ELECTROANALYTIC EFFECTS OF ULTRASOUND ON A HYDROGEN EVOLUTION REACTION IN KOH

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ABSTRACT—Due to the sun's intermittent nature, there must be energy storage on a large scale in order for solar energy to provide society's energy needs. One way to store this energy would be producing hydrogen through an electrochemical reaction. It has long been known that ultrasonic irradiation has positive effects in electrochemistry. However, the exact mechanisms that produce these effects are unknown. Much of the literature on the subject focuses on measuring product amounts after a number of minutes or hours. The following work uses linear scan voltammetry and chronoamperometry to analyze a hydrogen evolution reaction in KOH. The results indicate a strong, positive effect due to ultrasonic irradiation. Other processes that convert light directly into hydrogen, such as photoelectrochemical cells, can also benefit from this research.

INTRODUCTION

Researchers have studied the production of hydrogen from water for many years. The hydrogen evolution reaction is one of the most studied electrochemical reactions. Electrolysis is a process in which two electrodes are placed in a solution and a current is run through them. This produces hydrogen at the cathode (working electrode) and oxygen at the anode (auxiliary electrode). Since this produces no carbon dioxide this is a very clean process. With the growing demand of energy and a limited supply, a sustainable source of energy must become available in the not too distant future. Hydrogen is a potential candidate to act as an energy storage medium in a sustainable energy system. Renewable energy sources such as solar and wind are variable and need some sort of storage medium. Therefore, hydrogen and renewable sources of energy are a perfect fit.

Ultrasound has been shown to affect electrochemical reactions [1],[2] which may increase the efficiency of the process. It is thought the reason for these effects is cavitation [1],[2], which are bubbles that form in the presence of ultrasound. These bubbles violently collapse, producing locally high temperatures and pressures. Irradiation has shown many benefits in electrochemistry. It is believed that this has a number of causes [1],[2]:

- Cleaning of surfaces (including dissipating bubble accumulation)
- Activation of surfaces
- Increased mass transport in the bulk and near the surfaces
- Alternate reaction pathways caused by locally high temperatures and pressures

These effects may be different for each reaction. It is important to understand which of these four reasons is predominant in a particular reaction and how to enhance their effect. The hydrogen evolution reaction has been performed in special cases under ultrasonic irradiation. Banerjee, Kumar, and Gadhi [3] studied sonication in a Zn-$NiCl_2$(aqueous) system. An increase in the yield of hydrogen caused the authors to conclude that the sonication had eliminated mass transfer effects and had made the reaction ohmically controlled. Other authors [4],[6] arrive at a similar conclusion because of increased gas yields. However, electroanalytical techniques may give more insight to the mechanism of the process. Walton, Burke, and Murphy [7] have presented voltammograms performed on Pt and have shown a significant increase in limiting current at low potentials. This paper presents results from a hydrogen evolution reaction in KOH studied with linear scan voltammetry and chronoamperometry.

EXPERIMENTAL SETUP AND RESULTS

The experimental system, shown in Figure 1. Picture of setup, consisted of two platinum electrodes of area $0.2cm^2$ and a standard calomel electrode (SCE) as the reference electrode. The electrolyte used was two molar potassium hydroxide at room temperature, and it was purged for forty minutes with argon gas before the experiment. The sonicator used was a Quantrex 310 by L&R Ultrasonics which operates off 300W and at a frequency of 42KHz. Thirty cycles of cyclic voltammetry were performed first to pretreat the electrodes. Then six successive linear scans were done with 1mV/s scan rate from -0.9V to -1.5V with respect to SCE. The nature of our experiment tried to eliminate side reactions; therefore, the production of hydrogen should be proportional to the current. Thus, if current is higher during irradiation then at the same voltage without irradiation, efficiency of the electrolyzer alone increases due to the presence of ultrasound. However, the overall efficiency of the system does not necessarily increase because of the energy needed to ultrasonically irradiate the electrolyzer. Throughout all the experiments bubbles of hydrogen could be seen at the electrode when large potentials existed on the electrode except in the presence of ultrasound. This observation implies that the ultrasound probably cleans the surface of large bubbles that can clog active sites.

