Storage of Intermittent Renewable Energy:

A comparison of proton exchange membrane fuel cells with comparable methods of energy storage

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May 2015

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## Abstract

Proton exchange membrane fuel cells have increasingly been cited for their potential role in the storage of renewable energy. This paper demonstrates how renewable energy is an essential aspect of future sustainable development and how the storage of that energy is integral to its successful implementation into current energy systems. The various methods of energy storage are briefly reviewed and their utility for storing intermittent renewable energy is compared against proton exchange membrane fuel cells. Both the quantitative and qualitative measures of assessment show that proton exchange membrane fuel cells offer several key advantages over alternative methods, as they have high energy density, minimal local and extraneous environmental impacts, and are more easily integrated into small to medium scale uses of energy. The greater effects of theoretical implementation are also addressed, specifically in how these devices may quell the emissions of greenhouse gases and the progression of anthropogenic climate change, alter the distribution networks for electrical energy, increase the promotion of geographically diffused energy generation, and modify how societies obtain energy.

# Introduction

This paper broadly addresses the need for the storage of alternative energy within future energy markets and specifically examines the role that proton exchange membrane fuel cells (PEMFCs) can play within future systems. In order to situate this technology, the prevalent modes of energy storage are examined and compared with PEMFCs. For each technological method of energy storage, the efficiency, energy density, capacity, and other empirical parameters are presented in addition to qualitative assessments that seek to show the greater impacts and applications of each technology. The weight given to each method depends on its potential for energy storage and similarity to PEMFCs. The theory, applications, most recent advancements, and research goals for PEMFCs are covered as they offer several distinct advantages over other modes of energy storage, but are currently economically inhibited from widespread use for a number of reasons. In the final section, the greater potential influences of PEMFCs on the emission on carbon containing greenhouse gases, energy policy and economics, and they ways in which people both use and generate energy are articulated.

# Background

#### **History of Energy Use**

The Holocene is the first geological epoch in which a singular species has participated in the definition. This demonstrates how human impact on the world has been documentable for over 10,000 years and immensely widespread over the past 250 years. In a simplified world history, two key advancements have enabled this progression: the advent of agriculture and utilization of fossil fuels. The development of agriculture has allowed humans to assume a growth pattern in which resources availability increases with population. As such, there are now over 7 billion human inhabitants on earth. The source of energy throughout the Holocene has been largely carbon-based, and since the industrial revolution, has been dominated by fossil fuels.

Fossil fuels have been the primary source of energy over the last 250 years as they have high energy densities and ease of  $access^1$ . These fuels extract energy stored in carbon-containing fuels and consequently result in a net increase in atmospheric carbon-containing greenhouse gases upon use. These sources of energy will be referred to as 'traditional energy' and are primarily coal, oil, natural gas, and unsustainably harvested biofuels. These fuels enable our civilizations to function; they are necessary to grow our food, manufacture goods, transport people, heat homes, and have firmly cemented roles across all aspects of modern life. In 2012, the global primary energy supply<sup>2</sup> was 5.6 x  $10^{20}$  J, or nearly 18 TW per year.<sup>3</sup> For reference, this corresponds to the same energy as the typical annual electricity consumption of 14 trillion US

<sup>&</sup>lt;sup>1</sup> Poizot, P.; Dolhem F. Clean Energy New Deal for a Sustainable Future *Energy Envrion*. Sci. **2011**, 4, 2003-2019.

<sup>&</sup>lt;sup>2</sup> Primary energy is energy that can be extracted from a substance that exists in nature without transformations. For example, coal is a primary energy source while electricity is not.

<sup>&</sup>lt;sup>3</sup> International Energy Agency. Key World Energy Statistics, 2014,

http://www.iea.org/publications/freepublications/publication/keyworld2014.pdf (accessed March 8, 15).

households<sup>4</sup>. Of this energy, just three fuels provided 82% of global supply: oil, coal, and natural gas. Across the developed world, these fuels are still relatively cheap and available, and are both used directly and indirectly. The majority of these fuels are converted in some manner to make them more useable for specific applications. For oil, this involves refinement. Both coal and natural gas are largely combusted in large generation plants to produce heat used to generate electricity, which is then distributed along a grid to consumers.

The physical characteristics of these fuels are the key to their utility. Traditional energy sources are stable over time, easily stored and transported, and can produce power at various intensities and time-scales. This enables them to be used for a wide variety of uses. Both coal and oil are easily transported in simple containers, and natural gas can either be compressed or liquefied to increase its energy density and transportability. The energy density for these fuels, along with gasoline for reference, is shown below in table 1. A higher energy density is beneficial as the fuel requires less energy to be transported and is especially important for mobile applications. It is beneficial for stationary applications as well considering it is easier to store.

Fuel	Coal	Oil	Compressed	Liquid Natural	Gasoline
			Natural Gas	Gas	
Physical State	Solid	Liquid	Gas	Liquid	Liquid
Energy-mass ratio	2.420	5.143	2.371	2.505	2.485-2.566
[J/kg] x 10 <sup>7</sup>					

**Table 1.** This table shows key properties of common fossil fuels. Data represents an average value, which will vary depending on the quality of the fuel and its use.<sup>5</sup> Compressed natural gas is typical stored at 140-200 atm and takes up 1% of the volume of natural gas under standard conditions (1 atm, 25 °C). Liquid natural gas is stored cryogenically and occupies 0.17% of the volume of natural gas at standard conditions (1 atm, 25 °C).

We can see from the data in table 1 that fossil fuels have energy-mass ratios on the order of about  $10^7$  J/kg. This unit will be important when trying to access the utility of energy storage

<sup>&</sup>lt;sup>4</sup> US Energy Information Administration. How much electricity does a typical American home use? http://www.eia.gov/tools/faqs/faq.cfm?id=97&t=3 (accessed March 8, 2015).

<sup>&</sup>lt;sup>5</sup> Alternative Fuels Data Center. Fuel Properties Comparison.

http://www.afdc.energy.gov/fuels/fuel\_comparison\_chart.pdf (accessed March 8, 2015).

<sup>&</sup>lt;sup>6</sup> Petrowiki. Compressed natural gas (CNG). http://petrowiki.org/Compressed\_natural\_gas\_%28CNG%29 (accessed March 9, 2015).

devices, as it represents an energy density we are used to. Devices that can provide a similar density of energy will be more easily integrated into existing systems.

Ubiquitous use of fossil fuels will have largely negative impacts of an unknown magnitude on global climate patterns due to a rise in average global temperature as a result of the greenhouse effect. These impacts will affect billions of people and alter the way in which humans interact with their environment. Furthermore, the increasing scarcity of these fuels will exacerbate the existing inequalities with energy access. These two issues serve as the most important motivations to pursue alternative energy. These issues contrast the scarcity argument often cited as motivation to decarbonizes energy systems. As fossil fuels are a finite resource, the diminishing supply of these fuels has historically been cited as a primary motivation to pursue alternative sources of energy. In doing so, energy security and supply would be preserved. However, recent advancements in extraction technology, particularly the hydraulic fracturing of shale to extract natural gas (fracking), have enable previously inaccessible reserves of fossil fuels to be extracted. As the extent of fossil fuel supplies remains ambiguous and methods of extraction continue to open up new reserves, diminishing supply is no longer the definitive motivation for perusing alternative energy. However, even if it is not economically viable to promote alternative energies in lieu of fossil fuels, the environmental and social motivations to decarbonize energy systems are overwhelming. Despite difficulties in generating concrete projections for the remaining supplies of fossil fuels, the negative consequences of using these fuels are only becoming clearer. The potential impacts from further reliance on fossil fuels demonstrates the need for alternative energy sources that will allow for a more sustainable energy system.

#### **Alternative and Renewable Energy**

There are many alternative options for energy generation; therefore it is important to carefully define the criteria for both alternative and renewable energy. The former encompasses the latter, and is defined simply as energy derived from non-fossil fuel sources. These are primarily nuclear, wind, solar, geothermal, tidal, sustainably produced biofuels, hydroelectric, and biomass. Renewable energy has a stricter definition, as is defined as energy that comes from sources that are replenished on a human time scale and have limited or redeemable

environmental impacts. All alternative energy mentioned above is considered renewable under this definition except nuclear energy. These sources of energy may be generally referred to as 'renewables'.

