PIEZOELECTRET MECHANOCATALYSTS FOR DIRECT WATER SPLITTING VIA ULTRASONICATION

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ABSTRACT
This work reports the first use of polymeric piezoelectret films for direct water splitting using ultrasonication as the driving mechanism. Piezoelectret devices are analogous to piezoelectret ceramic materials which produce electrical charges in response to mechanical stimulus. Water splitting has gained increasing attention as an alternative for producing renewable hydrogen energy. Hydrogen energy has high energy conversion efficiency and does not contribute to the harmful greenhouse gas effect that is responsible for various environmental hazards such as climate change, acid rain, and smog. The piezoelectret device is made of a polymer with charged microscopic dipoles that is bounded by metal electrodes. Ultrasonication is used to produce mechanical stimulus on the device which then generate a voltage on the surface of the metal electrode layers. This voltage catalyzes the water splitting reaction to produce hydrogen from water. Our process achieves water splitting without complicated thermal annealing (in contrast to previous work using piezoelectric ceramics) and does not use complicated transformer circuits. We show voltage measurements from mechanical stimulus to demonstrate that the device voltage can surpass the 1.23 V required to catalyze the water splitting reaction. Additionally, hydrogen quantification is conducted using Gas Chromatography (GC). Based on the analysis, the device has potential for passive energy harvesting of vibrational motion in liquid media such as tidal motions in the ocean.

INTRODUCTION

Hydrogen as an alternative fuel source
The world currently uses fossil fuels as its primary source of energy [1]. Scientists estimate that there are about 50 years left of fossil fuel reserves, further escalating the need to find alternative energy sources [2]. Besides being an exhaustible resource, the use of 1 Kg of fossil fuels produces 3.2 Kg of CO2 [2]. This CO2 gas is known to cause adverse effects such as the greenhouse effect, stratospheric ozone depletion, acid precipitation, and smog [3]. Additionally, the extraction of fossil fuels has led to catastrophic events such the Deepwater Horizon oil spill in 2010 which has environmental effects still not fully understood [4].

Hydrogen is a promising fuel source for the world’s energy needs based on its conversion efficiency, easy transportation, and various phases of storage. Its combustion does not produce harmful greenhouse gases that contribute to the environmental problems discussed previously [2]. The major current hydrogen source is from greenhouse gases which hinders its viability as a source of clean energy. Hydrogen from water splitting only requires water and a source of voltage at 1.23 V to catalyze the reaction. Furthermore, water covers 70% of the Earth’s surface and is a renewable resource [2]. As such, the ability to produce hydrogen via water splitting has the potential to use abundant resources to produce clean energy.

Water Splitting
Water splitting has gained considerable interest as a source for energy production from hydrogen based on its use of water - an abundant renewable resource, as its main
piezoelectric effect has been used to create widespread modern technologies such as the microphone, speakers, and quartz resonators which help setting the clock for the time [7].

Piezoelectret devices are newer class of devices that are primarily made of charged polymers which display similar mechanical to electrical conversion characteristics as those of piezoelectric devices. They are constructed by charging polymers with many air gaps which can be polarized by a high voltage source such as the corona charging process. Their recent development has been fueled by their ease and versatility specifically for flexible electronics and energy harvesters [8].

Water splitting using mechanocatalysts

Piezoelectric ceramics have been used to demonstrate water splitting using ultrasonic waves and turbines in water as the input energy [9]. Mechanocatalysts materials such as ZnO microfibers, BaTaO3 micro-dendrites, and various reactant. Other methods for water splitting include chemical and thermochemical water splitting, electrolysis, and photocatalysis [5]. In most cases, the large-scale application of water splitting is hindered by multiple engineering and scientific barriers. For example, the chemical water splitting process suffers from producing harmful CO2 by-products. The thermochemical splitting process requires temperature upwards of 2000°K, while the electrolysis scheme has high energy and investment costs. The photocatalysis process generally only uses 4% of the solar spectrum which greatly limits its use as well [6].

Piezoelectric and Piezoelectret Devices

Piezoelectric devices can convert mechanical stimuli into voltage through the movement of dipoles in the material. They can also perform the reverse process to convert voltage into mechanical movements. This

Figure 2: Schematic diagram demonstrating the device electricity generation process. (I) Original state. (II) Compressing/disturbed state. (III) Further compressing state with further reduction of surface charges. (IV) Releasing state with increase of surface charged back to state (I).

Figure 3: Device Fabrication Process. (a) The FEP spacer are hot pressed and bonded together with two separate PET/EVA composite piezoelectret polymer layers; (b) Charging polymer via the corona method; (d) Sputter Au on both sides (d) 3D rendering of final device. The process flow is along the A-A cross-section. (e) SEM image of full device. (f) SEM image of the PET film. (g) SEM image of the FEP Film.

Figure 4: Voltage and current characteristics of a piezoelectret device using the manual pressing as the actuation source. Results show the induced voltage well over 1.23 V.
metal oxide powders have been applied [10]. These all suffer from issues such as time consuming, high temperature requirements, and expensive to produce hydrogen [11].

