Repeatability and Reproducibility of Fibre-Based Nanogenerator Synthesized by Electrospinning Machine

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Abstract. Zinc oxide fibres-based nanogenerators synthesized easily by electrospinning machine are promising to harvest electricity from mechanical energy. However, the repeatability and reproducibility were two major factors needed to be investigated to minimize product failure and to determine the feasibility of mass production of nanogenerators. The green fibres of zinc oxide were produced by electrospinning machine of zinc acetate and polyvinyl alcohol solution at a flow rate of $4 \mu$L/min followed by sintering at temperature 550°C with heating rate 240°C/h. Each 10 nanogenerators was tested by three trained operators with three times of repetition at compressive load 0.5 kg. The nanogenerators revealed the maximum output voltage ranging from 203 to 217 mV. The value of repeatability and reproducibility of nanogenerators was approximately 24.29% showing that nanogenerators were still acceptable to be mass-produced. The relatively low reproducibility was mainly due to the operators, so that the checklist needed to be made easier and simpler for all the variables affecting to the quality of the fibres. Reducing the value of the repeatability and reproducibility is interesting to study further by creating a rotating collector so that the thickness and orientation of fibres can be arranged better.

1. Introduction

The scarcity of fossil energy sources and the increase of energy consumption worldwide have attracted engineers to develop renewable energy sources. Nanogenerator (NG) is one of energy converter devices that convert mechanical or thermal energy as produced by a small-scale physical change into electricity. Piezoelectric materials can be used as NG in which they convert mechanical energy into electrical energy by utilizing crystalline materials with non-centro symmetric. Moreover, NG is the technology of compact portable electric power sources that is widely developed at this time [1].

Some piezoelectric materials have been explored such as: PZT [2], BaTiO$_3$ [3, 4], PVDF [5, 6], and ZnO [7, 8]. The highest voltage generated from the PZT material, PVDF, and PVDF-TrFE was 1.63
V, 2.21 V, and 400 mV, respectively [9]. In contrast, ZnO-based NGs were more resistant at high temperature. In addition, ZnO-based fibers NGs generated DC power that did not require a rectifier. The DC type of NGs was very suitable to build a self-powered system that operated independently and wirelessly without the use of external energy storage systems. Furthermore, to obtain continuous electrical energy and large energy density, then the NGs were fabricated based on nanofibers synthesized by electrospinning machine. Nanofibers via electrospinning have been widely used because of their ease of the fabrication process and low cost [10-12].

Moreover, the piezo effect-based NGs were influenced by several factors: size, shape, type, and crystallinity of the materials. In addition to the raw materials, there were some other important parameters in the fabrication process of nanofibers with an electrospinning machine, including voltage, collector type, collector temperature, tip distance, needle diameter, needle angle, and precursor flow rate [13]. Naturally, nanofibers from electrospinning machine were randomly oriented, so that the output voltages generated by the piezo effect-based NGs were vary. Therefore, the repeatability and reproducibility aspects for fabricating nanofibers by electrospinning method are extremely needed for the purposes of mass production. However, the studies of the repeatability and reproducibility of producing NG based on nanofibers are still limited, especially for the nano-fibres of zinc oxide (ZnO).

2. Materials and Methods

2.1. Preparation of precursor materials
Polymer used was polyvinyl alcohol (PVA, MW = 70,000, Merck Ltd., Germany). The interesting properties of PVA polymer were soluble in water and some types of salts, especially zinc acetate and fully decomposed at a temperature of 400–500°C temperature [14]. To prepare the precursor materials, first, the PVA solution was made from 2 g of polyvinyl alcohol and 20 ml of distilled water. The solution was stirred at 70°C for 4 h [15] and allowed to settle at room temperature for 8 h. To produce the ZnAc solution, 2 grams of zinc acetate dihydrate Zn(CH$_3$COO)$_2$.2H$_2$O (Merck Ltd., Germany) was mixed with 8 ml of water and stirred for 1 h at 70°C. ZnAc solutions were then mixed with the PVA solution at a weight ratio of 1:4, stirred at 70°C for 8 h, and settled at room temperature for 24 h. This produced the ZnAc/PVA solutions and then ready for electrospinning.

2.2. The fabrication of fibers by electrospinning machine
The electrospinning machine was employed to produce green fibres. The ZnAc/PVA solution of 1 mL was put in the syringe pump of the electrospinning machine. The needle in the electrospinning machine was horizontally connected to the positive terminal to inhibit the beads on the collector while the aluminium plate was connected to the negative terminal. The distance between the terminals is 8 cm. A voltage of 15 kV was applied to push out the solution at a flow rate of 4 μL/min. The fibres were attracted by the electrostatic field and they attached themselves to the surface of the negative plate collector as green fibres. The green nanofibers were then sintered performed at a temperature of 550°C with a heating rate 240°C/h [16] to remove PVA and acid content of acetate and remained ZnO nanofibers. The morphology of the ZnO nanofibers was studied by scanning electron microscopy (SEM, FEI: Inspect-S50).