As demonstrated above, the development of alternative energies is promoted as a necessary development in order to mitigate the most extreme effects of climate change, to diversify and increase energy security, and, arguably most importantly, to mitigate the increasing gap between the have's and the have not's of the world. However, both developing and implementing renewable technologies remains a great challenge. In 2012, alternative energy produced 18% of the world's energy needs. Approximately half came from sustainable biofuels, and the rest was distributed among more advanced technologies.<sup>7</sup> Of these, nuclear supplied the most, followed by hydroelectric power, solar, and wind. Geothermal, tidal, and other niche methods made small contributions as well. Hydroelectric supplies approximately 2.4% of global energy and is the leading renewable energy. However, most of the potential capacity for hydroelectric power has already been installed and thus this type of power will be unable to provide for growing energy needs. Geothermal, tidal, and other niche methods supply a very small amount of global energy, with a combined contribution of 0.5% of global energy supply. Growth in these techniques is geographically limited making it unlikely for them to make up a larger proportion of future renewable energies.<sup>8</sup>

The role that traditional energy, renewable energy, and energy storage play in future energy markets is often glossed over in current literature. To situate the role of energy storage within energy markets, a brief clarification is offered. As stated previously, traditional energy comes from primary energy sources. These have been in ample supply but will last for a finite amount of time. Due to the constraints we need to find new sources of primary energy. An immense amount of this exists in nature, in the forms of solar, wind, and hydrological energy. Attainable geographical wind energy is approximately 6 x  $10^{19}$  J, or 11% of the current global energy supply. Hydro has a similar value of 5 x  $10^{19}$  J. Attainable solar energy, assuming a

<sup>&</sup>lt;sup>7</sup> International Energy Agency. Key World Energy Statistics, 2014,

http://www.iea.org/publications/freepublications/publication/keyworld2014.pdf (accessed March 8, 15). <sup>8</sup> REN21. Renewables 2014 Global Status Report.

http://www.ren21.net/portals/0/documents/resources/gsr/2014/gsr2014\_full%20report\_low%20res.pdf (accessed March 8, 2015)

modest 10% conversion rate for collection panels, is  $2 \times 10^{21}$  J, a staggering 338% over current global supplies.<sup>9</sup> While these numbers have many assumptions built into them, we can see that solar energy can provide over an order of magnitude more energy than we currently use, and is the only energy source that can make up a majority of renewable energy systems. Both solar and wind produce power at variable rates that are subject to natural fluctuation. Due to these fluctuations, they must be converted into more useful forms, stored for later use, and released at a consistent rate.

In summary, energy storage must be designed for the storage of renewables, and must be particularly compatible with solar energy. Solar energy is an example of an intermittent renewable energy, defined as energy from a renewable source that has an element of production essential to the generation of power that is outside of operator control and variable in nature within a 24-hour period. These sources have difficulties in utility, as they are not easily integrated into current distribution networks, and many current energy storage methods are best with a constant energy input.

# **Methods of Energy Storage**

The role of alternative energy in supplementing and securing energy systems has been well demonstrated. Additionally, renewable energy will play an integral role in diversifying energy systems sustainably. However, energy storage remains the biggest challenge for the increased use of many renewable energy sources.<sup>10</sup> By the year 2040, renewable energy is projected to be the second largest source of new electrical generation (behind natural gas) and will account for 33% of global power supply, according to the most recent *International Energy Agency* report.<sup>11</sup> The growth rates in this model from various energy sources would result in renewables accounting for nearly half of the new power generation by 2040.

<sup>&</sup>lt;sup>9</sup> Lewis, N. L. Chemical Challenges in Renewable Energy Cal. Inst. of Tech.: Pasadena CA.

 <sup>&</sup>lt;sup>10</sup> Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future *Nature* 2012, 488, 294-303.
<sup>11</sup> International Energy Agency. World Energy Outlook 2014 Factsheet.
http://www.worldenergy.outlook.org/media/waawabsite/2014/141112\_WEO\_FactSheets.

http://www.worldenergyoutlook.org/media/weowebsite/2014/141112\_WEO\_FactSheets.pdf (accessed Feb 19, 2015).

Renewables, particularly solar and wind, supply intermittent power as these sources only produce energy when the sun is shining or the wind is blowing. Consequently, it is necessary to normalize their irregular contributions to the total power supply so that the load placed on the power grid is accurately met. This is achieved in several ways, depending on the degree of influence the intermittent energy has on the overall grid and the time-scale of interaction. On the scale of seconds to minutes, power stabilization is achieved through large banks of capacitors, spinning reserves<sup>12,13</sup>, batteries, and mechanical flywheels. These methods account for minimizing variation in power output from both conventional and renewable energy sources by storing and releasing small amounts of energy. For energy variation on the scales of minutes to hours, spinning reserves, quick acting natural gas plants<sup>14,15</sup>, and hydroelectric generating stations (including both pumped and non-pumped hydro), can adequately account for variation in intermittent renewable energy power output. As a consequence of these methods, energy storage over time frames ranging from seconds to hours is largely achieved with known and demonstrated methods. However, moving to longer time scales from hours to overnight, global energy storage capacities ranging from  $1.9-45.0 \times 10^{16}$  J will be needed by 2040 to ensure power is supplied consistently as the proportion of intermittent energy increases.<sup>16, 17</sup> Current energy storage capacity is a meager  $1.4 \times 10^{14}$  J, and meeting future goals will require innovative methods.

In order to understand the best method to meet future energy goals we must first identify the characteristics of a good energy storage system to effectively compare and contrast various methods. At the most essential level, an efficient energy storage system will have the ability to return a high proportion of the energy initially invested. This concept is referred to as energy

<sup>&</sup>lt;sup>12</sup> Spinning reserve refers to generators that are operating in synchronization with the grid but are either not being used to supply power to the grid, or are only operating at partial capacity. As such, they can quickly be brought online at the discretion of the system operator.

<sup>&</sup>lt;sup>13</sup> Rebours, Y.; Kirschen D. What is spinning reserve?; The University of Manchester: Manchester, UK, 2005.

<sup>&</sup>lt;sup>14</sup> Power supply is composed of both base load power plants and peak load power plants. Peak load power plants are able to adjust their power output through out the day and are typically powered by natural gas.

<sup>&</sup>lt;sup>15</sup> Hynes, J. How to Compare Power Generation Choices, *Renewable Energy World (N.A. Ed.)* [Online], October 2009. http://www.renewableenergyworld.com/rea/news/article/2009/10/how-to-compare-power-generation-choices (accessed Feb 23, 2015).

<sup>&</sup>lt;sup>16</sup> This storage capacity was calculated assuming 30% of global energy supply comes from storage for time-scales ranging from 1-24 hours.

<sup>&</sup>lt;sup>17</sup> Chu, S.; Majumdar, A. Opportunities and challenges for a sustainable energy future *Nature* **2012**, 488, 294-303.

return on investment (EROI), which is a ratio that measures the amount of energy returned by a process over the energy initially invested, and is calculated by the simple equation below.<sup>18</sup>

# $EROI = \frac{Energy return of process}{Energy loss of process}$

A more efficiency energy storage system will have a higher EROI. As both the numerator and the denominator are both in units of energy, the resulting ratio is a dimensionless measurement of efficiency. This is very useful metric to assess the use of energy storage, but additional factors must be evaluated. For example, if one type of energy is converted to another, e.g. electricity is used to generate hydrogen, the characteristics of each medium of energy must be considered. Furthermore, it is important to factor in more than energy efficiency when determining the utility of an energy storage system. In addition to a high EROI, better energy storage systems will have some or all of the following criteria: 1) high-energy density, 2) high capacitance, 3) fast discharge and recharge rates, 4) minimal energy loss over time, 5) efficient coupling with an existing system of power generation, 6) cost effective, 7) high cycle-life, and 7) minimal impacts on natural phenomena. These criteria make up the basis from which energy storage systems can be judged upon, and each method will have its own strengths and weaknesses.

