

Water Splitting Test Cell for Renewable Energy Storage as Hydrogen Gas

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Abstract

The simple water splitting electrolysis cell has been shown that can easily be used to assess iteratively changed aspects of design and operation for the water splitting process and the design concepts for water splitting devices. The design characteristics and materials have been discussed such that a cheap and easy starting point for the assessment of design and process modification can be fully assessed. Concentration of electrolyte, and distance between electrodes have been shown to be key to the resistance of the cell and therefore to the efficiency of the process. This test cell will form the basis for comparison for future research regarding a number of aspects of potential improvements to the water splitting process.

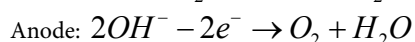
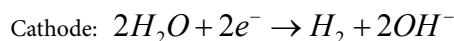
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Introduction

As the world turns more towards renewable for its energy supply, energy storage and transport become a more prevalent consideration. The lack of correlation between renewable sources of energy and energy demand create many challenges for the buffering of supply and demand. Simple water splitting devices can be used to convert spare (renewable) electrical energy into “Green Hydrogen” gas which can be transported, stored and used “On demand” for domestic, commercial and transport applications [1-3]. The electrolysis of water has been known for centuries [2,4] but only accounts for a very small proportion of worldwide hydrogen production [5] as the “Value” of hydrogen increases this is set to change, with large scale electrolysis becoming more prevalent given the added value of the “Green” agenda.

Alkaline water electrolysis could provide the key to low cost, sustainable and environmentally friendly hydrogen production worldwide [4,6]. This paper shows a simple and innovative water splitting cell that can be used to store renewable energy in the form of hydrogen gas. The paper goes on to discuss a number of design factors in the water splitting device and assess various improvements in design for their functionality, and the stacking of the cells into a useable devices.

A water splitting device operating through electrolysis consists of an anode, a cathode and an electrolyte solution. In an alkaline system, a DC charge is applied across the anode and the cathode and gas yielding reactions occur on both. Electrons on the cathode are consumed by the reduction of water into hydrogen with the resultant hydroxide ions passing through the electrolyte to the anode. At the anode the hydroxide ions deposit their electrons and are oxidized to form oxygen and water [4,7].



A single cell water splitting device was prepared from acrylic and silicone using stainless steel electrodes as shown in Figure 1. This water splitting device was used as the starting point in the design improvements and a reference point for all of the characterizations, comparisons and discussions. In all cases the supply of electrolyte to the cell occurs from a large reservoir to ensure that the electrolytic concentration does not change over time between experiments.

The energy efficiency of water splitting devices is keys to the production of green hydrogen from renewable energy alongside the

flexibility of such devices to absorb and handle spikes in political output. It is understood that a conventional industrial electrolyze requires between 4.5 and 5 kWh of energy in order to produce a single meter cubed of hydrogen [8]. Different forms of renewable energy have different constraints. Wind energy for instance suffers greatly from the creation of electrical spikes that correspond to spikes in the speed and wind, or gusts. The ability to smooth the spikes or indeed “Top slice” makes the storage of renewable energy in the form of hydrogen gas very versatile and potentially beneficial.

Experimental Methods

The simple water splitting cell set-up is shown and modifications and assessment procedures discussed. In this multi component water splitting device (Figure 1) the central chambers can be filled with electrolyte solution from the reservoir and a current passed between the electrodes. Hydrogen forms on the cathode, while oxygen forms on the anode. Both gasses rise through the electrolyte and pool at the top where they are separated by the gas trap before leaving the chamber due to buoyancy. The multi component water splitting device is held together using nylon threaded rod and nylon bolts so that there is no electrical short-circuit between the plates and the electrolyte supplied and balanced via an external reservoir. This represents a basic point of origin for a water splitting concept from which all future adaptations can be measured and assessed.

Water splitting device parameters

Dimensions: The test cells are 100 mm × 100 mm with varying distance between the electrodes. The spacer wall thickness was 20 mm giving an initial surface area for the accessible electrodes as 60 mm × 60 mm or 3600 mm². In addition there was the presence of the gas trap which reduced the face to face surface area by 300 mm² giving a total active surface area of 3300 mm².

