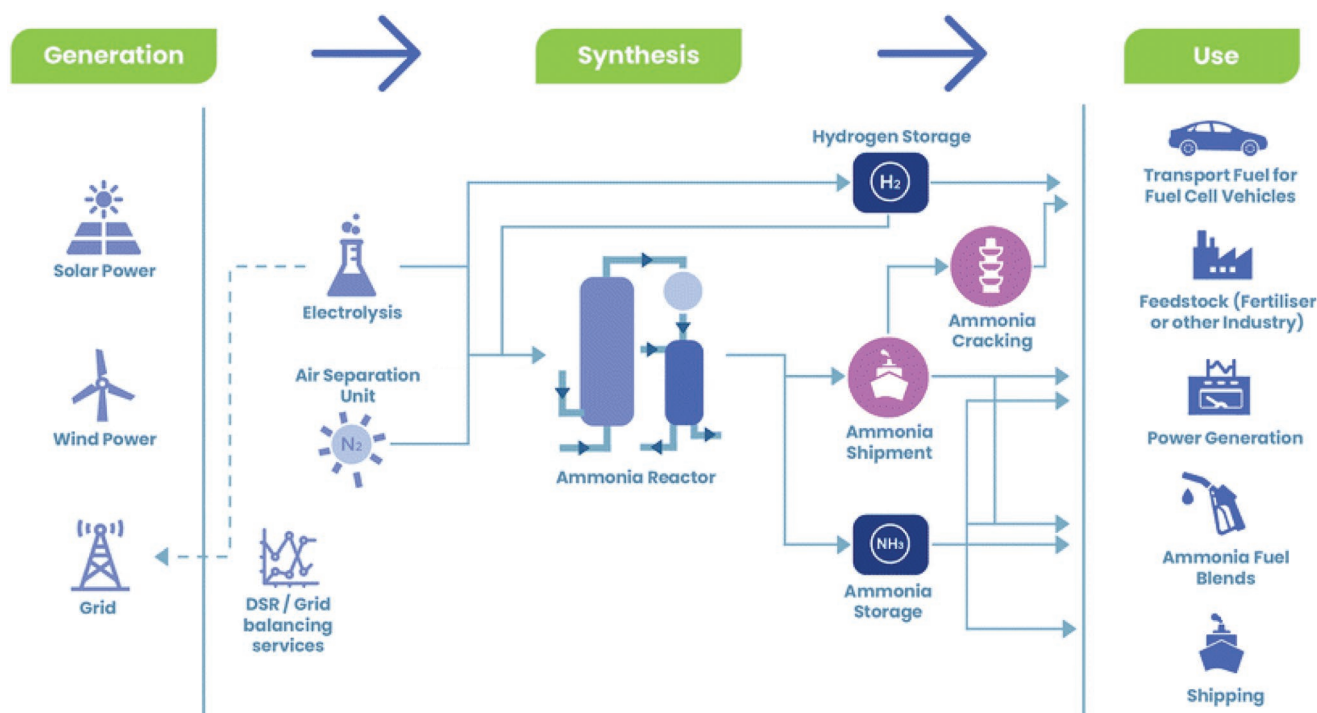


Figure 9. The use of ammonia in a decarbonized economy. Reproduced with permission.^[145] Copyright 2021, Elsevier.

carbon footprint, improve efficiency, and create a sustainable process, low-cost production both of ammonia from clean electricity and of electricity from ammonia fuels is required (Figure 9).^[145]