The basic ways in which we store energy belong to five categories: mechanical, thermal, electrical, electrochemical, and chemical. Many methods exist for storing energy within each category, each of which has distinct advantages and disadvantages. This section will explore the primary types of energy storage used today and compare their utility with hydrogen as an energy carrier based on the criteria outlined in the preceding paragraph. The most common type of energy storage that offers potential storage of energy from renewables are batteries, thermal energy storage, mechanical flywheels, power to gas, and pumped-storage hydroelectric. Compressed air energy storage (CAES) is included in this analysis given it is a highly efficient

<sup>&</sup>lt;sup>18</sup> Hall, C. A.; Energy Return on Investment. In *The Energy Reader: Overdevelopment and the Delusion of Endless Growth;* Bulter, T. et al., Eds.; Watershed Media: Healdsburg, CA, 2012.

method of storing energy, though it is not compatible with intermittent renewable energy. These methods will each be examined in brief detail and compared to PEMFCs.

#### **Batteries**

Batteries are perhaps the most familiar method of energy storage. A battery is a closed system that can convert stored chemical energy into electrical energy through the application of a load. Once a battery's stored chemical energy has been exhausted, applying a potential voltage to the cell can restore the electrochemical potential. The most familiar type of battery is the lithium-ion battery (Li-ion), which has the highest energy density among batteries.<sup>19</sup> The density of the batteries, combined with their durability and low operating temperature, makes them ideal for small-scale use, primarily in portable electronics and transportation. Additionally, they have a very low self-discharge rate and a high cycle-life. Li-ion batteries typically cost three times as much as other batteries, meaning they suffer an economic disadvantage when considering them for use in large scale, stationary applications. Lead-acid (PbA) batteries are comparatively cheaper, simpler to manufacture, and have the lowest self-discharge rate of any battery. The primary disadvantages of PbAs are a low recharge rate and a low cycle-life.<sup>20</sup> Batteries that are more suitable for grid energy storage and stabilization include sodium-sulfur and redox-flow batteries.<sup>21, 22</sup>

Redox-flow batteries utilize the oxidation and reduction of a liquid electrolytic solution, where energy is stored by reducing a solution and can be released by oxidizing the same solution. Benefits of this method are high scalability, as a larger tank can be built to store more electrolytic solution. The reduced solution can be stored almost indefinitely, and the rate at which energy is released is highly tunable. The primary downfall of this technology currently is that it has a very low energy density.

<sup>&</sup>lt;sup>19</sup> Scrosati, B.; Hassoun J.; Sun, Y.K. Lithium-ion batteries. A look into the future *Energy Environ*. *Sci.* **2011**, 4, 3287-3295.

<sup>&</sup>lt;sup>20</sup> Ghiassi-Farrokhfal, Y. et al.; An EROI-Based Analysis of Renewable Energy Farms with Storage. In *e-Energy* 

<sup>&#</sup>x27;14, Proceedings of the 5<sup>th</sup> international conference on Future energy systems. Cambridge, UK, June 11-13.

<sup>&</sup>lt;sup>21</sup> Dunn, B.; Kamath, H.; Tarascon, J. M. Electrical Energy Storage for the Grid: A Battery of Choices *Science* **2011**, 334, 928-935.

<sup>&</sup>lt;sup>22</sup> Alotto, P; Guarnieri M.; Moro, F. Redox flow batteries for the storage of renewable energy: A review *Renewable* and Sustainable Energy Reviews **2014**, 29, 325-335.

# **Thermal Energy Storage**

Thermal energy storage is a broad category in which thermal energy is stored in a medium and used to generate heat to produce steam and power a turbine. The media of storage vary greatly, and range from earth, to water, to more technologically advanced (and expensive) options such as molten salt. The most developed type of thermal energy storage is pumped heat electrical storage (PHES). In this process, a heat pumped powered by electric is used to drive energy from a cold sink to a heat sink. Adiabatic containers maintain the thermal differential until the energy is needed, at which time heat is transferred via a gas from the heat sink to the cold sink to power a heat engine. The overall efficiency can approach 75-80%, although it diminished as storage time increases, considering the heat and cold sinks are not perfectly adiabatic.<sup>23</sup>

# Flywheels

Flywheels are able to store electrical energy as mechanical energy in the form of kinetic energy. Although the basics of a flywheel are familiar to many, technical flywheels used for grid energy storage have several distinctive features. The primary loss of energy for flywheels is heat resulting from friction. Friction is minimized by placing the flywheel in a vacuum and using permanent and electromagnetic bearings as stators that the flywheel is not in physical contact with its support. A single flywheel can have a capacity of up to  $9 \times 10^5$  J, and is able to absorb or discharge energy instantaneously. The downside is that they are capital intensive, and have high losses over time, ranging from 3-20% per hour. As a result, flywheels are unable to effectively store energy for more than several hours and thus are very limited in the storage of intermittent renewable energy.<sup>24</sup>

<sup>&</sup>lt;sup>23</sup> Pumped Heat Electrical Storage (PHES). Energy Storage Association: Energy Storage Technologies.

http://energystorage.org/energy-storage/technologies/pumped-heat-electrical-storage-phes (accessed Feb 22, 2015). <sup>24</sup> Oberhofer, A.; Meison, P. Energy Storage Technologies & Their Role in Renewable Generator; Global Energy Institute, 2012.

#### Power to Gas

Power to gas (P2G) is a method of converting electrical energy into gaseous fuel.<sup>25</sup> There are currently three pathways for this particular type of conversion, and all utilize the electrolysis of water to generate hydrogen that is then combusted or reacted in a variety of ways. In the first method, generated hydrogen is used to directly supplement the natural gas grid. The second method utilized the Sabatier reaction, where hydrogen is reacted with carbon dioxide to form methane and water. The methane is then used to supplement the natural gas grid. In the third method, hydrogen is mixed with a biogas, where it can undergo a Sabatier reaction to improve the quality of the biogas. These methods have been demonstrated to store the energy generated from intermitted renewable energy at an efficiency rate of more than 60%. They have been shown to pair more efficiency with intermittent renewable energy than with traditional energy sources with regards to environmental impacts.<sup>26</sup> This is largely due to the ability of renewable energy to produce very cheap electricity during off-peak hours while traditional power generation is fully utilized during this period to supply a base load of power to the grid. This type of technology is relatively new, and does not yet make up a significant portion of energy storage, although several countries, namely Germany, are invested in developing the technology.<sup>27</sup> It has the distinct benefit of being easily integrated with existent natural gas networks. However, further research is necessary to improve efficiencies so that this technology can compete economically with other methods of energy storage.<sup>28</sup> A very important aspect of the process is that it does not generate a net increase in greenhouse gases, as seen in the scheme below.

<sup>&</sup>lt;sup>25</sup> Germany: Trade and Invest. Power-to-Gas Technology.

http://www.gtai.de/GTAI/Navigation/EN/Invest/Industries/Smarter-business/Smart-energy/power-to-gas.html (accessed Feb 22, 2015).

<sup>&</sup>lt;sup>26</sup> Reiter, G.; Lindorfer J. Global warming potential of hydrogen and methane production from renewable electricity via power-to-gas Int. J. of Life Cycle Assessment. [Online] **2015**, http://link.springer.com/article/10.1007/s11367-015-0848-0/fulltext.html (accessed Feb 23, 2015).

<sup>&</sup>lt;sup>27</sup> Germany: Trade and Invest. Power-to-Gas Technology.

http://www.gtai.de/GTAI/Navigation/EN/Invest/Industries/Smarter-business/Smart-energy/power-to-gas.html (accessed Feb 22, 2015).

<sup>&</sup>lt;sup>28</sup> Walspurger, S. et al. CO<sub>2</sub> Reduction to Substitute Natural Gas: Toward a Global Low Carbon Energy System *Isreal J. Chem.* [Online] **2014**, 54, 1432-1442.

$$CO_2 + 4 H_2 \longrightarrow CH_4 + 2 H_2O$$
$$CH_4 + 2 O_2 \longrightarrow CO_2 + 2 H_2O$$

**Figure 1.** The chemical pathway of the P2G method of energy storage is seen. The first reaction is mildly exothermic while the second is intensity exothermic.