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Electrodes: Much research has been carried out on the development of electrode materials by groups all over the world as seen in the review by Park et al. [9]. Many electrode materials have been tested by us, with medical grade stainless steel (316) performing well and with maximum cost to efficiency ratio. This material has been chosen as it is easily accessible and allows a reasonable starting point for the design and improvement of the electrolysis cell. 0.9 mm thick plates were used throughout these experiments and were cut to the same dimensions and design as the spacers with the addition of a 20 mm x 20 mm tab for connecting the electrodes on the end plates.

Spacer materials: Acrylic sheet is easy to procure, chemical resistant and easy to work with and was used as the spacer material. The cells were cut from single sheets using a laser cutter so each section was a unique piece rather than glued square rod. The spacers were cut from 20 and 12 mm thick sheet.

Gas trap: 1 mm thick acrylic sheet was laser cut to the same design as the spacers however with the upper internal edge lowered by 5 mm, so as to trap and separate the gas as it rises on the side electrodes. The gas trap allows the collection of gas at the top of the device and the channeling of the gas through the gas output.

Seals: 0.75 mm thick silicone sheeting was used with the same design as the spacers cut out using the laser cutter. Under compression the thickness was assumed to be 0.5 mm.

Electrolyte input: The electrolyte balance was made through 8 mm acrylic tubes affixed into the base of each of the oxygen side spacers and connected to the base of the reservoir. During electrolysis twice as much gas formation occurs on the hydrogen side as on the oxygen side so the electrolyte input is performed on the least busy side.

Gas output: Acrylic tube of 8, 10 or 12 mm can be attached to standard pneumatic push-fit tubing for easy sealing and hydrogen processing. Push-fit tubing allows for the easy connection of both wet and dry gas processing. The gas was passed into an expansion tank (Figure 2) prior to release to the atmosphere such that the electrolyte level was fixed at roughly the centre of the expansion tank.

End plates: In addition to the materials and pieces outlined in Figure 1, end plates consisting of 8 mm thick green acrylic, placed over the end electrodes. These plates had an additional 20 mm of height such that the cell was positioned 20 mm above the ground, preventing short circuiting of the electrode plates and spreading the compression

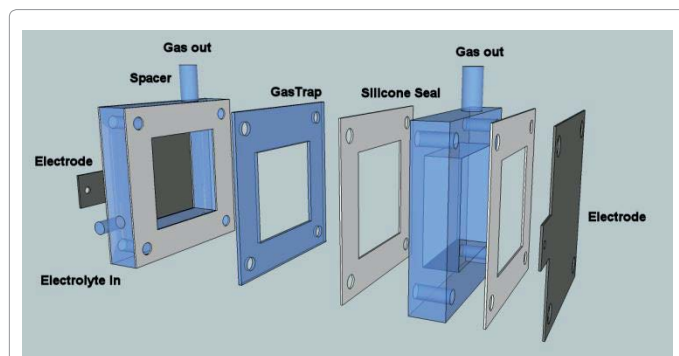


Figure 1: Schematic showing the makeup of a simple water splitting device for the storage of renewable energy. The multi component water splitting device consists of two electrodes, two spacer units and a central trap all held together with threaded nylon Rod and silicon seals to limit the leaks.

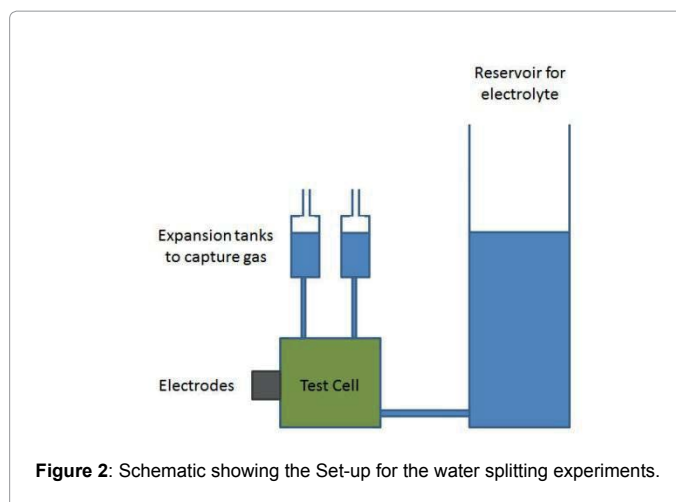


Figure 2: Schematic showing the Set-up for the water splitting experiments.

evenly across the spacer walls.

