Protonics for Electrochemical Transformations in a Sustainable Future

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1. Introduction

The fact that solar energy reaches the earth at a rate which far exceeds that at which human society currently uses global energy resources is well-established.(*1*) Recognition of this reality sparked the vibrant field of 'solar fuels' in which the energy of the sun is stored in chemical bonds for use on demand, addressing the inherent intermittency of solar energy.(*2*) In the last 15 years since the establishment of large central efforts in solar fuels development, the price of solar electricity has plummeted. Accordingly, the idea of using solar electrons to drive chemical reactions, once considered a staggering waste of a precious resource, is gaining serious traction. Today, solar fuels produced through a two-step process using photovoltaics for electricity generation in the first step and an electrochemical conversion device in the second step are much more attractive than a mere decade ago. The electrochemical conversion technologies being pursued in this context, moreover, need not be limited to solar electrons; they are equally well suited to wind, geothermal, and hydrothermal electricity sources. Thus, solar fuels research has morphed, in some quarters, into electrochemical studies of the transformation of benign reagents such as H_2O, N_2, O_2, and even CO_2 (though certainly not benign!) into value-added products. Of the many electrochemical reactions under consideration, we focus here on splitting water into hydrogen and oxygen, splitting ammonia into hydrogen and nitrogen, and producing ammonia from nitrogen and hydrogen.

Hydrogen has been seen as both hero and villain in a sustainable energy future – hero because the product of using its energy content to carry out useful work is water, and villain because creating hydrogen in the first place has historically resulted in carbon emissions. As an energy carrier, hydrogen is typically treated in the context of polymer electrolyte membrane (PEM) fuel cells, which produce electrical power exceptionally well when the hydrogen is extremely pure. Today's average automotive internal combustion engine operates at an efficiency of $\approx 30\%$(*3*), whereas an automotive fuel cell, as reported by Hyundai, for example, for its Nexo fuel cell vehicle, stands at $\approx 60\%$ system efficiency(*4*). Despite this impressive mark, widespread deployment of hydrogen fuel cells for automotive applications has stalled for a variety of reasons including insufficient PEMFC lifetime and excessive precious metals loadings. Perhaps most significant, however, is the staggering cost of a hydrogen delivery infrastructure.(*5*) Herein lies another aspect of hydrogen as villain. The willingness of policy makers to wait for the completion of such a massive construction project before setting carbon emissions targets has been viewed in some quarters as a stalling tactic. Today, hydrogen as hero is overtaking the image of hydrogen as villain. Use of carbon-free electricity to split water by electrolysis largely eliminates carbon emissions in the production step(*6*), whereas use of liquid hydrogen carriers stands to circumvent the requirement of deploying costly, single-purpose delivery pipelines(*7*). Simultaneously, infrastructure projects for hydrogen delivery have been undertaken in many parts of the world, accelerating the pace at which a transmission solution, of one type or another, will be available.

2. Electrolytes and the Constraints They Imply

Electrochemical transformations involving hydrogen, whether they be electrolysis, electric power generation, or ammonia production, have typically employed one of three types of electrolytes: aqueous acid/base electrolytes with mobile protons/hydroxyl groups; proton exchange polymer electrolytes; or proton conducting oxides. Aqueous electrolytes, as their names imply, are acids typically H_2SO_4 or HCl, or bases, typically KOH or NaOH, in water at some moderate concentration. The most highly deployed polymer in electrochemical systems is the sulfonated fluoropolymer Nafion.[8] Systems based on aqueous liquid or polymer electrolytes are inherently restricted to operation at near ambient temperatures. Accordingly, the are not able to benefit from enhanced reaction rates afforded by higher temperature conditions and thus rely heavily on precious group metal (PGM) catalysts. Moreover, their acid/base nature is inherently corrosive to auxiliary components. Proton conducting oxides (PCOs), typically doped derivatives of $BaZrO_3$ or $BaCeO_3$, on the other hand, require operation at temperatures of ~ 450 °C or higher[9], at which the degradation of auxiliary components is thermally accelerated. Furthermore, these electrolytes permit non-negligible electron hole transport, penalizing the Faradaic efficiency of the transformation of interest.[10]