#### **Pumped Storage Hydroelectric Power**

Pumped storage hydroelectric generating stations use electricity to pump water from a lower to a higher reservoir. This energy can be recovered by releasing the water from the upper reservoir to power a generator, and the overall efficiency can exceed 80%.<sup>29</sup> This system is currently used to store both intermittent renewable energy and traditional energy, where water is pumped during times of low demand at a low cost and then used to generate electricity during times of high demand, which can be sold at a high cost. The primary benefits of this system are its responsiveness to power demands from the grid, so it can easily normalize irregularities in power demand on an hour to daily basis. Once established, a pumped-hydro station can be cycled thousands of times, and the system has very little loss in energy over time. The water can be stored indefinitely, given losses due to ground water seepage and evaporation are minimal. However, pump-hydro is geographically restricted because it needs appropriate water resources and a suitable location for an upper and a lower reservoir.<sup>30</sup> The installation of a pumped hydro storage system requires drastic land use change, as at least one, if not two reservoirs are constructed (an existing body of water can be used for one reservoir). Furthermore, the hydrologic ecosystem that the energy storage system exists with can be altered as water temperature, nutrient concentration, turbidity, flow, and many other factors are affected.

# **Compressed Air Energy Storage**

Compressed air energy storage (CAES) is a widely used and economically efficient method of storing energy on a large scale. The principle relies on filling an underground geologic cavern with compressed air. This air can then be heated and released and used to spin a gas

<sup>&</sup>lt;sup>29</sup> Rehman, S. et al. Pumped Hydro Energy Storage System: A technological review *Renewable and Sustainable Energy Reviews* **2015**, 44, 586-598.

<sup>&</sup>lt;sup>30</sup> Pumped Hydroelectric Storage. Energy Storage Association: Energy Storage Technologies. http://energystorage.org/energy-storage/technologies/pumped-hydroelectric-storage (accessed Feb 22, 2015).

turbine generator. CAES effectively decouples the compression and expansion cycle of a conventional gas turbine to allow the temporal separation of the use of a fuel and the generation of electricity. The primary benefit of CAES is the large power capacity that a single CAES site can hold, as their capacity can vary from 1.8 to  $10.8 \times 10^{11}$  J. CAES is also relatively temporally stable; the compression can last for more than a year. The efficiencies for these systems typically range from 60-80%, and capital investments range from \$400 to 800 per kW. Combined, these factors make CAES the leading energy storage method.<sup>31</sup>

The CAES drawbacks are that sites are geographically confined. The underlining technological foundation is geologically restricted, specifically to requiring a large and stable geological cavern or aquifer. As such, the application of this system is limited to specific geological contexts. Although geologic caverns are not rare over a wide swath of land, they must be in close proximity to a large gas turbine plant in order for a CAES system to be economically feasible. It is this factor that results in the implementation of a small number of CAES systems in a highly economic manner. It is important to highlight that CAES cannot be paired with coal-fired, nuclear, wind, or solar plants.

## **Summary of Storage Methods**

There are many factors that affect the utility of an energy storage system, ranging from technical parameters to environmental effects. As a result, the direct comparison is difficult and each system should be evaluated with the appropriate context. The following table offers a comparison of empirical parameters of all the systems reviewed here and PEMFCs.

<sup>&</sup>lt;sup>31</sup> Chen, H.; Zhang, X.; Liu, J.; Tan C. Compressed Air Energy Storage. In *Energy Storage–Technologies and Applicatons*; Ahmed Faheem Zobaa Ed. Intech: 2013, pgs 101-112.

Method	Energy Density	Capacitance	Discharge	Response	Energy loss	Cycle-life x	Round-trip	Cost	Scalability
	[J/kg] x 10 <sup>4</sup>	[J] x 10 <sup>13</sup>	[MW/h]	time	(per hour)	10 <sup>3</sup>	Efficiency	[\$/J/cycle-life] x 10 <sup>13</sup>	
Li-ion	36.0-72.0	7.2	16	ms	8%-20%	4-8	95%	54-72	High
Na-S	43.2-54.0	3.6	34	S	0%	4.3-6	85-90%	32-47	Medium
RFB	3.6-18.0	2.2-43.2	0.2-100	ms	0%	13	85%	25	High
TES	25.2	3.6	20	min	varies	10	-	180	Low
Flywheel	4.0-10.8	1.8	0.3	min	3%-20%	10-100	85%	9-72	High
P2G	-	-	-	days	-	-	42-58%	-	Low
Pumped	0.1	36000	300	min	0%	-	70-85%	0.2-1.1	Medium
Hydro									
CAES	3.6-10.8	3600	30-300	min	0%	-	60%	1.5-6.5	Low
PEMFC	288.0-468.0	3.6	1	ms	0%	200	70%	72	High

**Table 2.** Maximum performance parameters for lithium ion batteries (Li-ion), sodium sulfur batteries (Na-S), redox flow batteries (RFB), thermal energy storage (TES), flywheel, power to gas (P2G), pumped hydro, compressed air energy storage (CAES), and proton exchange membrane fuel cells (PEMFCs) gathered from recent literature.<sup>32</sup>

One very important quality common to all energy storage systems, but varying in degrees, is their ability to be used for arbitrage. As energy markets have daily periodic fluctuations in demand, the price of electricity, or the value of energy, changes accordingly. If electricity can be produced during off-peak hours when demand is low and the value of energy is lower and stored until it can be sold during peak hours when the demand and value of energy are higher, the price differential between high value and low value energy markets can be profited upon. To be able to participate in energy arbitrage, a storage system must be able to be charged with a type of low-value energy, such as energy produced during off-peak hours or intermittent renewable energy.

# **Proton Exchange Membrane Fuel Cells for Energy Storage**

The former discussion has demonstrated that energy storage is a very diverse and challenging field in which a myriad of approaches have been used to temporally separate the generation and consumption of power. A unique approach that offers comparable efficiency and other key benefits to prevalent methods is achieved through the pairing of intermittent alternative energy, the electrolysis of water, and the operation of hydrogen fuel cells. This process will be discussed in detail below, including the energy attributes of hydrogen, methods of sustainable

<sup>&</sup>lt;sup>32</sup> Alotto, P; Guarnieri M,; Moro, F. Redox flow batteries for the storage of renewable energy: A review *Renewable* and Sustainable Energy Reviews **2014**, 29, 325-335.

generation, and the controlled generation of energy through the operation of hydrogen fuel cells. Although there are many types of fuel cells, this paper will specifically address PEMFCs as they are most suitable for renewable energy storage.

## Hydrogen as an Energy Carrier

Hydrogen has continually been cited as an energy rich fuel that has a wide range of uses in future energy systems with minimal environmental impacts <sup>33</sup>. The primary benefits of utilizing hydrogen as a fuel include a high energy-mass ratio, very low greenhouse gas emissions at the point of use<sup>34</sup>, diversification of energy supply energy, and the ability to act as a substituent for many current fuels<sup>35</sup>. Hydrogen is not a primary fuel itself, as molecular hydrogen does not exist freely on earth. It must first be generated from a range of compounds, typically either water or methane. Consequently, it is best to consider hydrogen as an energy carrier, as it is simply a medium that facilitates the transfer of energy from one form to another. An apt analog to hydrogen is pure electricity, as both things do not exist freely in nature but can be generated and used for work.

Once generated, hydrogen can be combusted to produce heat or react electrochemically with oxygen to produce electricity. The energy content of hydrogen gas varies greatly depending on the parameters of evaluation. By mass, the energy content of hydrogen stands out at 141.6 MJ/kg, which is approximately three times that of methane, the closest competitor among common fuels. However, when evaluated by weight or volume, hydrogen is the least energy dense among the same fuels, a result of its fundamental physical properties. Hydrogen is the lightest element, so it has both a minuscule molar mass and prefers to be in a gaseous state. Hydrogen doesn't become liquid until -259 °C (20 K) and doesn't solidify until -252 °C (14 K) at 1 atm. Various storage methods decrease the volume of hydrogen by increasing pressure, reducing temperature, or both. Alternatively, hydrogen can be physisorped or chemisorped with

<sup>&</sup>lt;sup>33</sup> Ram B. Gupta Hydrogen Fuel: Production, Transport and Storage, illustrated ed.; CRC Press, 2008.

<sup>&</sup>lt;sup>34</sup> Water vapor is a potent greenhouse gas, but the amount emitted by PEMFCs, even on a global scale, is insignificant compared to naturally occurring water vapor. Additionally, emitted water vapor can be condensed to a liquid.

<sup>&</sup>lt;sup>35</sup> Although hydrogen cannot be directly used for most current uses, it can act as a substitute for many small to medium scale uses, as PEMFCs will physically fit in a household, car, or even handheld electronic device and provide the appropriate amount of power.

various materials. These processes make hydrogen easier to store, but must also be able to release hydrogen at the appropriate rate to be effectively paired with PEMFCs.