Fixing Screws: M8 size Nylon 66 threaded bar was used to apply a compressive force to hold the water splitting device together while maintaining electrical integrity between the electrodes.

Assessment process

The simple water splitting device was quantitatively assessed for a number of functional properties and assessment criteria, before modifications were performed in order to fully understand the impact of each modification as they occur. All measurements were taken using a large volume of electrolyte in the reservoir to maintain steady state concentration of the electrolyte throughout.

IV Curve: IV curves were performed using an Invium potentiometer at 0.5 volt increments from 0-10 V unless 2.5 A was reached. At each step the water splitting device was given 30 seconds to fully equilibrate and reach a static current value. In all of the analysis of the IV curve the raw data was processed through MatLab for interpretation. At each voltage setting the 60 measurements were collated, the first 10 readings, 5 seconds, were discarded and the final 25 seconds averaged (mean) to yield an operating current for that voltage setting. This was performed as there was a noticeable capacitance effect on the water splitting device as it charged and maintained steady state current, especially in the pre Ohmic region of the plot. This process invariably took less than 3 seconds to occur.

R_{opp} : The operating resistance of the cell (R_{opp}) is a direct measure of the efficiency of the cell and calculated from the IV curve $R_{opp} = 1/\text{gradient of the IV line once it has stabilized}$. Matlab was programmed to calculate the Gradient based on the straight line between 3V and the maximum voltage reading in the calculation of the resistance.

V_{min} : The V_{min} value of the IV curve also yields information as to the efficiency of the cell. A low V_{min} implies a higher efficiency process. The lowest V_{min} possible theoretical value should be 1.23 V, corresponding to the potential for water splitting [7,8] in reality no gas evolution is observed below 1.65 to 1.7 V, [8] hence there is a need for the over potential. Industrial cells are often operated at between 1.8 and 2.6 V[8]. The V_{min} was assessed by extrapolation of the straight line part of the graph to $I=0$ value and is effectively the voltage at which the cell begins to operate as a water spitting device rather than a capacitor, when the minimum over potential has been achieved.

$$V_{\min} = 1.23 + \text{Overpotential}$$

Cell efficiency- thermal: The thermodynamic cell efficiency, $Cell_{\text{Eff}}$ is defined as:

$$Cell_{\text{Eff}} = \frac{\text{Hydrogen Energy}_{\text{out}} (KJ)}{\text{Electrical Energy}_{\text{in}} (KJ)} \times 100$$

Hydrogen gas has a calorific content of 286 KJ/Mol. This is regarded as the amount of energy that can be recovered from 1 mole of hydrogen by reaction with oxygen yielding only water as a by-product. Energy input is calculated by the multiplication of the voltage, current and time plots from the potentiostat. Measurements were performed at constant voltage for 5 minutes periods with a gas syringe measuring the volume of hydrogen produced. To lower errors the gas measurements were performed in triplicate and the cell efficiency values averaged.

Result and Discussion

The water splitting set-up is operated as a test rig, Figure 2. The cell was connected to a reservoir of electrolyte of greater volume than the cell cavity so that changes in volumes and concentration due to the electrolysis process are minimised. The gas output connections are connected to expansion tanks so that they don't overflow when gas bubbles are produced and the electrodes are connected to a potentiostat. Prior to each experiment the working electrolyte is returned to the ballast so that continued use does not lead to significant increasing concentration. The temperature was maintained at room temperature so as to avoid significant changes in electrolytic conduction [10] and buffered using the large ballast tank.

Baseline measurement

The setup as described in Figure 1 and Figure 2 was used to display the initial findings for the experiment sets. Two 20 × 20 square spacers were joined together with a gas trap and the IV line calculated. The raw data Figure 3a was then interpreted as set out in the experimental section to give the IV curve shown in Figure 3b. The values for the operational resistance and the minimum voltage required to drive the cell were calculated and are 6.8 Ohms and 2.03 Volts respectively with a concentration of 0.1 M NaOH.