A relatively underexplored class of proton conducting electrolytes are solid acids which incorporate polyanion groups into their structure. The prototypical material in this class is CsH_2PO_4, cesium dihydrogen phosphate, which adopts a cubic crystal structure with rotational disorder of the H_2PO_4 groups above a polymorphic transition at 228 °C, Figure 1.[11] While some details of the proton transport, an example of the Grotthus mechanism, remain unclear, it is well-established that the rotational disorder is essential to the high conductivity and low activation energy for proton migration. Several compounds display similarly high conductivity (exceeding $\approx 1 \times 10^{-3}$ S/cm with an activation energy of ≤ 0.5 eV) with similar structural disorder, forming the class of materials known as superprotonic conductors.[12] Of these, only CsH_2PO_4 has been considered, to any significant extent, for electrochemical applications, a consequence of its stability in both oxidizing and reducing environments.[13, 14] The temperature of operability of electrochemical devices employing solid acid electrolytes (140 – 280 °C) not only achieves enhanced catalysis rates without accelerating degradation of auxiliary components, but also exposes the device electrodes to gaseous reactants rather than to reactants dissolved in an aqueous (liquid) phase. At first glance, this latter feature might be considered a minor technical difference from operation of lower temperature systems. However, ensuring reactant delivery to reaction sites and removal of gaseous products has, in fact, emerged as a major obstacle to effective operation of aqueous and polymer electrolyte systems.[15]
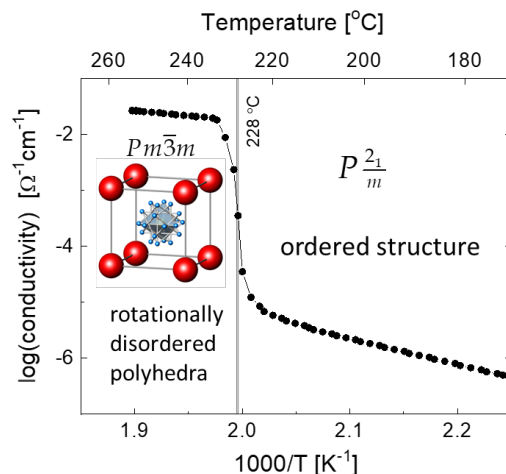
Figure 1. Conductivity of CsH_2PO_4 (cesium dihydrogen phosphate, CDP) showing the superprotonic transport above the polymorphic transition at 228 °C. Inset shows the CsCl-type structure (Cs ion are large red spheres), with the six equivalent orientations of the rotationally disordered $(H_2PO_4)^-$ group. Conductivity measured on heating under a steam partial pressure of 0.4 atm, applied to prevent electrolyte dehydration/decomposition.

The features of the main electrolyte systems are broadly captured in Figure 2. While challenges remain and the case for investing in intermediate temperature systems is strong, remarkable progress has been made in recent years in electrochemical device operation using all three classes of proton transport electrolytes. In light of publications of several excellent reviews of the high and low temperature systems and electrolyte classes, the discussion here provides greater coverage of the intermediate temperature system than the other two.

Ambient to 100 °C	140 °C to 280 °C	450 °C to 650 °C
Aqueous and polymer electrolytes	**CsH$_2$PO$_4$ and derivatives**	**Doped BaZrO$_3$ and derivatives**
Require pgm catalysts	**Under-explored space**	**Electronic leakage**
Corrosive to auxiliary materials	Zero electronic leakage	Poor Faradaic efficiency
Incompatible with gas delivery	Compatible with gas delivery	Poor lifetime of auxiliary materials
	Excellent lifetime	

Figure 2. Comparison of candidate systems for electrolysis based on the nature of the electrolyte (pgm = precious group metal. Aqueous and polymer electrolytes are typically H^+ conductors, but may be OH^- conductors. The high-temperature, solid-state electrolytes are H^+ conductors

3. Electric Power Generation in Fuel Cell Mode

A fuel cell with a proton conducting electrolyte generates electricity by facilitating hydrogen electrooxidation at the anode and oxygen electroreduction at the cathode:

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$ (1)

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (2)

At open circuit, when no electrons flow through the exterior circuit, the cell voltage is ideally given by the Nernst potential, E_N, associated with the sum of the anode and cathode half reactions:

$$E_N = \frac{\Delta_{rxn}G}{4F} = \frac{\Delta_{rxn}G^0}{4F} + \frac{RT}{4F}\ln\left(\frac{\hat{p}_{H_2O,c}^2}{\hat{p}_{O_2,c}\hat{p}_{H_2,a}^2}\right) \tag{3}$$

where $\Delta_{rxn}G$ is the Gibbs energy of the net reaction (hydrogen and oxygen forming water), $\Delta_{rxn}G^0$ is the standard Gibbs energy of the reaction at the temperature of interest, and $\hat{p}_i$ is the pressure of species i relative to the standard pressure (of 1 bar) and is, for systems operated without pressurization, numerically equal to the partial pressure of species i. The subscripts c and a indicate cathode and anode chambers, respectively. In liquid electrochemistry, it is typical to treat the reactants as occurring in their standard states, such that the second term in Eq. (3) falls out, giving the standard Nernst potential, E_N^0. In solid state systems, however, in which gases are supplied to the electrode chambers, accounting for the nonstandard conditions is the norm. In all cases, the Nernst potential and hence expected open circuit voltage is ≈ 1 V (or slightly greater).