#### **Sustainable Hydrogen Generation**

As hydrogen is a carrier for energy rather than a fuel itself, it is only as environmentally friendly as its method of generation. Currently hydrogen production is reliant on the steam reformation of methane and water gas shift reactions of carbon monoxide and water. The first process is highly energy intensive, as it must occur at temperatures ranging from 1000 K to 1400 K, while the second can be preformed with the residual heat of the first reaction at temperatures of 600 K. A scheme for both processes is displayed below in figure 2.

 $CH_4 + H_2O \longrightarrow CO + 3 H_2$  $CO + H_2O \longrightarrow CO_2 + H_2$ 

**Figure 2.** The most prevalent process for the production of hydrogen is seen above. Note how methane is consumed while carbon dioxide is produced.

Hydrogen produced via the process in figure 2 is used as a commodity, largely for the production of ammonia, and not as a fuel source. As methane is an effective fuel itself, there is little value in converting it into hydrogen by such an intensive process. The production of hydrogen from intermittent renewables is a distinct process that utilized the electrolysis of water, seen in figure 3.

 $2 H_2 O \longrightarrow O_2 + 2 H_2$ 

**Figure 3.** The electrolysis of water. This is a thermodynamically unfavorable reaction has a Gibbs free energy of  $2.4 \times 10^5$  J per mole of water reacted. This value represents the minimum amount of energy required for the reaction to proceed thermodynamically, and an actually cell will require more energy due to the sluggish kinetics of the reaction.

Under this process, electricity splits water into its atomic components. This reaction is facilitated by an electrolytic cell, which utilizes efficient design and catalysts to achieve a standard efficiency of 70%.<sup>36</sup> Recent research has demonstrated ways to increase both the

<sup>&</sup>lt;sup>36</sup> Mazloomi K. et al. Electrical Efficiency of Electrolytic Hydrogen Production *Int. J. Electrochem. Sci.* **2014**, 7, 3314-3326.

efficiency of this process and/or lower the cost.<sup>37, 38</sup> Most importantly, electrolysis cells pair well with intermittent energy sources, allowing for highly profitable energy arbitrage.

### Storage of Hydrogen

The storage of hydrogen is achieved through a variety of methods and advancements in this field are desirable to increase the utility of PEMFCs. Although hydrogen is very energy rich by weight, it is energy poor by volume. As a result, a reliable way to store hydrogen after it has been generated but before it is used must be researched. There are many options, including compression, cryogenic, chemisorption, and physisorption. Compressed hydrogen requires extremely high pressures to achieve only somewhat reasonable volume in comparison to other fuels. For instance, a container four times as large as a typical gas tank is required for a hydrogen vehicle to drive the same distance. In addition, high pressure tanks raise safety concerns from both stationary and portable storage. Storing hydrogen cryogenically (at temperatures ranging from -120 to -196°C) requires less space, but additional energy is required to cool and insulate the storage container.

A more desirable method is to use chemisorption or physisorption to store hydrogen within another material. Chemisorption involves a reversible reaction in which gaseous  $H_2$  is split and covalent bonds to a surface. Physisorption is a distinct process where gaseous  $H_2$ remains in its diatomic from but is absorbing into a porous material. Many materials exist that can both absorb and desorb hydrogen at rates compatible with PEMFCs. The hydrogen is not held under high pressures but the density is increased, making it more transportable. The hydrogen can either be stored on the surface or within a material at a range of densities.<sup>39</sup>

<sup>&</sup>lt;sup>37</sup> Rausch, B., M. D. Symes, G. Chisholm, and L. Cronin. Decoupled Catalytic Hydrogen Evolution from a Molecular Metal Oxide Redox Mediator in Water Splitting. *Science* **2014**, *345*, 1326–1330.

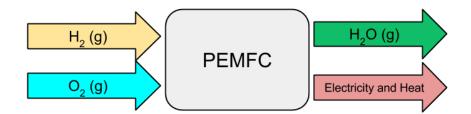
<sup>&</sup>lt;sup>38</sup> Minoru et al. Gas crossover and membrane degradation in polymer electrolyte fuel cells. *Electrochimica Acta* **2006**, 51, 5746-5753.

<sup>&</sup>lt;sup>39</sup> US Department of Energy. Fuel Cell Technologies Program: Hydrogen Storage. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/fct\_h2\_storage.pdf (accessed March 19, 2015).

storage at atmosphere or slightly elevated pressures and temperatures, and most importantly decreased volume.

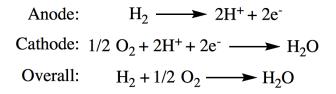
#### **Proton Exchange Membrane Fuel Cell Design and Operation**

The combustion of hydrogen consists of a reaction with oxygen to produce water. Hydrogen can be combusted directly to produce heat, or can be electrochemically reacted with oxygen to produce both heat and energy. In the latter process, a fuel cell is used to facilitate the reaction and results in the direct production of electricity. There are several types of hydrogen fuel cells. Each type varies in how efficiently it can convert the potential chemical energy of hydrogen into electricity, the temperature at which it operates, and the membrane used. This paper will focus on proton-exchange membrane fuel cells (PEMFCs), as they have a lowoperating temperature, low pressure fuels, have quick start-up times, and can be used for stationary or portable uses.

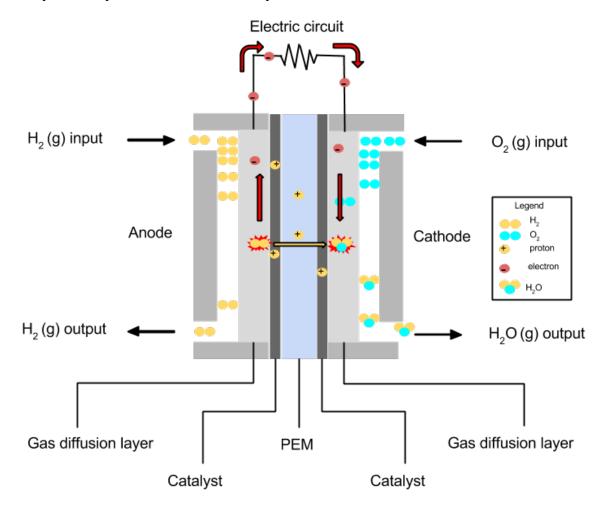


**Figure 4.** The basic concept of a  $H_2$ — $O_2$  fuel cell. Unlike a battery, the reactants are stored externally, and the fuel cell will continue to produce water and electricity are long as reactants are supplied.

PEMFCs facilitate the electrochemical reaction of pure gaseous hydrogen with oxygen (either pure or ambient). The basic components of a fuel cell (shown in figure 6) are an anode where hydrogen is oxidized, and a cathode, where oxygen is reduced. A partition called the membrane electrode assembly (MEA) divides the two compartments, and insulates against the flow of electrons but provides for the flow of protons. At the anode, hydrogen is split into two protons and two electrons. The protons permeate the MEA, while the electrons flow through an external circuit. Both species eventually flow to the cathodic side, where oxygen combines with electrons and protons to form water. During this process, electricity, water, and a little heat are generated. The two half reactions and the overall reaction is viewable in figure 5 below.



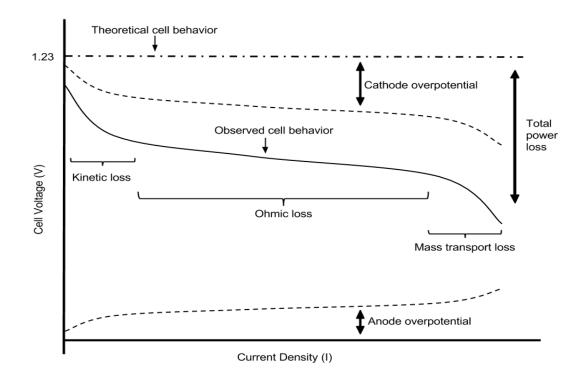
**Figure 5.** The exothermic reaction of hydrogen and oxygen is seen above. The reaction is thermodynamically favorable but kinetically slow under standard conditions.



**Figure 6.** A schematic diagram of a PEMFC.  $H_2$  is consumed within the left gas diffusion layer and  $H_2O$  is formed in the right gas diffusion layer. Red arrows indicate electron movement. There are no moving parts within the cell, and electricity is produced as long as reactants are supplied.

