

# Frontiers of chemical engineering engineering essay

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## **Abstract**

This report investigates the potential for using Iron Oxide ( $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>) in the process of photo-catalysis to generate Hydrogen. The progression of this technology, originating in the 1970's, has been dormant until recent advances by Dr. Sivula and Dr. Rothschild have brought rust to the frontier of solar based renewable energy. In small scale tests carried out by the aforementioned scientists, it has proven itself to successfully convert solar energy to Hydrogen fuel. Comparisons between the results of these tests and standard Silicon-based cells are debated. Rust is not currently as effective but the low cost of raw materials and the possibility of increased efficiency is discussed. The implications of the resultant increase in its

economic viability are examined and show that rust can become competitive in the solar energy industry. Table of Contents

## **Introduction**

The world's population is constantly growing, creating an increase in demand for energy which people are reliant on every day. The fossil fuels used to meet these demands are running out, creating a growing energy crisis and therefore an inherent need for new renewable energy technologies. Solar energy is one of the most viable renewable technologies. This is primarily due to the fact that it is based upon capturing the energy of the sun; which is effectively unlimited providing close to 1000W/m<sup>2</sup> of power to the Earth's surface in clear conditions.[1]Several researchers have demonstrated that rust has the potential to harness solar energy with efficiencies of around 4-5%.[2]Although currently lower than conventional silicon based cells; it has been stated that this could improve over the next decade.[3]This is not economically viable. However, given the low cost of rust and its relative abundance, this could be a promising area to invest in.

## **Methods**

The sources consulted in this report were extracted from various scientific publications, journals and books. The websites sourced are from or can be traced back to credible journals published by leading experts in this area of research. For example, sources include journals co-authored by Dr. Sivula and Dr. Grätzel, both of whom are at the forefront of research and development related to electricity generation using rust.

## Scientific Background

Creating hydrogen is currently the best method of storing solar energy. To produce hydrogen using photovoltaic cells, the power generated is used to electrolyse water, splitting it into hydrogen and oxygen. Standard photovoltaic cells are able to capture 15% of solar radiation with a further 30% of this being lost in conversion, making this process inefficient.

[4]Therefore a more efficient way of making hydrogen is to bypass photovoltaic cells and use the light from the sun to directly electrolyse the water. Direct electrolysis of water requires using a material which ejects electrons of a specific energy when hit by a photon. For materials to release electrons from their atoms a certain amount of energy is needed, with this value varying for different materials.[5]The ejected electrons leave 'holes' in the material, forcing water to donate electrons to fill them. This process repeats, oxidising the water to produce hydrogen and oxygen. Viewed as a nuisance; rust (iron oxide) is constantly being created through the corrosion of iron and iron-based alloys, weakening and degrading structures. This nuisance could be the material used to harness solar energy. The basis of power generation from rust relies on the ability of iron oxide to produce a small current when exposed to visible light. " Splitting water requires electrons with at least 1. 23eV",[6]making iron oxide almost perfect with its band gap of between 2. 1-2. 2eV along with its stable reaction to the effect of light.[7]FigureFigure 1 illustrates a photo-electrochemical cell that consists of a semiconducting photo-anode and a metal cathode with its corresponding energy diagram displayed on the right.[8]The obstacle to high efficiency is the difficulty in forcing the correct electrons to the edge of the rust. Recent

advances in nanotechnology have improved efficiency. Recent research suggests the maximum theoretical efficiency of converting solar energy to hydrogen is 16.8%, which seems disappointing.[9] However, considering the availability of rust and the cost associated with acquiring it, the idea is still definitely viable. Achieving this maximum theoretical efficiency is challenging and it is unknown if it can be reached. Research into improving the efficiency is on-going and there have been significant advances since Kenneth Hardee and Allen Bard first discovered that rust could conduct electricity. Storing the hydrogen and oxygen produced is another problem which must be addressed before this idea can become a feasible reality. The product mixture is highly explosive and it is possible that the products could recombine to create water again, rendering the process pointless. Current methods of storing hydrogen include gas compression, liquid hydrogen tanks and more recently the use of metal hydrides. One interesting idea is to use borohydride, a compound which is stable at room temperature, non-toxic and cost-effective according to chemist Don Gervasio of Arizona State University. "The borohydride solution releases its hydrogen as it flows over a catalyst made of ruthenium. The hydrogen passes through a membrane and combines with oxygen in the fuel cell, generating electricity and waste water." [10] Practical, safe storage of hydrogen is vital if power generation via rust is ever to become a main renewable technology in the construction of a hydrogen economy.