Here, we use a simple method to fabricate piezoelectret devices which can be excited by vibrational disturbances in water to generate hydrogen. Our choice for the controlled vibrational motion is the ultrasonication and the working concept is visually represented in Figure 2.

Vibrational Energy in the Ocean
It has been calculated that if only less than 0.1% of the renewal energy in oceans could be converted to electricity, it will satisfy and surpass the present world demand for energy of more than five times over [12]. Given this, it is attractive to consider engineering systems that can harvest energy produced by tidal motions every day. As technology advances, this energy resource can become a significant source of renewable energy in the future. Figure 1 shows what this realization may look like.

FABRICATION AND DEVICE
Figure 3 demonstrates the fabrication process of the piezoelectret water splitting prototype device. The process starts by enclosing a layer of FEP material within two 58 µm-thick PET layers using a hot-pressing method described in the prior work [13]. The 23 µm-thick FEP layer acts as a spacer where the air trapped in the structure can be charged. The charging of the device is performed using the corona charging method. The PET/EVA/FEP sandwich has one side grounded and the other side near a corona needle which applies 15 kV. This high voltage causes the breakdown of the air in the structure which creates electrical dipoles.

After the charging process, the device requires the metallization layers to generate voltage. Au was chosen for its chemical inertness as opposed to other metals which could react with water. A 50 nm-thick layer of gold was deposited using a customized DC magnetron sputter deposition system. Figures 2 e-g show SEM images of the cross sections of the structure.

RESULTS AND DISCUSSION
Manual Voltage and Current Characteristics
The device function was first tested using a manual pressing process. The device was connected to a voltage measurement system using wires and the voltage response was recorded over time. Figure 4 shows the results. The reverse and forward connection are tested to verify the validity of the signal acquired from the measurement system. They prove the signals are from the device rather than artifacts of the measurement system [13]. The manual pressing process also serves to confirm that the device can generate voltage higher than the 1.23 V to split water.

Ultrasonication Voltage Characteristics
In the interest of using the device to harvest vibrational energy in liquid medium, the voltage response was tested under ultrasonication in DI water. The device was placed in a standard gas tight Gas Chromatography vial partially filled with DI water. After, an N₂ gas purge was performed. The entire vial was then submerged in an ultrasonic tank and exposed to ultrasonication at 40 kHz for various time periods. The system after this process is shown in inset (c) of Figure 1. Bubbles made of gases can be visually seen on the surface of the device electrodes. The voltage response of the device is shown in Figure 5.

Surface Charge Potential
The surface charge potential of piezoelectret devices is used to study their stability over time, for example some prototype devices show good stability after 50 days with quasi-permanent electrical charge [13][14]. The surface potential was plotted in Figure 6. A longer study period would be required to view the flatline surface potential of the device. However, it is assumed that the value at stability
would be quasi-permanent and allow for the continued device operation.

**Gas Generation Quantification**

Gas Chromatography measurements were used to verify the \( \text{H}_2 \) generation capabilities of the prototype device as a standard test [11][15]. After the sonication process, the gas in the headspace of the GC vial was extracted using a gas tight syringe and injected into a GC equipped with a conductivity detector and an Argon carrier gas.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( \text{H}_2 ) Generation (ppm/hr)</th>
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<tbody>
<tr>
<td>Polymer</td>
<td>0.00</td>
</tr>
<tr>
<td>Au Nugget</td>
<td>0.00</td>
</tr>
<tr>
<td>Water</td>
<td>0.00</td>
</tr>
<tr>
<td>Device</td>
<td>12.99</td>
</tr>
</tbody>
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*Table 1: Time series data in the GC tests show collected \( \text{H}_2 \) measurements. Various control samples show no \( \text{H}_2 \) generation.*

As a control, all components of the prototype device as well as the full device itself were tested under the same conditions to validate the \( \text{H}_2 \) production was a result of the prototype device with sonication. Previously, other works using piezoelectric ceramics such as ZnO and BaTiO\(_3\) have shown gas generation of 22.5 and 30 ppm/hr, respectively. This indicates that our device produces hydrogen on the same order of magnitude without using those hydrothermal methods to make piezoelectric ceramics requiring over 72 hours. Additionally, our devices splits water directly on the surface of electrodes without the need for a transformer or rectifier needed in other systems [9].

**CONCLUSIONS**

In summary we have demonstrated the use of a piezoelectret device as a mechanocatalyst for the generation of \( \text{H}_2 \) via ultrasonication. The device performance was characterized using voltage response measurements which supported its capacity to generate the voltage required to split water at 1.23 V. These voltages were generated using both manual and ultrasonic vibrations. The validity of the device for producing \( \text{H}_2 \) was also tested using Gas Chromatography measurements which revealed that Hydrogen gas was indeed generated by our device under ultrasonication. Our method presents a novel way of using mechanical vibrations to generate chemical energy in the form of using fluid motion to generate hydrogen. The application of the device has the potential to passively harvest energy.

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**REFERENCES**


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