#### **Theoretical and Experimental Efficiency**

The standard (1 atm, 25 °C) electrochemical potential for the reaction of hydrogen and oxygen is 1.23 V. Actual fuel cells achieve a significantly lower electrochemical potential ranging from 0.9 V to 0.5 V. The reason for this is a result of overpotentials, or the difference in voltage between a reaction's thermodynamic redox potential and the redox potential at which the reaction is observed to occur at experimentally. Three primary factors contribute to this. The first is the result of sluggish reaction kinetics, such as the formation of high-energy transition states or the presence of multiple reaction pathways. Typically, a more complex or higher energy reaction pathway will yield greater energy losses. The second factor, ohmic loss, is energy loss from resistance of current in the materials providing for the flow of electrons. This can be limited by using materials with very low electrical resistance. The third factor, mass transport loss, is the result of an imbalance of products and reactants within the cell. This occurs at higher current densities, and is diffusion limited. Reactants need to flow into the cell and the products need to flow out at proportional rates for proper function. Imbalanced concentrations of these species will result in a drop in cell efficiency. A diagram of these phenomena and the typical current densities they occur at is displayed below in figure 7.



**Figure 7.** The theoretical and real cell behavior for a characteristic PEMFC. The curves are drawn not to reflect specific values, but general function. It must be noted that the cathode overpotential is typically greater than the anode overpotential, but catalyst must be used at both the anode and the cathode to prevent large overpotentials.<sup>40, 41</sup>

We can see in figure 7 that the overpotential at the cathode is greater than at the anode. The reasoning for this is easily explained by examining the pathways for the hydrogen oxidation reaction (HOR), which occurs at the anode, and the oxygen reduction reaction (ORR), which occurs at the cathode. The potentials for these two reactions are not equal, and the negative overpotential generated at the cathode for the ORR is typical two orders of magnitude greater that the positive overpotential generated by the HOR at the anode when state of the art catalysts are used for both.<sup>42</sup> As such, further minimization of the overpotential of the ORR can have a greater impact on reducing energy losses for the overall reaction. Platinum metal has been the most successful at reducing these losses, as it has the appropriate coordination affinity for the

<sup>&</sup>lt;sup>40</sup> Strasser, P. Fuel Cells *Chemical Energy Storage*, **2013**, 1, 163-184.

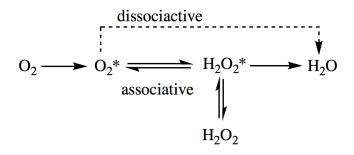
<sup>&</sup>lt;sup>41</sup> Mahadevan, A.; Gunawardena, D. A.; Fernando, S. Biochemical and Electrochemical Perspectives of the Anode of a Microbial Fuel Cell. In *Technology and Application of Microbial Fuel Cells;* Wang, C.T. Ed. **2014**. ISBN: 978-953-51-1627-1, InTech, DOI: 10.5772/58755.

<sup>&</sup>lt;sup>42</sup> Strasser, P. Fuel Cells *Chemical Energy Storage*, **2013**, 1, 163-184.

species in their transition states. Platinum is able to lower the energy of the transition states, and as a result minimize the energy loses from kinetics.

 $1/2 \text{ H}_2 \longrightarrow \text{H}^* \longrightarrow \text{H}^+ + e^-$ 

**Figure 8.** The mechanistic pathway for the HOR is seen above. The symbol \* denotes coordination of a species with an active site of the catalyst.



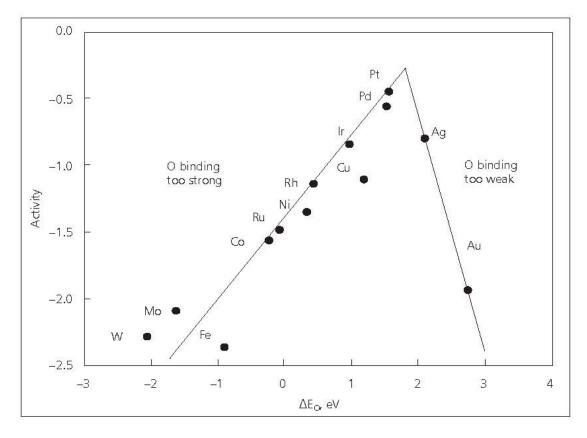
**Figure 9.** The sluggish kinetics of the ORR can be attributed to two possible pathways, each with several intermediates and possible formation of reactive oxygen species<sup>43</sup> The symbol \* denotes coordination of a species with an active site of the catalyst.

As these two figures show, reactants need to physically coordinate with the surface of the catalyst for both the HOR and the ORR. As such, maximizing the surface area can increase the efficiency of the catalyst. This can be achieved by using thin-films or nanoparticles, although the longevity of the catalyst is normally diminished from these techniques. Moreover, catalysts that employ noble metals are both rare and expensive and their use is the major economic inhibitor for the widespread use of PEMFCs.

Different surfaces will coordinate with the reactants with various affinities, and the strength of this coordination is essential to the catalytic performance of the material. If the bond is too weak, the reactive species will be unable to coordinate appropriately with the material and the activation energy for the reaction will remain high. If the bond is too strong, the coordinated species will be unable to leave after coordination, and from a permanent bond. A plot of these bond strengths for various metals with oxygen is shown below. Hydrogen exhibits a similar

<sup>&</sup>lt;sup>43</sup> Holton, O. T.; Stevenson, J. W. The Role of Platinum in Proton Exchange Membrane Fuel Cells *Platinum Metal Rev.*, **2013**, 57 (4), 259.

bonding pattern with each metal.<sup>44</sup> We can see in the figure above that the platinum family of noble metals is most suitable for catalyzing the ORR as it can coordinate with the reactants appropriately.



**Figure 11.** The activity for the ORR across various substrates is plotted. The platinum family of elements exhibits the highest activation activity. Reused with permission from Norskov et al.

# **Market Demands for Cell Design**

A design feature necessary to address is the power output for PEMFCs. As the cell potential for a single unit is 1.23 V, only a meager amount of electrical production is achieved with a single cell. However, fuel cells can be combined in series to form a stack, which have power outputs up to  $2.5 \times 10^5 \text{ Js}^{-1}$ . The 2<sup>nd</sup> law of thermodynamics tells us that as cells within a stack increase, more energy losses will occur and the overall system will be less efficient. While this is undoubtedly true, a reasonablely high output can be generated without significant losses.

<sup>&</sup>lt;sup>44</sup> Norskov J. K. et al. Origin of the Overpotential for Oxygen Reduction at a Fuel Cell Cathode *J. Physical Chemistry* **2004**, 108(46), 17886-17892.

However, careful management over cell temperature, gas flow, and water evacuation is necessary for efficient cell function for larger stacks, requiring additional blowers, pumps, and controls.

The two major challenges associated with fuel cells are cost and durability. PEMFCs are both relatively expensive and have high maintenance cost as a result of the materials used to build them. The primary expense is from the use of precious metal catalysts that lower the activation energy required to split hydrogen and oxygen. The main durability issue lies in the degradation of the MEA by reactive oxygen species, which form as byproducts of the ORR. These reactive oxygen species, which can be peroxides or oxygen ions, can react with the catalyst, catalyst substrate, or MEA to hamper the function of each component. This can diminish the performance of the cell, decrease its lifetime and potentially lead to gas cross over, which can result in explosive mixtures of  $H_2$  and  $O_2$ . Minimizing the formation of these reaction oxygen species is essential to the production of commercially viable PEMFCs and is achieved through catalyst design advancements. The challenge is to reach this goal with only earthabundant and inexpensive materials.

#### **Future Research Challenges**

The majority of issues that arise in research are rooted in attempts to optimize complex chemical interactions that facilitate a specific process into a simple, reliable, and cheap device. The chemical reaction that a PEMFC facilitates is very basic on a superficial level (figure 3). However, from a power supply stand point the reaction proceeds at a geological pace. This is because both H<sub>2</sub> and O<sub>2</sub> are stable in their diatomic form and will only react as ions. The bond dissociation energy for diatomic hydrogen at room temperature is 436.0 kJ/mol, while the same value for diatomic oxygen is 498.40 kJ/mol<sup>45</sup>. As a result of these relatively high values, mixtures of hydrogen and oxygen will have negligible reaction rates at temperatures less than 300 °C (573 K) without a source of ignition. Even though the reaction is thermodynamically favorable, it is kinetically hindered by its high activation energy. Fuel cells are able to speed the reaction of hydrogen and oxygen by utilizing noble metals catalysts. These metals coordinate with both oxygen and hydrogen and lower the activation energy, making the reaction proceed at

<sup>&</sup>lt;sup>45</sup> Darwent, B. deB. *Bond Dissociation Energies in Simple Molecules*, NSRDS-NBS 31; The Catholic University of America: Washington DC., 1970.

an appreciable rate at lower temperatures. The remaining challenge is to bring down the cost of the devices.