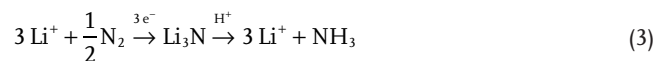
Direct electrochemical conversion between N_2 and ammonia offers the promise of improved energy efficiency and a direct use of renewable-based electricity. However, before such a method can be realized, two fundamental challenges must be addressed: cathodic nitrogen fixation to electrocatalytically produce ammonia (Equation (1)), and anodic oxidation of ammonia to release protons and electrons (Equation (2)). Indeed, the electrochemical reduction reaction of N_2 (N_2RR) is so difficult that N_2 is commonly used as an “inert gas” to sparge liquid electrolytes prior to performing electrochemical measurements. The design of unique electrode–electrolyte interfaces to enable N_2RR remains an active research area.^[139] These efforts seek to address several performance issues that have plagued electrocatalytic N_2RR : 1) low Faradaic efficiencies (FE), 2) low rates of production, and 3) competition with the hydrogen evolution reaction (HER).^[139,140] These problems, combined with inherent tradeoffs between N_2 activation and N–H bond formation in simple heterogeneous catalysts, require clever manipulation of the electrode interface to achieve efficient N_2RR .^[139,141,142] Here, we discuss a unique electrochemical interface which enables N_2RR as shown in Equation (1).^[143,144]



The solid–electrolyte interphase (SEI) is a heterogeneous layer between a solid electrode and an organic electrolyte and

forms because the electrode potentials operate outside of the electrolyte’s “voltage stability window.” The SEI is composed of reduced organic solvent molecules and electrolyte ions and can contain elements of the electrode as well. Generally, the SEI is ionically conductive but electronically insulating, which inhibits further electrolyte decomposition at the SEI|liquid interface (i.e., the surface potential is sufficiently screened). The SEI has been studied in detail for reversible Li-ion batteries,^[146,147] but is not common in heterogeneous catalysis; insulating surface layers are generally regarded as a source of overpotential and catalyst deactivation. However, an exceptionally promising N_2RR heterogeneous electrocatalyst—lithium metal—necessitates not only reconciling with the presence of SEI but developing new understandings of the SEI and strategies to leverage the SEI to improve N_2RR catalysis.

Unlike heterogeneous catalysts that are designed for direct reduction of N_2 or its adsorbed intermediates, lithium-mediated N_2RR (Li- N_2RR , Equation (3)) enables the conversion of N_2 to a lithium nitride where subsequent protonation of the nitride liberates ammonia.



The formal redox potential of Li^{+0} is -3.05 V versus SHE, substantially more negative than the potential at which most organic electrolytes undergo reductive decomposition (>-2 V vs SHE). The reactive nature of Li^0 therefore ensures the formation of a passivating SEI when exposed to organic electrolyte (Figure 10), a significant area of interest in Li-metal-based LIBs.^[147] In early Li- N_2RR reports, efficiency for NH_3 production was limited to 50% even at high N_2 pressures.^[148,149] However, recent work has found significant improvements by exploring

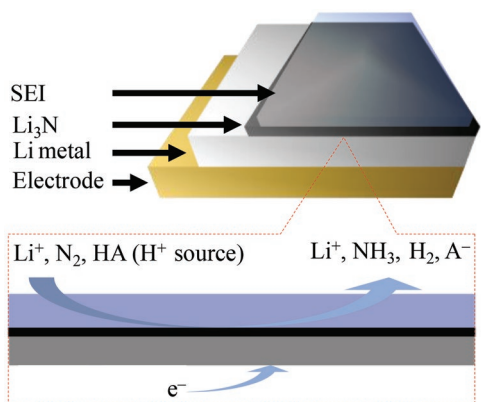


Figure 10. Schematic illustration of an operational electrode assembly for Li-N₂RR. The zoomed image below illustrates the reactants passing through the SEI layer to the Li/Li₃N layer for ammonia synthesis.

the role of the SEI layer in Li-N₂RR, and defining descriptors which can be used to favorably tune the SEI properties with electrolyte additives.

The work of MacFarlane, Simonov, and coworkers report the significant impact electrolyte anions have on Li-N₂RR by achieving nearly 100% Faradaic efficiency.^[150] The authors performed a differential capacity analysis of different anions and found a positive correlation between the double layer capacitance and the ammonia yield rate. Consistent with an increased interfacial capacitance improving N₂RR yield rates, they show that increasing electrolyte concentration improves performance until NH₃ production rates become limited by mass transport at high (>2 M) electrolyte concentrations with greater viscosities. Post-electrolysis electrochemical impedance spectroscopy measurements revealed that the electrolytes that generate a high capacitance at the interface reduce the resistance of the SEI layer formed at the surface. These measurements suggest that a more compact ionic assembly at the electrode surface is necessary to exclude undesirable solvent molecules from the interphase region and improve the components of the SEI which are beneficial for catalysis. This is consistent with the recent proposal that enhanced screening can also accelerate CO₂ electro-reduction discussed above, suggesting that modulation of local potential gradients via interfacial ion assembly could be a general theme for selective hydrogenic transformations.