Investigating the effect of distance between the electrode plates

It is understood that the distance between the plates has a significant effect on the overall efficiency of the process. There is a trade-off between gas separation and cell efficiency as higher distances giving better gas separation but lower efficiency.

To investigate the relationship between the spacer lengths and the resistance of the cells a 20 mm spacer with an electrolyte inlet was used as the cell, and sequentially increased in size by a 12 mm spacer. Measurements were taken accordingly.

There is a clear relationship between the distance between the electrodes and the resistance of the water splitting cell. The results show a linear response between spacer length and the resistance. The gradient of this line, inset in Figure 4 is 0.1515 ohms/mm and is resultant from the surface area of the electrodes, the concentration of the electrolyte and the temperature of the electrolyte. The closer the electrodes are together, the lower the resistance and therefore the lower the resistance and the higher the efficiency. However, as the water splitting cell has no diaphragm to separate the gasses across the face of the electrodes the closer the plates are to each other the less gas separation occurs leading

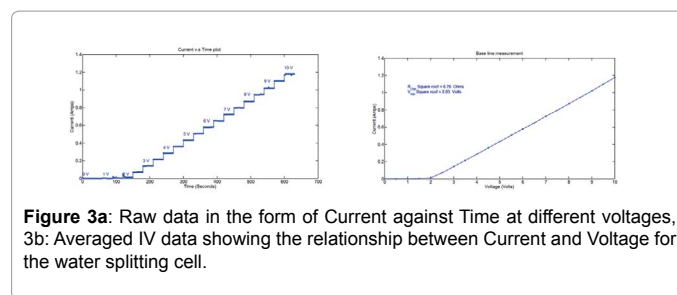


Figure 3a: Raw data in the form of Current against Time at different voltages, 3b: Averaged IV data showing the relationship between Current and Voltage for the water splitting cell.

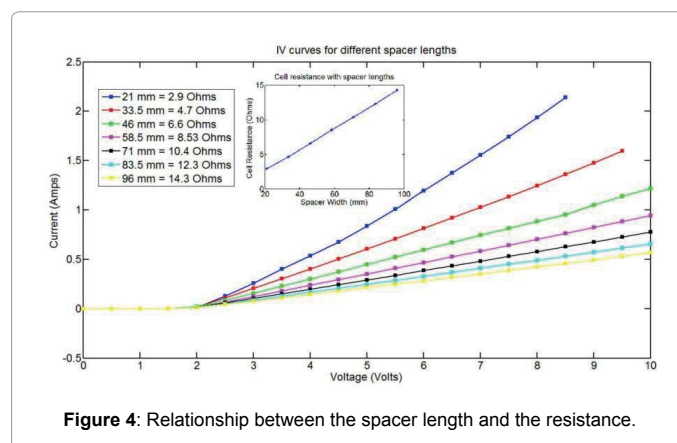


Figure 4: Relationship between the spacer length and the resistance.

to inefficiencies and safety concerns. At 96 mm there is no hydrogen / oxygen mixing whilst at 21 mm there would be approximately 50% loss for the hydrogen stream if the gas separator were not in place. As the hydrogen evolution is twice the volume of the oxygen evolution there is no need for the spacers to be of the same diameter. A 20 mm hydrogen spacer can easily be paired with a 12 mm oxygen spacer to give a cell, (20 × 12) of lower resistance than the 20 × 20, yet comparable gas separation capabilities.

Interior roof design of the spacer

A build-up of gas during the electrolysis process in the top of the cell is observed to purge over once a critical volume is reached. This had a detrimental effect on the cell operation as it sucks electrolyte solution though the entire system and results in the mixing of gas bubbles. Hydrogen contamination in the oxygen stream results in wasted efficiency whilst oxygen contamination in the hydrogen stream has safety implications for the long term storage. A redesign of the shape of the cell cavity roof, Figure 5, to channel the gas out of the cell, improved the gas separation characteristics.