Upon drawing current from the cell to deliver electrical power, the voltage drops, and the resulting voltage vs. current density relationship defines the polarization curve, which in turn, defines the power density curve, Figure 3. In the low temperature systems, a non-linear activation voltage loss is typically evident at small values of current density (resulting from low catalytic activity at the electrodes). This feature is typically absent from high temperature systems and the electrodes behavior linearly. Nevertheless, they are often analyzed in terms of Butler-Volmer kinetics, which inherently imply a non-linear voltage-current relationship. Deviation of the open circuit voltage from the Nernst potential is generally attributed to activation losses or fuel cross-over in low temperature systems. In high temperature systems, electronic leakage through the electrolyte is more commonly the culprit.
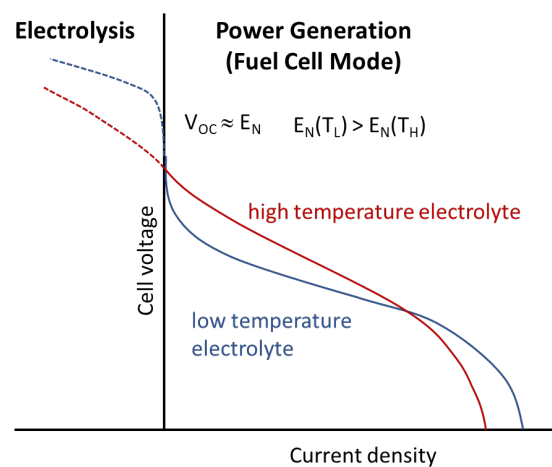
Figure 3. Schematic polarization curves for electrochemical device operation with a hydrogen rich gas supplied to the fuel electrode and oxygen rich gas to the air electrode. In low temperature (near ambient) systems, large overpotentials associated with the electrochemical reactions are typically encountered,

reflected in strongly non-linear behavior near open-circuit (zero-current density) conditions. The open circuit voltage (V_{OC}) is ideally given by the Nernst potential (E_N, Eq. (3)).

The power densities achieved from representative, state-of-the-art PEMFCs, solid acid fuel cells (SAFCs) and protonic ceramic fuel cells (PCFCs) vary widely, Table 1. The relative advantages and disadvantages of these systems extend beyond this single metric, but the comparison is a useful starting point for assessing those additional factors in future efforts.

Table 1. Characteristics of representative, state-of-the-art fuel cells built around proton conducting electrolytes.

System	T, °C	Electrolyte	Cathode	Anode	Power density @ 0.6 V (W/cm^2)
PEMFC(*16, 17*)	70	Nafion	0.30 mg Pt/cm^2 1 atm O_2	0.30 mg Pt/cm^2 1 atm H_2	0.91
SAFC(*18*)	240	CsH_2PO_4[a]	1.75 mg Pt/cm^2 0.6 atm O_2	0.50 mg Pt/cm^2 0.6 atm H_2	0.38
PCFC(*19*)	500	BZCYYb4411[b]	PBSCF[c] air	Ni, 0.97 atm H_2[d]	0.52

[a] 0.4 atm H_2O supplied to both electrodes to suppress electrolyte decomposition
[b] $Ba(Zr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1})O_3$
[c] $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$
[d] balance (0.03 atm) H_2O