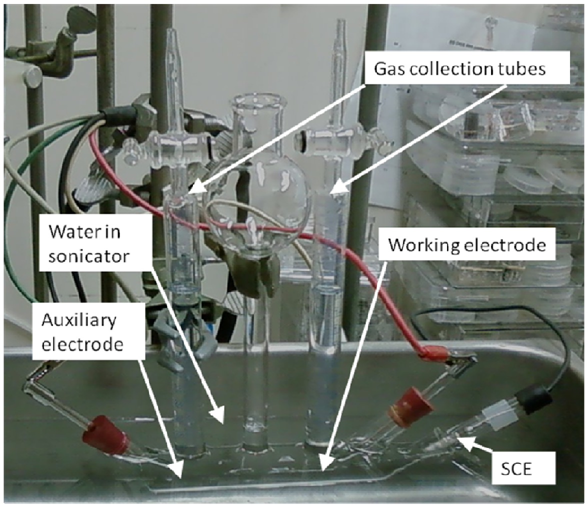

Figure 1. Picture of setup

The results of the linear scans can be seen in Figure 2. The first three curves show a steady decrease in performance of the device, but when irradiated the fourth curve shows significant improvement over the third and even the second. The degradation of performance in the first three curves was unexpected and must be studied further. However, despite the degradation it can also be seen, because of higher currents, that ultrasonic irradiation effectively increased the performance of the electrolyzer.

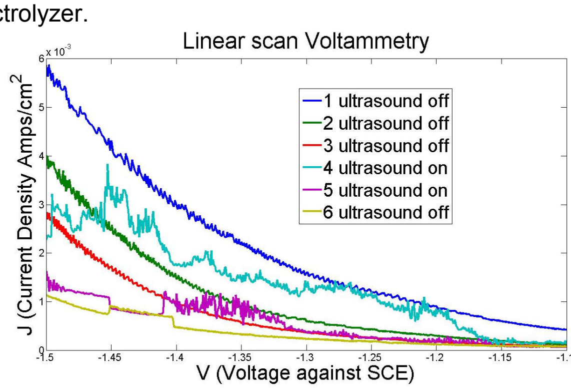

Figure 2. Successive scans of Linear Scan Voltammetry

Perhaps the most telling results are that of Figure 3, which shows a zoomed in graph of the last two curves from Figure 2. In these curves ultrasound was toggled on or off during the experiment. There was a distinct jump in current at all four of these points. When the ultrasound is turned off, the current decreases rapidly and vice versa. The fact that this jump occurs on the scale of a few seconds demonstrates that bulk heating due to the ultrasound is not the reason for the performance gain.

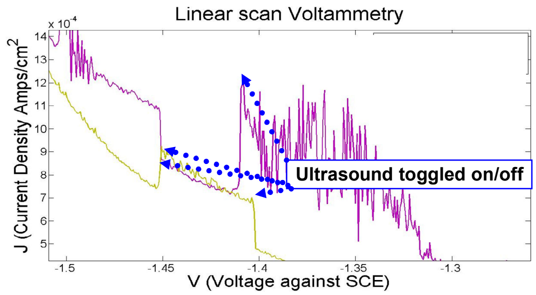

Figure 3: Zoomed in picture of runs 5 and 6 in fig. 2

The next electroanalytical technique used to study this system was chronoamperometry (CA). CA starts at a voltage that provides little current, in this case -.9V. Then the voltage is suddenly raised to a potential where hydrogen is evolved. The sudden peak occurs because all the active species near the electrode are able to react because of the voltage change. The data with ultrasound irradiation was very noisy, so it was filtered with a fifth order lowpass butterworth filter. Figure 4- **6** depict three different CA experiments.

In Figure 4 ultrasound has little effect with this low voltage. However, it still seems to have a positive effect, because when it is turned off around 80 seconds the current drops to where it was in the control case.