The reason for this is partly a consequence of the limited understanding of the mechanism of proton-coupled electron transport (PCET), which is the basic pathway for chemical energy conversion and occurs in many redox reactions. However, PCET is a theory that addresses both classical and quantum effects and behavior, and is not understood in its entirety.<sup>46</sup> Future research must not only experiment with PEMFC development, but address a more fundamental understanding of what are highly complex physical interactions occurring at scales in which particles behave in both classical and quantum mechanical manners. Discussion of this topic goes beyond the depth of this paper. Further, fundamental research of PCET will impact research specifically aimed at PEMFCs.

A more tangible aspect of PEMFC development relates to the use of catalysts and cell engineering. These two aspects are innately tied to the theoretical and actual electrochemical performance of PEMFCs (figure 7).

#### **Development of Catalysts**

Catalysts are essential to the process of obtaining electrical energy from hydrogen but they are often reliant on expensive precious metals such as platinum or palladium. Two primary solutions to this exist. One must either engineer a method that uses a very small amount of the expensive catalysts or create new catalysts with comparable efficiency from inexpensive elements. The best catalysts for PEMFCs will be inexpensive, durable, prevent the formation of reactive species that can either degrade the membrane or poison the catalyst, all while promoting the reaction at an appropriate rate. The efficiency of platinum catalysts has been increased immensely by tuning nanoparticles so their surfaces are most active in this process. A more desired approach is to identify a material that is both earth abundant and reduces the kinetic losses of the ORR. Materials that have shown promise in this regard are cobalt complexes, often situated on a graphene substrate.

<sup>&</sup>lt;sup>46</sup> Weinberg, D. R. et al. Proton-Coupled Electron Transfer *Chem. Rev.*, **2012**, *112*(7), 4016-4093.

One of the main challenges in the development of catalyst is avoiding self-poisoning. Catalyst poisoning occurs when a reaction species generated by the catalyst reacts with the catalyst and inhibits functionality. These species often only occur in trace amounts but can degrade the device over time. As the ORR often generates reactive oxygen species (ROS), the material must be inert to these highly reactive species. While platinum and similar metals do not suffer severely from damage by ROS, metals with a higher affinity for oxygen may form permanent bonds, inhibiting their function. A further motivation to limit the formation of ROS is to prevent damage to the relatively fragile MEA.

In summery, PEMFCs facilitate a series of interactions to enable to reaction of hydrogen and oxygen to produce water, electricity, and heat. The main expenses for PEMFCs are primarily from the use of noble metal catalysts and degradation of the MEA by reactive oxygen species, a byproduct of the catalytic reaction. Designing a new catalyst is a highly sought after research goal, and advancements in this field can range from employing cheaper catalyst materials, minimizing reactive species, and reducing overpotentials.

# **Comparison of Energy Storage Methods**

The past argument and discussions have elucidated the attributes of various energy systems and the specific developmental goals of PEMFCs. We can now engage in a quantitative and qualitative comparison of the role each energy storage system can play when paired with intermittent renewable energy.

## **Quantitative Assessment**

The empirical parameters for various energy storage methods serve as the key guidance in their economic viability for various uses. Although factors such as compatibility with current energy infrastructure, renewable energy sources, and externalities from use are important, the capability for each energy system is strictly limited by operational parameters. To demonstrate the differences between various methods of energy storage, the parameters for each method have been normalize to that of PEMFCs, as shown in table 3. In this way, we can easily see the differences between methods.

Method	Energy Density	Capacitance	Discharge	Response	Energy loss	Cycle-life	Round-trip	Cost
			rate	time	(per hour)		Efficiency	
Li-ion	0.08-0.2	2	16	1	8%-20%	0.02-0.04	1.36	0.75-1
Na-S	0.09-0.1	1	34	1.0 x 10 <sup>-3</sup>	0%	0.02-0.03	1.21-1.28	0.4-0.7
RFB	0.008-0.04	0.6-12	0.2-100	1	0%	0.065	1.21	0.3
TES	0.05	1	20	1.7 x 10 <sup>-4</sup>	varies	0.05	-	2
Flywheel	0.009-0.02	0.5	0.3	1	3%-20%	0.05-0.5	1.21	0.1-1
P2G	-	-	-	7.1 x 10 <sup>-6</sup>	-	-	0.6-0.83	-
Pumped	0.0002	10,000	300	1.7 x 10 <sup>-4</sup>	0%	-	1-1.21	0.003-
Hydro								0.2
PEMFC	0.6-1	1	1	1	0%	1	1	1

**Table 3.** Key empirical parameters have been normalized to that of PEMFCs. Normalization involves a ratio of parameters; it results in a unitless number. Acronyms are lithium ion batteries (Li-ion), sodium sulfur batteries (Na-S), redox flow batteries (RFB), thermal energy storage (TES), power to gas (P2G), and proton exchange membrane fuel cells (PEMFCs). Compressed air energy storage has been omitted from this comparison, as it cannot be used for the storage of energy from intermittent renewable sources.

To start, the first four parameters are addressed. The most advantageous quantitative characteristic that fuels cells have over all other methods of energy storage is a very high energy density. Lithium ion batteries have at best a third of the energy density relatively to PEMFCs, and most other methods are multiple orders of magnitude below PEMFCs. Energy density is most important for portable uses, so PEMFCs are good candidates for uses such as transportation and portable electronics. As seen in the table 3, the capacitance and discharge rate for PEMFC are lower or equal to all other methods except flywheels. However, since the difference is less than an order of magnitude for most cases, this is not a great hindrance to PEMFCs. Both these empirical restrictions can be overcome by linking PEMFCs in series. The response time for PEMFC is equal to that of many batteries, but between three and six orders of magnitude above that of other methods. This is most important for small timescale load leveling for the electrical distribution networks, which is currently achieved with the cheaper methods of flywheels and spinning reserves. As spinning reserves are intrinsic phenomena in generating stations but flywheels are not, so PEMFCs could replace flywheels, providing it would be economically profitable.

To address the second set of four parameters, we see the PEMFCs have no energy loss over time, in contrast to flywheels, thermal energy storage, and lithium ion batteries. PEMFC are well suited to uses that both lithium ion and flywheels are used for, so this characteristic is a important advantage that could eliminate energy losses that currently occur. The cycle life for PEMFCs is much higher than most other energy storage methods (both pumped hydro and P2G have no cycle life limitations). Key research goals outlined in the previous section will further increase the cycle life for PEMFCs by limiting MEA degradation. The round trip efficiency for PEMFCs is less than most other methods. All these factors result in a final cost for PEMFCs that is equal or slightly higher to batteries and some flywheels. The cost for PEMFCs is much greater than pumped hydro energy storage.

The most important findings from the previous discussion are that PEMFCs have much greater energy storage density than any other method. Batteries are similar to PEMFCs in many regards, but have higher discharge and capacity rates as well as lower costs. PEMFCs and flywheels are both well suited to load leveling. Pumped hydro energy storage and power to gas have vastly different empirical parameters in comparison to other methods, so they are more applicable to large-scale uses that operate on longer time scales. Although the quantitative parameters presented are very important, qualitative considerations must also be addressed for each method.

#### **Qualitative Assessment**

As elucidated above, much of the motivation in pursuing renewable energy lies external to economic motivations. As such, the evaluation of storage methods for renewable energy must also include these non-monetary considerations. However, comparison is not as easy for non-quantifiable measures. Applicable factors addressed are geographical, climatic, and material impacts.