4. Electrolysis

Electrolysis using a proton conducting electrolyte proceeds by a 'simple' reversal of the fuel cell reactions. Subtleties arise because the electrocatalysts useful for the forward reactions (fuel cell mode), may not be suitable in the opposite direction. This is particularly true of solid acid systems, in which the Pt catalyst readily undergoes oxidation at the anode under electrolysis conditions. Another subtlety surrounds the voltage required to drive the electrolysis reaction. It is often stated that 1.23 V ($= \dfrac{\Delta_{rxn}G^0}{4F}$) is the minimum voltage for the water splitting reaction. In fact, this is only true in systems in which the hydrogen and oxygen are produced as gases with a pressure of 1 atm, as occurs in liquid electrolysis. At high temperatures, because the gases can attain arbitrary *partial* pressures, steam electrolysis can proceed at lower voltages. Nevertheless, to enable comparison to lower temperature systems, high temperature systems are often operated with 1 atm hydrogen supplied to the fuel electrode (now the cathode) and 1 atm oxygen supplied to the air electrode (now the anode), and the applied voltage/current increases the respective hydrogen and oxygen partial pressures beyond the values at which the gases are supplied. Operation in this manner furthermore enables assessment of suitability of the system to generate high pressure hydrogen. Nevertheless, the possibility of splitting steam at low voltage, well below 1.23 V, should not be discounted as it opens up possibilities of integrating with a broad range of photovoltaic systems with moderate open circuit values. Returning to the typical condition in which reactant gases are supplied at close to standard pressures, operation at 1.4 V results in waste heat generation that balances the endothermic reaction enthalpy, and hence is

termed the thermoneutral point. While high temperature systems provide appreciable current at this voltage, typical low temperature systems require a larger driving force to drive the water splitting reaction. Representative, state-of-the-art electrolysis performance characteristics across the selected systems are summarized in Table 2.

Table 2. Characteristics of representative, state-of-the-art electrolyzers. Here the aqueous system incorporates a hydroxyl (OH⁻) ion conductor rather than a proton conductor.

System	T, °C	Electrolyte	Anode	Cathode	Current density (A/cm^2)
Alkali	25	1 M KOH, O_2 saturated	RuO_2	Pt@C	0.10 @ 1.6 V
PEM[6, 20]	55 (10 bar)	Nafion	--	--	0.47 @ 1.8 V
PCFC[21]	500	BZCYYb4411[a]	PBSCF[b] 0.03 atm H_2O[c]	Ni, 0.97 atm H_2[c]	0.72 @ 1.35 V

[a] $Ba(Zr_{0.4}Ce_{0.4}Y_{0.1}Yb_{0.1})O_3$
[b] $PrBa_{0.5}Sr_{0.5}Co_{1.5}Fe_{0.5}O_{5+\delta}$
[c] balance (0.03 atm) H_2O

Returning to the question of electrocatalyst selection and design, the ideal electrochemical system would support reversible operation between electrolysis and electrical power generation. Such a system would enable chemical energy storage when electricity is available in excess and then provide electricity when demand exceeds the supply available from the wind or solar resource. This strategy has advantages over battery storage because, amongst other benefits, the size of the conversion device and that of the storage unit are decoupled. However, the round trip efficiency of reversible electrochemical cells generally lies below that of batteries, underscoring the need to develop more active catalysts. To date, amongst systems employing proton conductors, only those based on ceramic electrolytes have been operated in reversible mode.[21] In such materials, Faradaic efficiency losses are particularly severe because the electrolyte itself becomes oxidized during electrolysis, increasing its p-type electronic conductivity.[10]

5. Ammonia Oxidation for Hydrogen Production and Power Generation

Amongst potential liquid hydrogen carriers ammonia offers obvious benefits because the product that remains after extracting the hydrogen is benign and abundant N_2. As nitrogen makes up 78% of earth's atmosphere, there is no need to return the depleted carrier for regeneration. This stands in a stark contrast to alternative candidates such as methylcyclohexane, which is transformed to toluene upon dehydrogenation. Furthermore, the mass fraction of extractable hydrogen is highest for ammonia amongst candidate carrier and many parts of the world already have an extensive ammonia delivery infrastructure due to the tremendous importance of this molecule to agriculture.

Electrooxidation of ammonia in an electrochemical system based on a proton conducting electrolyte involves the following anode reaction:

Anode: $2NH_3 \rightarrow 3N_2 + 6H^+ + 6e^-$ (4)