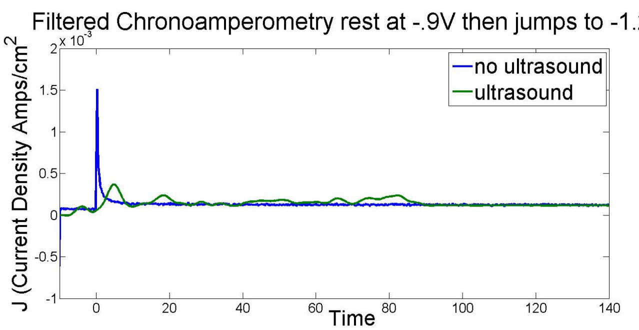

Figure 4. First chronoamperometry run

In Figure 5 ultrasound has a positive effect. This can be seen around 80 seconds when the ultrasound is turned off. At this point in time the current drops to where it was in the control case. The ultrasound is turned on again around 120 seconds and the current jumps up as expected.

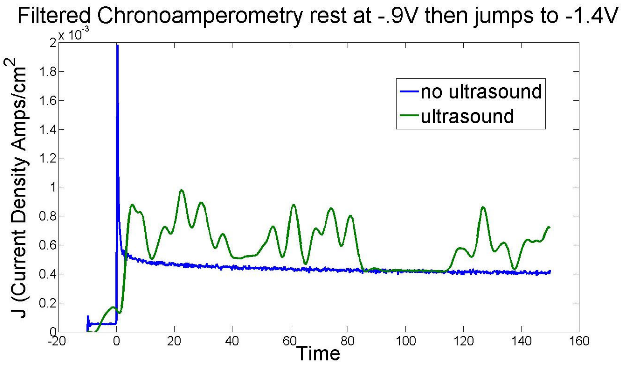

Figure 5. Second chronoamperometry run

The last run, shown in Figure 6, of chronoamperometry caused unexpected results. It seems as if the ultrasound degrades the system. The ultrasound is turned off around 100 seconds and back on at 120 seconds. The current does not return to its control case value when the ultrasound is turned off. Therefore, it seems that the system has degraded just as before in the results shown in Figure 1.

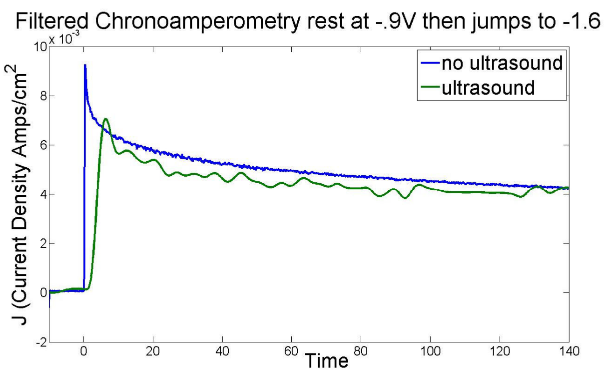

Figure 6. Third Chronoamperometry run

CONCLUSION

Our results illustrate that ultrasound can significantly improve the efficiency of an electrolyzer, especially at intermediate current densities. Even after factoring in the power that is used by a sonicator, ultrasonic irradiation might be able to increase the efficiency of electricity to hydrogen. Other research has shown that ultrasound combined with light can produce a positive result greater than the superposition of the two [8],[9]. Photoelectrochemical cells are a system that could benefit from this effect. These electrochemical cells include a light sensitive catalyst, which is usually a semiconductor that acts like a solar cell except in place of a p-n junction is a semiconductor solution junction. These systems actually convert light directly into hydrogen. However, because of the high voltage needed from the device, it is hard for devices using visible light to achieve this goal. Using ultrasound combined with these devices, though, has shown promising results [10] which requires further research.

The goal of future research will be to provide a more complete understanding of the mechanism that causes the positive effect shown herein. Using more complex electroanalytical techniques such as electrochemical impedance spectroscopy (EIS) will help achieve this goal.

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