The sloped inside roof appears to have had little effect on the resistance of the cell, Figure 6. The marginal improvement in performance, (lower R value) is likely due to the high effective surface area between the plates. There is no change in the face to face surface area of the electrodes, as the gas trap is still in place, however the sloped roof will allow for additional linear contact between the plates at non-90° angles. At a concentration of ~0.1 M the resistance of the cell will be very sensitive to changes in the effective face to face area. The change in the roof design will also allow for better gas handling, getting the bubbles of hydrogen and oxygen out of the system such that they do not interfere with the electrical processes occurring on the electrodes. The gas handling of the cell was considerably improved with gas passage from the cell into the expansion tank facilitated.

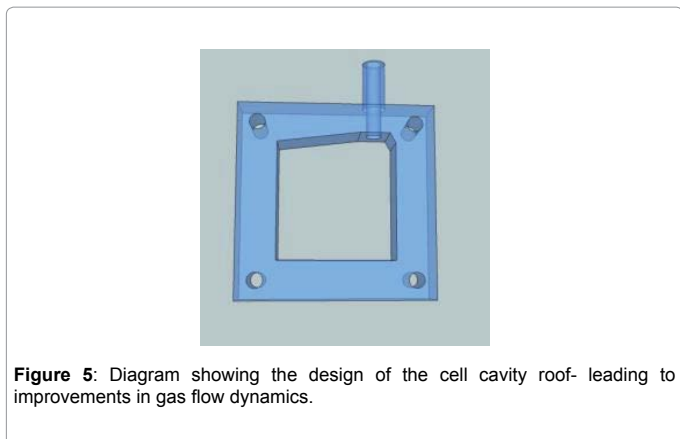


Figure 5: Diagram showing the design of the cell cavity roof- leading to improvements in gas flow dynamics.

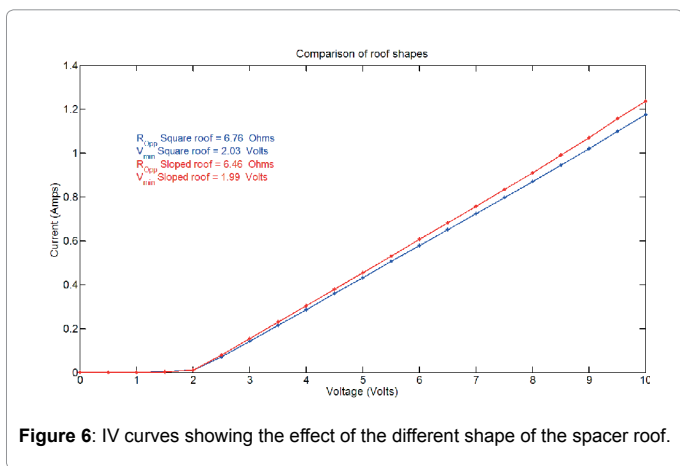


Figure 6: IV curves showing the effect of the different shape of the spacer roof.

Investigation of the concentration of the electrolyte solution

In all cases the 20 × 20, sloped roof setup was used to assess the different concentrations. Electrolyte mixtures from 0.1 M to 1 M, incrementing in 0.1 M intervals were prepared in a volume of 4 Litres. The same protocol as above was run with the samples denoted by their concentration of NaOH.

The concentration of electrolyte has a profound effect the resistance of the cell and therefore the efficiency of the overall water splitting process. Again a trade-off exists between the concentration of the electrolyte, the efficiency of the cell and the safety of the operators. A highly concentrated electrolyte whilst more efficient has more significant safety implications, which depending on the application of the water splitting cell poses a more or less significant threat, both to the operator and the environment. Alkali electrolysis is therefore limited in practice by the concentration of the electrolyte [11]. A 25-30% KOH solution has been widely reported [6,11]. One would expect that doubling the concentration of the electrolyte results in halving the resistance as a result of their being twice as many charge carriers available for conduction. This is evidenced by the numbers for the resistance measurements in-set, Figure 7. At 0.1 M the resistance was 7.3 Ω and reduced to 3.75 Ω at 0.2 M, approximately halving in resistance. Doubling the concentration from 0.2 M to 0.4 M, the resistance drops from 3.75 Ω down to 2.01 Ω again approximately halving, etc. In reality the efficiency gain in doubling the concentration does not quite halve the resistance with a lesser effect at the higher concentrations with the exponential decay dropping off slightly. Hence there is not

a 10 fold decrease in resistance associated with the 10 fold increase in concentration. Commercial alkaline water splitters running at a very high concentration of KOH have a very significant risk to operators and the environment in the event of a leak [4].

