Piezoelectric Nanogenerators: Harvesters of Mechanical Energy

Matthew Kromer Literature Seminar November 10, 2016

Piezoelectric materials have long been studied for their ability to convert mechanical energy into electrical energy.[1-3] These materials are able to do so through the piezoelectric effect, or the separation of charges within the crystal lattice resulting from some external strain being applied to the material. By polarizing these materials through mechanical force, they can exhibit a voltage which causes current to flow through a load to power some device. Due to prohibitive costs, piezoelectric materials would not be efficient for producing energy on a large scale. However, these devices have been proven to be quite useful on much smaller length scales. Electronics are shrinking much smaller than batteries are, and there needs to be some other option of a smaller power source for portable and implantable MEMS. Piezoelectric nanogenerators (PENGs) are attractive alternatives to batteries because they can be made on small length scales and provide power to the device without the need of being recharged.

PENGs most commonly consist of nanowires made of some piezoelectric material sandwiched between to metal electrodes that are electrically connected.[4-6] When the wires are bent due to some external force, they generate charge which then translates to an electric field. These strained piezoelectric nanowires cause electrons to flow between the two metal electrodes in order to neutralize the charges generated. This electron flow causes an alternating current to be generated by PENGs, where the change in polarity is due to the electrons flowing in opposite directions depending on whether or not the piezoelectric nanowires are strained. By measuring voltage and current flowing through the circuit when the device is strained, it is possible to determine the amount of power being produced by the device.[5]

The most common piezoelectric material utilized in PENGs is zinc oxide (ZnO) due to its low cost, biocompatibility, and ease of fabrication.[5] Compared to other materials, ZnO has a low piezoelectric coefficient of approximately 12 pC/N.[7] Other materials such as barium titanate or lead zirconate titanate have piezoelectric coefficients an order of magnitude larger than ZnO, making these materials more suitable for producing the most effective PENG. Koka et al. performed a direct comparison between $BaTiO_3$ and ZnO nanowires that were grown in very similar hydrothermal syntheses.[8] The wires were grown onto an FTO substrate and were placed under an indium beam that moved up and down as a result of vibrations (Figure 1). What was found was that the $BaTiO_3$ was able to produce about 16 times more output power when strained via vibrations at about 1 g. The $BaTiO_3$ device was able to output a power density of 6.27 $\mu W\ cm^{-3}$ which is comparable to microscale piezoelectric energy harvesters.[9-11] This study showed the fabrication of a potentially useful PENG for MEMS and NEMS, and highlighted some of the shortcomings of ZnO based devices. If ZnO could be modified in some way to increase its performance to match that of $BaTiO_3$,

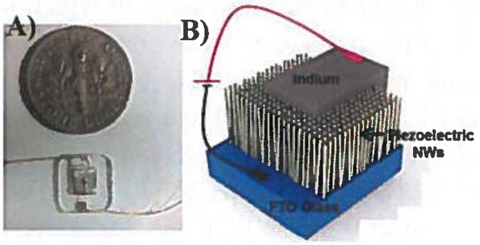

Figure 1: A) Device design for a PENG with $BaTiO_3$ or ZnO nanowires. B) Relative size of device.[8]

then these devices could be made with inexpensive materials while still maintaining workable output powers for various applications.

Zinc oxide is a semiconductor and due to oxygen vacancies, it is naturally n-doped. These free charges screen charge generated due to piezoelectricity, thus inhibiting the effectiveness of ZnO in a PENG.[5] There have been studies performed in which ZnO was annealed in air to remove oxygen vacancies, and a three-fold increase in output power was observed when these wires were integrated into a PENG.[12] A more long term solution to this issue is to dope the ZnO with some positive ions to screen the free electrons in ZnO. A study performed by Sohn et al. involved doping ZnO nanowires with lithium ions to reduce any screening of charge generated from the piezoelectric effect.[13] Nanowires were grown hydrothermally onto a metal electrode in a solution containing lithium ions. Devices using nanowires doped with lithium produced significantly more current and voltage as they were strained with 100 dB sound waves at 100 Hz.[13] These authors also optimized device design by considering the metal-semiconductor junction between the base of the nanowire and the metal contact electrode. This type of junction is a Schottky junction, and if the nanowires are compressed, a negative potential can form near the metal-ZnO interface. A negative potential will lower the barrier height of this Schottky junction, allowing some electron to flow directly into the metal contact electrode. To resolve this issue, the researchers deposited a molybdenum oxide (MoO_3) layer before growing the nanowires.[13] The low work function of the MoO_3 results in a higher barrier height, thus preventing any current to flow out of the ZnO, even if a negative potential develops at the interface. The devices with this interlayer saw a 30-fold improvement over undoped ZnO with no interlayer, ultimately reaching a power density of 0.96 mW cm^{-3}.[13] Shown here was a large enhancement of ZnO nanowire performance in a PENG by doping with lithium and tailoring the metal contact-ZnO interface.