Of the energy storage systems reviewed, all but thermal energy storage and pumped hydro have minimal or redeemable impacts on the immediate environment they inhabit.<sup>47</sup> Geographically, pumped hydro energy storage has the most drastic impacts as it is necessary to change the landscape by either constructing multiple artificial reservoirs, damming a river, or

<sup>&</sup>lt;sup>47</sup> Ibrahim H.; Ilinca, A.; Perron, J. Energy storage systems—Characteristics and comparisons *Renewable and Sustainable Energy Reviews*, **2008**, *12*(5), 1221-1250.

both.<sup>48</sup> This has a drastic effect of the previous use of the land, such as species displacement or changes in hydrology. The increasing prevalence of this technology will exacerbate these impacts, as there is no foreseeable development for mitigation of these effects.

Climatically, all the energy storage systems evaluated do not result in an increase in carbon emissions from use. It is important to recall that these technologies can be implemented for the storage of electricity generated from any type energy source without exacerbating the impacts of climate change themselves once constructed and integrated into use. They instead provide a mechanism to incorporate a higher proportion of intermittent renewable energy into future energy landscapes. While they are not the instrumental factor for discontinuing the use of traditional energy, they are essential to the overall process. PEMFCs emit water vapor in normal use, which is a powerful greenhouse gas. However, the amount of water vapor emitted from even widespread use of fuel cells is small in comparison to natural evaporation. Furthermore, a condenser can be used to liquefy emitted water vapor.

The materials used in the construction and use of these energy storage methods must also inform their utility. Flywheels, pumped hydro energy storage, and thermal energy storage all primarily use earth abundant materials, many of which can be recycled. Batteries contain more toxic substances that must first be synthesized, but can often be recycled to various degrees. PEMFCs contain little to no toxic substances, but do employ rare noble metal catalysts and the membrane is composed of a polymer that must be carefully synthesized.

Depending on the specific scale of use and timeframe requirement, each energy storage method offers particular benefits and drawbacks. As such it will be necessary to employ a variety of storage methods to effectively store intermittent renewable energy, and it will be necessary to develop all types of energy storage in order to meet the estimated  $1.9-45.0 \times 10^{16}$  J of energy storage capacity for energy generated from renewables needed by 2040. Global installed energy storage is currently  $1.4 \times 10^{14}$  J and bridging the gap between these two numbers will require a wide range of effective techniques. The various empirical parameters dictate what uses various methods can be employed from, and qualitative considerations can inform as to what methods

<sup>&</sup>lt;sup>48</sup> Yang, C. J.; Jackson, R. B. Opportunities and barriers to pumped-hydro energy storage in the United States *Renewable and Sustainable Energy Reviews*, **2011**, *1*(15), 839-844.

are the most energetically, economic, and materially efficient, while having minimal climatic and geographic impacts.

# **Impact on Future Energy Landscapes**

PEMFCs will undoubtedly have impacts on the field of the storage for intermittent renewable energy, and the development of energy storage in general will have far reaching consequences that permeate into many facets beyond energy markets and systems. Of these, the most important impacts to consider are the promotion of geographically diffuse energy generation networks, policies surrounding energy generation, the emissions of greenhouse gases, the progression of anthropogenic climate change, and situated impacts of carbon emissions.

## **Impacts on Current Electric Infrastructure**

Power is currently produced at large generating stations and transmitted to population centers. Consequently, billion of dollars have been invested in the generating stations and distribution networks around the world, particularly in developed countries. This structure has been based on the availability of traditional energy sources and does not consider the viability of the system into perpetuity. Increasing the proportion of intermittent renewable energy currently used will require large investments in infrastructure. From an economic standpoint, the most short-term losses can be avoided by integrating as much of the existing infrastructure from traditional energy systems into future energy systems that incorporate intermittent renewable energy. Of the energy storage systems examined, the ones that are most compatible with current infrastructure will be economically promoted while systems that require alternative infrastructure will be economically promoted while systems that require alternative infrastructure will be economically promoted while systems that require alternative infrastructure will be economically promoted while systems that require alternative infrastructure will be economically promoted while systems that require alternative infrastructure will be economically promoted as new market of economic activity within energy systems.

#### **Energy-Industrial Complex**

The use of fossil fuels has dominated world energy systems for 150 years and moving away from this system brings the security of alternatives into question. Although fossil fuels will continue to become more scarce and expensive, the total supply will not be exhausted in the near future. They represent a conservative choice for more empowered nations to base their energy systems on. As energy is the currency of the universe, energy from fossil fuels is the currency of our world. However, when considering the externalities of a carbon-based system, they become less favorable the further one looks into the future. Economic activities are dependent on energy, and changes in the way energy is generated will alter market behaviors. This will both be influenced by current energy policy and influence future energy policy.

Economic considerations motivate the public and private companies that have stake in the current energy system. Government subsidization of fossil fuels and renewables must be altered to incentive research and implement energy storage systems. The US government currently offers more subsidies to traditional energy than renewable energy. Though this is not the case in all counties, it offers some context to the slow response time of the developed world to projected and accepted models of climate change. While the scientific community has been in agreement over the occurrence of anthropogenic climate change for well over twenty years, policy changes to enact carbon emission reducing measures have struggled on both the national and international levels. This has been formally attributed to concerns over energy security, but the arguments laid out in this paper indicate that energy sovereignty can only be fully achieved with the promotion of renewable energies. Transferring this ideology to national and international policy makers remains a great challenge. All energy storage systems are equal in this category, as the most important consideration for policy makers are economic viability, geological constraints, and popular perception. Although policy is often the greatest tool for instigating change, it is informed by and responsive to the other aspects examined here.

### **Ulterior Considerations**

Energy storage systems that are more spatially adaptable can be placed wherever they are the most economically viable. This is either at the site of generation or at the site of use, to avoid losses in the transformation of power from high to low voltages. This brings into question the effects that energy storage systems have on their immediate environment, as a noisy, dangerous, or large energy storage system will have consequence for the experience for people near it. All types of batteries and PEMFCs are silent in principle, as there are no moving parts in their operations. Additionally, impacts of the pumps and controls required for efficient operation can be neglected as many common devices found in everyday life use the same mechanisms. These storage devices have many advantages over traditional sources of energy as well. Internal combustion engines are loud, and emit toxic pollutants. The smog that surrounds nearly every major city would disappear if any of the energy systems used replaced our current prominent methods of energy use. Additionally, they operate at temperatures an order of magnitude greater that either batteries or PEMFCs. All of these aspects represent qualities that people would be willing to pay for, so as to say that not all of the benefits from these technologies come from their environmentally benign nature or monetary considerations. The benefits of living in a quiet, healthily, and clean environmental provide a direct incentive to subside these technologies and promote their use.

#### **Equality Standards**

The promotion of renewable energies can aid in the development and equality within many regions. Much of the forecasted increase in global energy use is projected to occur within developing nations. The access to energy within these regions will only grow in importance in both the short term and long term future. Continual reliance of traditional energy exacerbates the unequal distribution of fossil fuels, as these resources are not uniformly distributed. The scarcer fossil fuels become, the more likely energy conflicts are to occur. Renewable energies, particularly solar and wind are geographically diffuse resources that have a roughly equal distribution on a global scale. These renewables can provide consistent, if intermittent, energy to all areas without regard for geopolitical boundaries. By creating efficient methods to capture, store, and use these sources of energy, economically viable energy can be brought to people who would otherwise be unable to afford the rising cost of traditional power. As the number of people in such a scenario is on the order of *billions*, perusing the capture of renewable energy has the potential to change the lives of many in the near future.

#### Conclusion

The failures of current energy systems have been addressed in terms of both mitigating climate change and promoting equality. As such, alternative energy systems have been shown to

be necessary to in reducing carbon emissions and improving energy security. An intergral aspect of alternive energy is the development of energy storage, of which PEMFCs may play a large and beneficial role in. The specific challenges in research for PEMFCs have been examined along with the projected benefits if research goals are met. The implementation of PEMFC will not only effect the way in which we power our phones and drive our cars, but will traverse through nearly every aspect of daily life. A brief digression will help to elucidate this. The laws of thermodynamics represent a model that was produced from a series of observations of the natural world; they explain the way in which the world behaves. Furthermore, they tell us that energy not free, as it has to be extracted from a primary source, or natural form, to one that can be used by humans. Within this process, it tends to be revert back to its natural form. As such, it is precious. We use energy for everything we do, and the most prevalent mediums we extract energy from are entirely finite. The motivation to expand our energy systems does not only lie within the failures of the contemporary system, but the potential effects derived from future energy landscapes. PEMFC are both a simple and a complicated device, and they offer a prospective solution to a simple and complicated problem: we need energy, how do we get it?

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