Pyroelectric energy harvesting for water splitting

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A B S T R A C T

Hydrogen fuel cells are a promising energy conversion technology due to its high energy density and zero greenhouse gas emission. As a result, the production of hydrogen from renewable and alternative resources has gained significant interest in recent decades. This paper demonstrates a new approach which uses a pyroelectric energy harvester for water splitting and represents a novel alternative hydrogen source. Pyroelectrics are attractive for harvesting waste heat due to their ability to convert temperature fluctuations into electrical energy. A range of pyroelectric materials and geometries for water electrolysis are analysed to determine, (i) the minimum material thickness to generate a critical potential to initialise water decomposition and, (ii) to maximize the charge and hydrogen mass production. We then successfully demonstrate that an appropriate pyroelectric material, when combined with rectification of the alternating current, can harvest heat fluctuations and generate a sufficient electric potential difference and current for water splitting. By harvesting the pyroelectric electrical energy, a continuous hydrogen bubble production was observed during thermal cycling. Practical routes to maximize the level of hydrogen production for this new concept are also explored.

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Introduction

Research background

As evidence has shown that the emission of greenhouse gases, such as carbon dioxide, has been a significant contributor to global warming and climate change [1], renewable and alternative energy sources [2—6] have become one of the main topics of interest across the world. The fuel cell, particularly using hydrogen fuel, is one of the most promising energy conversion technologies [6,7] due to its high energy density, low greenhouse gas emission and ease of storage. Today, the majority of hydrogen continues to be produced from fossil fuels and biomass [8,9] and one problem of using fossil fuels and biomass is the difficulty of carbon dioxide capture and its confinement. As an alternative, hydrogen evolution from clean and renewable resources has gained significant interest
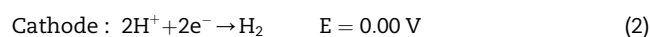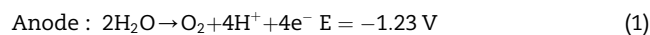
over recent decades. One approach is to use photo-catalytic water splitting using a wide band semiconductor or a series of semiconductor heterojunctions [10–12] which can directly absorb sunlight and use the photo-excited carriers to electrochemically reduce and oxidize water simultaneously. In this case, titanium dioxide (TiO_2) has been one of the most popular and widely used semiconductor in photo-catalyst research since the 1970s [13] and studies have focused on doping, surface decoration, core–shell structures and sacrificial reagents [12]. However, the number of available materials is limited and there remain concerns over performance and lifetime.

Recently, it has been reported that the piezoelectric effect can be coupled with electrochemical processes [14–17] and allows the engineering of charge-carrier conduction characteristics at the heterojunction between a strained piezoelectric material and a chemical solution. Hong et al. presented a "piezo-electro-chemical" effect where mechanical energy could be converted to hydrogen and oxygen [15]. In an ultrasonic water bath, the mechanical vibration of barium titanate and zinc oxide microfibers was reported to lead to the generation of strain-induced electric charges and the electric potential across the strained fibres was said to be sufficient to trigger the redox reaction and produce hydrogen and oxygen from water. Starr et al. [16] studied a "piezo-catalytic" effect for a single crystal cantilever of $Pb(Mg_{1/3}Nb_{2/3})O_3$-32$PbTiO_3$ coated with gold electrodes that was subjected to vibration in water. Their results showed that the rate of hydrogen production is dependent on the frequency of vibration and amplitude of the strain subjected to the cantilever, with hydrogen production increasing with increased piezoelectric potential, increased holding time and a decrease of electrolyte concentration. In addition to piezoelectric effects, "pyro-electro-catalysis", which combines the pyroelectric effect and an electrochemical oxidation–reduction reaction, has been studied and used for the disinfection of bacteria and decomposition of various toxic hazardous organic compounds in aqueous environments [18–20]. Gutmann et al. and Benke et al. focused on disinfection with nano- and micro-crystalline lithium niobate, lithium tantalite powder [18] and barium titanate/palladium nanoparticles [19]. When the powder was subjected to a temperature change, reactive oxygen species were created at the surface of the pyroelectric powders and react due to the uncompensated screening charge carriers. Later, Wu et al. [20] used bismuth ferrite nanoparticles to degrade a Rhodamine B dye solution using pyroelectric effects and it achieved a 99% degradation efficiency for a temperature change from 27 °C to 38 °C. Furthermore, water splitting using the pyroelectric effect has very recently been theoretically studied by Arvin et al. using density functional theory [21]. In their model, the surface phase of lead titanate switches between the ferroelectric and paraelectric phase when subjected to cyclical temperature changes below and above the Curie temperature of the material respectively. In the lower temperature ferroelectric state, H_2O molecules are dissociated on the negatively poled surface to produce bound atomic hydrogen. When the material is switched to the higher temperature paraelectric phase, the hydrogen atoms recombine to form weakly bound H_2, thereby creating a clean surface that is ready for the next thermal cycle.

Pyroelectric water splitting

Heat, in particular low-grade waste heat, has been an attractive source of energy owing to its ubiquity in a variety of industrial applications as well as in the surrounding environment. Pyroelectric materials are of interest here since they have the potential to convert temperature fluctuations from waste heat into useful electrical energy. Pyroelectric materials are polar and exhibit a spontaneous polarization, P_s, in the absence of an applied electric field or mechanical displacement [22]. This spontaneous polarization leads to the presence of charge on each surface of the pyroelectric material and nearby free charges will be attracted to the surface as 'bound' charge. The origin of pyroelectric behaviour is understood from the behaviour of the surface charge as the ambient temperature is changed and assuming that the polarisation level is dependent on material temperature [22]. If the temperature of a pyroelectric is increased, the polarisation level decreases due to a reduction of the net dipole moment. The fall in the polarisation level then leads to a decrease in the number of charges bound to the material surface. If the material is under open circuit conditions the free charges remain at the electrode surface and an electric potential is generated across the material. If the material is under short circuit conditions an electric current flows between the two polar surfaces of the material. When the pyroelectric is subsequently cooled under short circuit conditions, the polarisation level is increased and leads to a reversal of the electric current flow under short circuit conditions.

In this study, we propose to use pyroelectric effect to generate a sufficiently large electric potential between two electrodes to split water into hydrogen and oxygen gas. Rather than position the pyroelectric material inside the electrolyte, we will place the material outside of the electrolyte to demonstrate the splitting of water assisted by pyroelectrics (SWAP). Electrolysis is the decomposition of water into hydrogen and oxygen and in order to trigger electrolysis and produce hydrogen gas, the overall potential difference between the anode and cathode is critical and, thermodynamically, the necessary potential difference is at least 1.23 V [23]. Eqs. (1) and (2) provide the minimum electrode potential for electrolysis when pH = 0. However, in reality an excess energy, termed an overpotential, is required to overcome activation energy barriers during the reaction. Additional factors are that some of the products may catalytically reconvert to water, oxygen might oxidise the anode, and a double layer capacitor may be formed [16,24,25]. For example, in Ref. [25] water electrolysis requires at least 1.6 V when using nano-scaled TiO_2 and titanates.

$$\text{Anode}: \ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad E = -1.23\,\text{V} \tag{1}$$

$$\text{Cathode}: \ 2H^+ + 2e^- \rightarrow H_2 \qquad E = 0.00\,\text{V} \tag{2}$$

According to Faraday's laws of electrolysis, the mass of the substance produced by electrolysis is proportional to the quantity of carriers. This is expressed by Eq. (3), where m is the mass of the substance, Q is the total electric charge passed through the substance, F is the Faraday constant, M is the molar mass of the substance and z is the valence number of