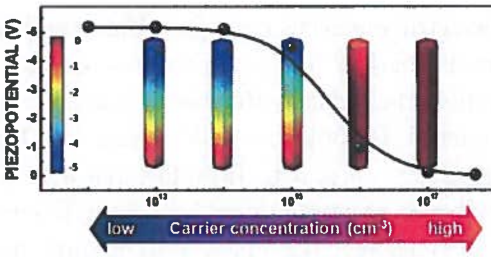

Figure 2: Finite element simulation predicting large enhancement in piezopotential by removing charge carriers in ZnO.[13]

Another area of interest with this field is the incorporation of PENGs into full devices to act as sensors. This area is of interest because there are several reports of "efficient" devices, but they are not shown to do much more than simply power a light emitting diode or a liquid crystal display.[14, 15] Lee et al. have shown the utilization of a ZnO based PENG in a setup in which it powers a sensor for detecting Hg^{2+} ions in solution.[16] The ZnO nanowires were grown onto a flexible Kapton substrate with the intention of increasing number of contacts between the nanowires and the material compressing them. The PENG was then connected to a multi-walled carbon nanotube supercapacitor so that whatever power is generated from the PENG can be stored. The sensor itself is a single-walled carbon nanotube field effect transistor (SWCNT FET).[17] This is able to detect Hg^{2+} ions because when Hg^{2+} comes into contact with the FET, its conductivity increases, allowing current to flow throughout the circuit. This increase in conductivity is only due to Hg^{2+}, making this sensor not prone to interfering signals. The detection method was an LED

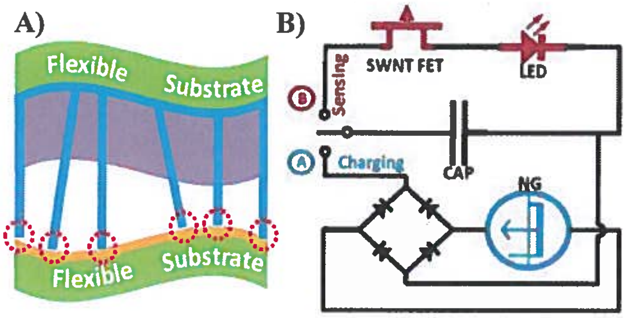

Figure 3: A) Schematic showing advantages of flexible substrates in PENGS. B) Circuit diagram for the Hg^{2+} sensor.[16]

which illuminates in the presence of Hg^{2+}. The sensor successfully illuminated the LED starting at concentrations of Hg^{2+} of 1 μM.[16] This study showed the possibility of using PENGs to power sensors for intermittent detection, but fell short by having rather low detection limits and the inability to consistently provide power to this sensor. However, this study does show the value of PENGs since they were able to successfully fabricate a functional sensor on the microscale.

The field of PENGs is still progressing, and thus far, has been able to produce some interesting studies highlighting power generation of these devices. However, there are several issues with the literature because several reports display large output powers without carefully considering the input force used to generate power.[14, 15] The future of the field will most likely involve the optimization of PENGs by altering aspects of the PENG such as the nanowire morphology or the interlayer between the ZnO and contact electrode.[18] Some studies performing finite element simulations suggest that achieving smaller length scales for the diameters of these devices can significantly increase their performance. There have also been recent development of alternative materials to achieve the same goal as a PENG, such as the triboelectric nanogenerator.[19] The further development of these devices is necessary to develop self-powered microelectronics which can be utilized as biological implants and sensors.

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