Figure 8 shows the straight lines formed in the ohmic region of the IV curves, extrapolated backwards to the 0 amps position. The inset shows the point on the X axis where the lines pass. The inset diagram shows that the position for the cell under all conditions is around 2V however there is a general trend that the higher the concentration the lower the V_{min} number. Low V_{min} values would lead to the earlier onset of hydrogen gas and thus a higher efficiency for the water splitting process. The position of the V_{min} relative to 1.23 V is down to be overpotential of the cell. This can be changed or tuned by a number of factors not just the concentration of the electrolyte. Primarily it is important to note that the stainless steel electrodes are considered to have middle over potential [8] compared to metals such as lead zinc and tin with a high over potential or indeed platinum and palladium with a very low over potential [8]. The lower the overpotential, the better the material is for electrolysis and the higher the cell efficiency (Figure 9).

The thermal cell efficiency was calculated at 2.5, 5 and 7 V as described in the experimental section, for a number of different cell configurations. In each case the cell was filled with 0.1M NaOH and the current measured at fixed voltage for 5 minutes. The hydrogen produced was passed into a gas syringe and the total volume of hydrogen recorded. Measurements were taken in triplicate to lessen the effect of inaccuracies in hydrogen volume measurement using a gas syringe.

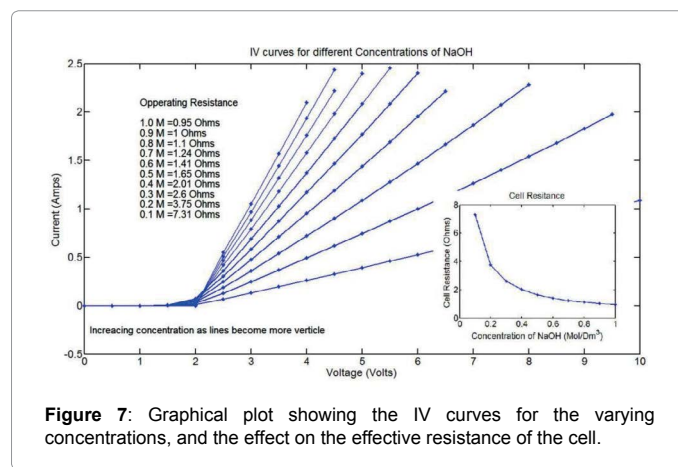


Figure 7: Graphical plot showing the IV curves for the varying concentrations, and the effect on the effective resistance of the cell.

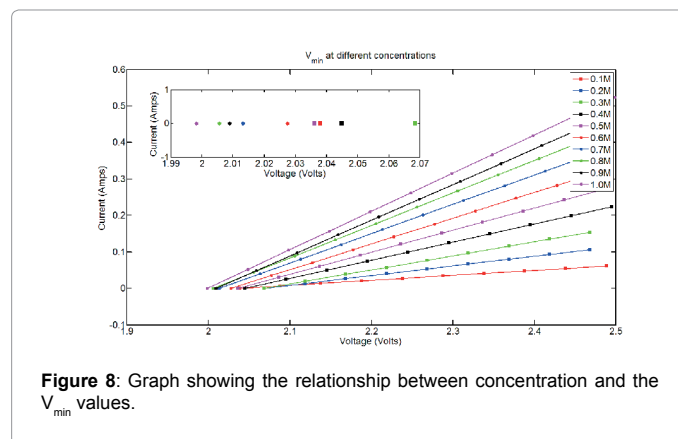


Figure 8: Graph showing the relationship between concentration and the V_{min} values.