## **State of the Art**

The initial concept of using iron oxide to produce electricity dates back to the 1970's when Dr. Allen Bard and Dr. Kenneth Hardee of the University of

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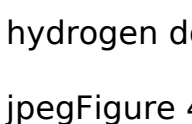
Texas, Austin, managed to successfully generate a current from rust electrodes.[11]They ran into problems however; as the current produced by the rust was not sufficient enough to promote a meaningful amount of electrons to the higher energy levels, where they can be utilised for electrolysis. Research into this area then disappeared as the development and production of efficient silicon based cells overshadowed anything that iron oxide was capable of at the time. Changes in the current economic situation and the need for low cost, green technologies recently rekindled interest in this area of photo-catalysis. In 1991 Michael Grätzel of the Swiss Federal Institute of Technology successfully produced a current from a layer of rust with the aid of a tandem cell; attaining 7.1% efficiency.[12]These tandem cells use sunlight to produce an electric current which is then passed on to the iron oxide; giving its electrons enough energy to escape and thus allowing the electrolysis of water. The cells are expensive however, and therefore limit the economic viability of this kind of component. <http://nsa31.casimages.com/img/2012/11/12/121112104627831141.png>Figure 2 shows an early model of Dr. Sivula's iron oxide electrolyser; capable of converting sunlight into useful chemical energy.[13]FigureFigureWithin the past decade improvements in our ability to manipulate nanotechnology have brought about further research and improvement in this field. Dr. Katz of Denison University, Ohio and Dr. Sivula of The Swiss Federal Institute of Technology both created iron oxide nanostructures which circumvented the paradox which had previously limited the technology. This problem comes from the need for the rust layer to be both thick enough to absorb enough solar energy and thin enough to allow electrons to escape.[14]Dr. Katz devised a

structure comprised of Nano-scale iron oxide rods with similarly small gaps between them; allowing water molecules to pass amidst them. This kind of structure provided ample surface area to absorb a usable level of light and also admitted the emission of electrons from the iron oxide structure – producing a current. Its efficiency however, was still not economically viable. Dr. Kevin Sivula's design improved upon this. Creating a 'rust spray', he was able to coat surfaces in 'cauliflower shaped trees' whose design bypassed the various problems associated with conventional iron oxide structures involving electron emission. This concept created an economically viable way of mass producing rust electrolyzers but the efficiency of this device only surmounted to 3.9%. However, an idea<sup>[15]</sup> by Dr. Avner Rothschild from Technion University, Haifa, Israel, could better the efficiency of Sivula's design by utilising quantum physics. He devised constructing tiny V-shaped mirrors within a 30 nanometre rust film which would reflect light back and forwards within the iron oxide structure. This would not only amplify the energy of the captured light photons, but also ensure that the maximum amount of energy would be absorbed by the iron oxide structure. Resonant light trapping in quarter-wave films. Figure 3 shows light being absorbed by a substance and propagating within a thin film of particles on its surface. Figure 3 If these two designs could be combined, despite the relatively low efficiency, the resulting device has the potential to be easily mass producible and marketable due to the low price and abundance of rust.

## Scientific Potential

Currently using iron oxide to produce hydrogen using solar energy has not been implemented on a large scale and is purely experimental. This is due to

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the relatively low efficiency of the solar panels compared to current production models (around 1.2% conversion[16] compared with 15% with conventional panels). Despite this comparably low efficiency there is still potential for iron oxide to be used as there is an ample supply of it and it is relatively inexpensive. There is a lot of room for improvement on the efficiency of these panels as one team of researchers managed to produce an impressive 12.4% efficiency[17] and research shows that there is an upper limit of 16% energy conversion.[18] One of the main issues with using solar energy to create hydrogen to be used as a fuel is finding a way to store it. Hydrogen is an extremely flammable gas and reacts explosively when exposed to a naked flame. This means that having a safe means to store and transport it is vital if it is to be used to create clean energy. In order for a storage method to be effective on an industrial scale it must not use a large amount of energy to convert the hydrogen to a storable state. One method for storing hydrogen safely is within a metal-organic framework. This method uses surface adsorption to store the hydrogen. Metal-organic frameworks are ideally suited to this task as they have a very large surface area per unit volume.[19] Hydrogen can easily be removed from the framework by lowering the pressure which is exerted upon it. This is because the hydrogen is only weakly bonded to the metal-organic framework by physisorption (The hydrogen does not chemically react with the substance).[20] . Figure 4 shows a metal-organic framework surrounding a pore which could be used to store hydrogen gas.[21] Figure 4 Another technology which has gathered significant interest as a medium for hydrogen storage is ammonia borane. This chemical contains 19.6% hydrogen by weight[22] and