For direct use of the ammonia in power generation, this anode reaction is coupled to the same cathode reaction relevant to a hydrogen-powered fuel cell. For production of hydrogen, the cathode reaction is the hydrogen evolution reaction, identical to that which occurs in electrolysis. The toxicity of ammonia renders it unlikely to be used in consumer applications, in particular passenger vehicles. A more plausible scenario is one in which ammonia is 'electrolyzed' into hydrogen and nitrogen at distributed locations at which passenger vehicles are supplied with hydrogen to operate conventional PEMFCs. Here the challenge is the extreme toxicity of ammonia to the PEMFC anode catalysts. Thus, the electrochemical production must yield high purity hydrogen, in addition to operating at low overpotential so as to minimize the electrical energy input and thus the cost of the process. Additionally, it is imperative to avoid oxidation of the nitrogen that would generate NO_x, an all-too-common product in low temperature systems.[22] In this application space, solid acid electrochemical cells have taken the lead. The author's laboratory has demonstrated 100 % Faradaic efficiency for extraction of H_2 from NH_3, achieving a hydrogen production rate of 3 ml(H_2) min^{-1} cm^{-2} at a total operating voltage of just 0.39 V using a dual-layer anode, with Cs-promoted Ru serving as an ammonia decomposition catalyst and Pt as a hydrogen electrooxidation catalysts.[23] At the temperature of operation of 240 °C, the Pt electrocatalyst is not poisoned by the residual NH_3 remaining after the gas passes the decomposition layer and no NO_x gases are formed. The combination of performance metrics achieved is unrivalled. Nevertheless, opportunities for further decreasing the voltage requirement and increasing the catalyst lifetime remain.

6. Electrosynthesis of Ammonia

Electrosynthesis of value-added chemicals using proton conducting electrolytes is a nascent area. In addition to N_2 reduction to generate NH_3, the reverse of Eq. (4), CO_2 reduction has garnered significant recent attention. The former has clear significance in terms of a hydrogen delivery infrastructure; the role of the latter in a sustainable future is unclear. Ammonia today is produced by the famed Haber-Bosch process, in which H_2 and N_2 are reacted under high temperature, high pressure conditions. Ammonia synthesis is recognized as a significant source of CO_2 emissions, but this is largely because the hydrogen used in the process is derived from fossil fuel steam reforming.[24] The energy input (for reaching the high pressure conditions for reacting H_2 and N_2) amounts for just 15-20 % of the total[25], thus even today's technologies, if combined with carbon-free hydrogen, have real potential for reducing the carbon foot-print of ammonia production. Electrochemical synthesis offers two possible advantages: (1) The voltage in the device generates an effective high pressure, at least of hydrogen, that is much higher than can be reached by mechanical pumping. In turn, this pushes the system thermodynamics to favor NH_3 production over retaining the H_2 and N_2 reactants, opening a possible route to increasing the energy efficiency of the process. (2) The reactor conditions can be achieved in small, modular systems, as compared to the immense plants currently deployed in the Haber-Bosch plants, democratizing access to the technology. In the latter case, large systems are required to render the cost of investing in high pressure equipment profitable.[26]

The chemical challenge of ammonia electrosynthesis arises from the facile evolution of H_2 at the device cathode, which can then outcompete N_2 reduction. To date, no electrocatalyst system

meeting the efficiency requirements for cost-competitive ammonia production has been reported.(*27*) Furthermore, in several cases, background NH_3 has exceeded the amount generated, sending researchers along unproductive paths.(*28*) This challenge notwithstand, systems based on proton conducting oxides, typically fabricated with Ag-Pd electrodes, have shown the most promise; ammonia production rates in the range of 1 to 5×10^{-9} mol s^{-1} cm^{-2} having been reported by several laboratories using such cells.(*29*) Perhaps the most intriguing results have been obtained using a protonic ceramic electrolyte in conjunction with a metal nitride cathode, VN.(*30*) The hypothesis here is that the cathode reaction proceeds via a Mars-van Krevelen mechanism in which protons react with nitrogen atoms in the lattice, and the resulting vacancies are refilled by dissociated gas-phase nitrogen. The rate of ammonia production was an impressive 8×10^{-9} mol s^{-1} cm^{-2} at 0.3 V overpotential and a temperature of 550 °C. Suppression of the hydrogen evolution to increase the Faradaic efficiency beyond the $\approx$ 5% observed is surely the next target for this line of investigation.

7. Concluding Remarks

The dramatic decline in the price of wind and solar electricity opens up new possibilities for the use of carbon free electrical power to generate useful chemicals. At the same time, the intermittency of these sources necessitates renewed focus on energy storage for on-demand use. Hydrogen production by electrolysis, a possible storage strategy, is approaching commercial viability. In fact, even today, about 4% of the world's hydrogen is produced by electrolysis. Shipping hydrogen, however, remains daunting. Ammonia is an intriguing potential solution to this challenge. The decomposition of ammonia to generate high purity hydrogen has been demonstrated. Achieving technoeconomic success in ammonia electrosynthesis, the other half of the ammonia-as-hydrogen-carrier approach, awaits breakthroughs in catalyst design, with nitrides currently the leading contenders to address this need.

8. Acknowledgements

9. References

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