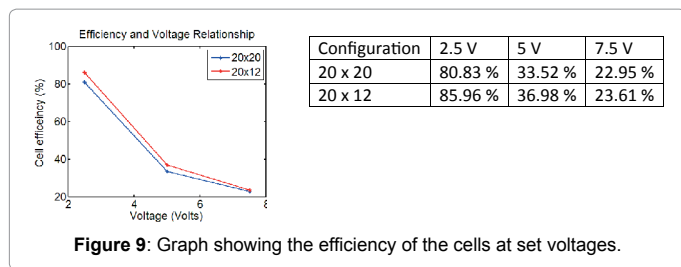


Figure 9: Graph showing the efficiency of the cells at set voltages.

There is a clear relationship between the voltage of the cell and the thermal efficiency when calculated in this way. It is clear that the effect of resistance in the cell leads to a significantly more inefficient process and again leads to a trade-off. The most efficient process would occur at 2 V and produce almost no hydrogen however using almost no current. Whilst technically efficient this process is not useful for the storage of renewable energy.

As the measurement of hydrogen is directly related to the charge which is given by the integration of the current time graph it would seem obvious that any arrangement that raises the current whilst lowering the voltage would be beneficial to the efficiency. An increase in concentration of electrolyte would have this effect, as would increase the surface area of the electrodes. At optimum efficiency these cells would be operating at close to 2 V. The electrolyser working in this study is operating at low voltage and achieving approximately 81-86% thermal efficiency. This can be compared to commercial electrolysers having a nominal efficiency of 70% [11] or to standard industrial operating parameters whereby 4.5 to 5 kwh/m³ of hydrogen [4,8]. This equates to between 70 and 78% thermal efficiency. Improvements in design and the use of higher concentration of electrolyte will no doubt yield higher the efficiencies.

There are many ways of calculating the efficiency of an electrolysis cell [7]. In many ways the efficiency of the cell is also considered to be a moot point given that in real terms the efficiency of the cell should be a value-based metric rather than energy-based metric. In this regard the percentage efficiency should be calculated as follows:

$$Efficiency_{EE} = \frac{Value(\epsilon)_{output}}{Value(\epsilon)_{input}} \times 100$$

It is obvious from the equation above that the value efficiency metric is thus largely skewed by the potential value of energy input, as well as the value of the energy output. Energy that would otherwise be wasted from a power station, wind farm or solar plant would therefore have a very low value energy input and therefore a large Efficiency_{EE} value irrespective of the use for the energy output. Likewise there is a dilemma regarding the value of the output. Hydrogen gas could have a number of different uses and therefore a number of different values per unit volume. Hydrogen used to replace electricity would be valued against the price of electricity whilst hydrogen used to replace petrol in vehicles would have to be valued against the price of petrol. The additional cost of processing should also be taken into account as hydrogen direct from the electrolysis process would be suitable for some applications however unsuitable for others.

Stack configuration

The water splitting cells, once optimised can be stacked together

such that the anode of one cell is the cathode of the next. In this way a 2V cell can be designed to fit any reasonable voltage input. Small scale renewable energy inputs, such as photovoltaic sheets and wind generators are mostly found to give an output of 12 or 24 V. A set of six cells can be stacked together in “series” configurations to provide water splitting device that operates most efficiently at 12 V. As seen before there is a direct relationship between the current passing through the cell and the hydrogen production, so in a stack configuration this needs to be multiplied by the number of cells available. 1 A of current passing through a single cell will produce 1/6 of the amount of hydrogen as 1 A of current passing through 6 cells, the voltage required to drive the six cells will of course be six times the voltage required to drive a single cell.

Conclusion

The simple water splitting electrolysis cell has been shown that can easily be used to assess iteratively changed aspects of design and operation for the water splitting process and the design concepts for water splitting devices. The design characteristics and materials have been discussed such that a cheap and easy starting point for the assessment of design and process modification can be fully assessed. Concentration of electrolyte, and distance between electrodes have been shown to be key to the resistance of the cell and therefore to the efficiency of the process. This test cell will form the basis for comparison for future research regarding a number of aspects of potential improvements to the water splitting process. These water splitting cells have the potential to be used as methods of storage of renewable energy.

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