some of this hydrogen can be separated from the compound when heated. This is a safer alternative to current technologies such as liquefying or compressing the hydrogen as in this case it is chemically bonded to the ammonia borane and so it cannot react explosively. Once the ammonia borane has been dehydrogenated by heating it can be replenished by treating it with a mixture of liquid ammonia and hydrazine. More hydrogen can be removed from the ammonia borane if it is reacted in certain ionic liquids. Researchers have managed to liberate 5.4% of the hydrogen contained within the ammonia borane while in the ionic liquid whereas they only managed to remove 3% of the hydrogen without it.[23] In future, advances in current hydrogen storage technologies such as liquefaction, compression and developments in new areas such as ammonia borane and metal-organic frameworks, meaning there is a lot of potential for hydrogen to be stored in a safe and efficient way.

## **Business Potential**

Currently methods for harvesting solar energy to generate electricity and power are relatively inefficient when compared to electricity generation from other forms of renewable energies. It also boasts a higher cost per m<sup>2</sup> and cost per unit power generated than any other renewable energy. As illustrated by figure 5[24], solar energy produced 0.9 million MWhr per year in the USA in 2009 – substantially less than alternative forms of renewable energies. The cost of using the technology to convert solar energy to electricity was over \$250 per MWhr. This is partly due to the high cost of the materials required to manufacture conventional solar panels. The metallurgic "solar grade Silicon", which makes up most of the solar cells in the panel,

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has to be put through a purification process which results in it costing around \$20-30/kg.[25] Were the panel to be mainly comprised of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> rust particles, which cost (\$0.75 - \$1.35)/kg,[26] then the cost of production of each solar cell – and by extension each solar panel would be dramatically reduced. Figure 5 From the data in Figure 5 provided by the U. S. Energy Information Administration, the cost of obtaining electrical energy from solar energy in 2009 was \$225million. Figure 6 Figure 6 illustrates again the cost of constructing the silicon based panels, preparing sites for installation of panels and construction of generators is over double the next most expensive energy source in terms of total cost \$/kWh. From Figure 6, the construction cost of electricity generation from solar energy using current technology is \$0.22 per kWh.[27] However, as it is a renewable form of energy, the cost of electricity production is low - only \$0.07 per kWh.[28] As it is renewable, the total cost per kWh of generated electricity from solar energy is not dependant on finite raw materials and will therefore decrease as the technology associated with it advances. The cost of generation could be reduced further if the materials required to make the technology were cheaper and more readily available than they currently are. As previously mentioned, a team of American scientists developed a prototype photo electrochemical cell that achieved an energy conversion efficiency of 12.4% which was remarkably high for iron oxide.[29] The downside of this prototype was that the cost required to manufacture 1cm<sup>2</sup> of this prototype using that particular technology would amount to \$1,000; too expensive to consider as an investment. However, Dr Kevin Sivula and his team of scientists' tandem cell with an efficiency of around 1.4% - 3.6% is very low in comparison to

the efficiency of current, state of the art, silicon based solar cell technology - 25% at a cost of \$150/m<sup>2</sup>. [30] His prototype has the potential to be developed into a cell which can attain efficiencies of 10% in the next few years and only cost \$80/m<sup>2</sup>. He claims this price will make his cell "competitive with traditional hydrogen production methods" using solar energy. [31] He also predicts that his tandem cell is capable of reaching efficiencies of up to 16% whilst still remaining at a low and affordable cost. This makes investing in this technology for hydrogen production an attractive prospect.

## **Conclusion**

From the research that we have carried out in this report it can be seen that this technology has a promising future. Currently there are limitations with its efficiency and there is also the problem associated with storing the Hydrogen produced. As the technology is still in its infancy these problems are likely to be overcome, with the efficiency predicted to improve significantly in the near future. This increase in efficiency will decrease the cost per kWh; whilst the cost of rust itself remains exceptionally low in comparison to that of solar grade Silicon. These advantages will help to bring this technology into competition with conventional solar panels and may eventually allow it to compete with other, cheaper sources of renewable energy. In summary, when rust has been used in photo-catalysis it has been proven to be a viable alternative to Silicon. Taking into account the abundance of rust, how easily it can be obtained, its durability and low cost; we believe this technology has great promise and potential for business investment. [Word Count: 2830 words]

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