The identity of the proton donor has also been shown to be an important consideration in Li-N₂RR. In a recent report, Manthiram and coworkers experimentally screened a variety of proton donors and determined the Kamlet–Taft (KT) parameter of the acid to be predictive of enhancement to Li-N₂RR.^[152] Combining these results with a deep learning method to predict the KT parameters of many acids across chemical space, the authors found that 1-butanol was a preferred proton donor for Li-N₂RR, counter to the commonly employed EtOH. A related report using stainless steel electrodes with LiBF₄ electrolyte demonstrated linear aliphatic alcohols to be the most active class of proton donors in promoting Li-N₂RR (Figure 11).^[151] The lack of correlation between N₂RR activity and proton donor pK_a, as well as the sensitivity of the system

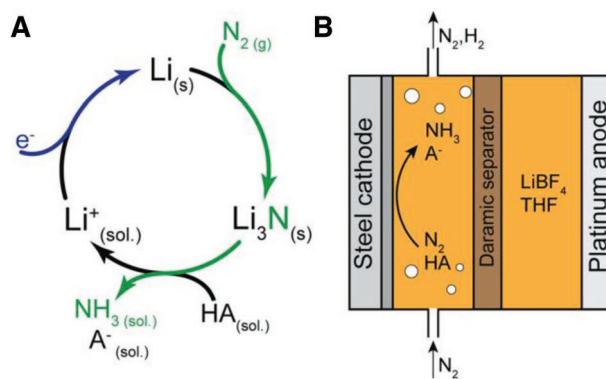


Figure 11. A) Catalytic cycle for Li-mediated electrochemical N₂RR at stainless steel electrodes. B) Reactor schematic for the cathodic conversion of N₂ to ammonia. Reproduced with permission.^[151] Copyright 2022, American Chemical Society.

to subtle changes in proton donor structure, are explained by changes in the SEI. Selecting proton donors that encourage formation of SEIs with preferential transport of N₂ may thus be an important strategy for encouraging N₂RR over HER. A complementary study using a copper foil cathode in 1 M LiBF₄ in THF, revealed a first order dependence on N₂ concentration and \sim –1.5 order with respect to EtOH proton source, likely due to increased competition from direct lithium protolysis.^[153] These findings suggest that the SEI may be a feature, not a barrier, to Li-N₂RR.

In all, it is unclear what the properties of the SEI should be, and more importantly, if the SEI should be incorporated into Li-N₂RR. Where dense ionic assemblies reduce the organic content of an SEI and promote a steeper interfacial potential gradient, identifying properties of a more organic SEI that can be used to optimize a system for enhanced efficiency (e.g., using a tailored proton donor or accelerating N₂ mass transport) are also valuable. Indeed, a better understanding of the SEI and its role on Li-N₂RR is needed before its value at a catalytic interface can be truly known.

The field of electrochemical dinitrogen reduction to NH₃ is relatively new. Several other strategies such as engineering the electrode morphology,^[154] use of homogeneous catalysts^[155] or redox mediators,^[156,157] and investigation of heterogeneous defects, substitutions, and additives^[158,159] are also unique electrochemical interfaces and remain important avenues of investigation. Indeed, electrochemically converting between N₂ and NH₃ is an exceptionally difficult reaction but given the utility of NH₃ in so many different sectors, enabling N₂RR through direct electrochemical reduction is worth the resource investments. Tuning the energetics of substrate activation, is in our opinion, the key challenge for nitrogen conversion to useful compounds using electrochemistry-driven approaches. The binding strength of nitrogen to a catalyst is key. Catalysts that are weak binders have increased side reactions of proton reduction to hydrogen, whereas strong binders of nitrogen have increased overpotentials.^[160] We believe that unique electrochemical interface design will play a large role in balancing the N₂ binding energy and unlocking this important reaction.

3. Conclusions and Outlook

The electrochemical potential of electrons can be readily tuned via a combination of applied potential or electronic state engineering of surfaces and active sites. This provides a high degree of control over reactions that solely involve ET. For EHTs however, protons play an equally important role. The moderate reduction potential for HER compared to many other hydrogenic chemistries means that HER will often compete with EHTs as a parasitic side reaction. In the immediate future, overcoming this competition is a grand challenge for EHTs. Understanding the mechanisms and pathways for EHTs is therefore critical to enable broad use of electrosynthesis for hydrogenic chemistries.

For EHTs, reaction selectivity and overpotential are often determined by a CPET kinetic step where a coupled proton and electron share a common transition state that minimizes the Coulombic barriers associated with charged-particle transfer.^[161,162] To facilitate CPET, electron–proton coupling must be maximized.^[163] In some cases, interface design can be used for discriminating against competing CPET reactions such as HER. One such example of a non-traditional electrochemical interface that leverages this parameter control is polymer encapsulated electrocatalysts for CO₂RR.^[164] These materials have been designed to provide a defined H⁺ transport pathway from polymeric functional groups and a secondary coordination sphere that affects proton–electron coupling. The combined effect results in improved selectivity for CO₂RR products over the HER in aqueous media. Improving control over interfacial environments for proton-coupled electrochemistry is ripe for additional innovation, as this requires an interplay of mass transfer, proton transfer kinetics, and local intermolecular interactions that are tightly chemically coupled to bulk electrolyte properties. We envision that research into novel electrochemical interfaces for EHT will provide a means of controlling proton–electron electrochemistry to enable advanced hydrogenic transformations and overcome HER limitations.

Other, more general, and forward-looking challenges pose interesting opportunities for researchers interested in unique electrochemical interfaces for EHT. By overviewing examples from different impact areas/communities/sub-fields, we can highlight key general themes; these novel systems elevate the degree of complexity of physics and chemistry of interfacial electrochemical phenomena. Even more complexity arises at the intersection of these phenomena (i.e., electrolyte depletion at the surface of functionalized colloidal semiconductor nanoparticle surfaces). While these new interfaces create new parameter spaces to explore, the complexity demands new predictive models and descriptors to advance scientific knowledge on the spatiotemporal and energetic properties of these interfaces. Developing new models of unique electrochemical interfaces as well as new materials and chemistries can spark a revolution in electrochemically generated hydrogen-containing energy carriers.

More broadly, it is an exciting time for basic science research into new forms of energy management. The increasing demand for energy storage from renewable energy generation coupled with increasing investment from governmental and

industrial sectors are driving innovation at remarkable rates. In general, however, it is difficult, if not impossible, to anticipate the needs of future energy utilization technology. Instead, as demonstrated here, it is the attributes or properties of novel energy carriers that will be valuable for assessing their viability in new systems or processes. There are many aspects of energy storage systems beyond the energy density that provide merit. For example, the ability of an energy carrier to be integrated into an industrial process is a critical component of process flow. Here, properties that enable rapid and reliable manufacturing far outweigh simple energy density. In another example, many of the highest performing energy storage systems require unacceptably large quantities of rare elements and replacing scarce materials with organic species or earth-abundant metals is an important goal. It is therefore prudent to think deeply about the unique properties of energy carriers (thermal stability, chemically robust, earthly abundance, biological compatibility, solubility, energy transformation pathways, etc.), and how these properties provide advantages over other forms of energy storage. Hence, we envision that bringing together cross-disciplinary teams to identify core scientific themes and questions that connect different communities will become increasingly important. Such a tact will enable engineers and scientists of the next generation to incorporate these carriers into their technology.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

electrochemical interfaces, energy carriers, energy storage, hydrogen carriers

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