2.3. The fabrication of NGs
The NGs were made of aluminium plate-ZnO nanofiber-and aluminium plate as shown in Figure 1. Between the two surfaces of aluminium, plates facing each other were glued by PDMS to prevent a short circuit.
2.4. NGs testing
After completion for synthesizing ZnO fibres, piezoelectric materials were ready to be tested piezoelectricity, repeatability, and reproducibility with statistical sampling techniques. The performance of NGs was tested by direct measurement to determine the output voltage (V) with time (t) during the excitation process [17]. The output voltage was recorded by real-time data-acquisition hardware using Advantech USB-4716 and PCLS-Adam View 32 software. The NG was subjected to a compressive load (loading and unloading) of 0.5 kg for 3 s per cycle representing the pressure load of weak finger-taps [18]. Each 10 NGs were tested by three trained operators with three times of repetition [19]. The maximum voltage results were then calculated to determine the percentage of the repeatability and reproducibility (R&R) based on UCL (Upper Control Limits) and LCL (lower control limits) [20].

Where $\bar{X}$ is the average of the sample means. $\bar{R}$ is the average range of samples. $A_2$ is 0.31 for the sample size of 10.

The measure of the R&R was calculated by the following formulas.

Repeatability (EV):

$$EV = 5.1k_1\bar{R} \quad \text{or} \quad \%EV = 100 \left( \frac{EV}{TT} \right)$$

Where $k_1$ is 0.5908. Next, reproducibility (AV) was calculated by the following:

$$AV = 5.1\left((k_2\bar{R}_{diff})^2 - (EV^2/\pi r)^{1/2}\right) \quad \text{or} \quad \%AV = 100 \left( \frac{AV}{TT} \right)$$

Where $k_2$ is 0.5231. Furthermore, repeatability & reproducibility (R&R) was determined by:

$$R&R = (EV^2 + AV^2)^{1/2} \quad \text{or} \quad \%R&R = 100 \left( \frac{R&R}{TT} \right)$$

Meanwhile, the part of variation (PV) was:

$$PV = 5.1k_3R_p \quad \text{or} \quad \%PV = 100 \left( \frac{PV}{TT} \right)$$

Total tolerance was determined by the following:

$$TT = \text{upper spec} - \text{lower spec}$$

Where $k_3$ is 0.3146.

3. Results and Discussions

3.1. Output voltage from NGs
The study to determine the repeatability and reproducibility of piezoelectric-based NGs for producing energy was conducted by measuring the output voltage in real-time. The NGs were subjected to the compressive load of 0.5 kg. The sample of the output voltage profile of ZnO fibres-based NGs is shown in Figure 2. The piezo effect occurred because the pressure applied by the external load was...
transferred into nanofibers. Furthermore, electrons generated in the nanofibers were then transferred through the electrode [2].

Figure 2 shows also the steady decline of the output voltage as time passes. This is because at the beginning of loading, the piezo materials in NGs had the intact fibre networks. Further, the applied load caused the fibre networks gradually experiencing the compaction. Over time, some fibre structures had torn as shown in Figure 3. When the fibre networks decayed, the NGs showed the drop of voltage [21]. Despite the damage to the fibre networks, the piezoelectric-based NGs might still produce output voltage because the crystalline structure was not broken due to the damage of the fibre networks.

Figure 2. Sampling output voltage from NGs

Figure 3. SEM image of fibers in NGs after 12000 cycles
In addition, the piezo material-based NGs had a recovery time phenomenon that was the time required to stand back into their initial state. The release of a load (unloading) was part of the recovery process of nano-fibers aimed to maintain the stability of the excitation for the piezoelectric-based NGs to produce the output voltage.

3.2. Repeatability and reproducibility (R&R) of NGs.

The analysis of R&R for NGs was conducted on the value of the maximum output voltage of the NG (see Table 1). The highest and lowest maximum output voltages of 10 samples tested by three operators with three repetitions were 217 mV and 203 mV, respectively. The maximum voltage indicated the performance of NGs as an electric energy harvester from mechanical energy. Furthermore, a large voltage was required when the NGs would be used as an electric charger. However, when viewed from the production process, the magnitude of the maximum voltage was varying for each part; therefore, it was very necessary to measure the repeatability and reproducibility of the synthesis process of NGs.

| Appraiser/ Trial # | Parts |
|--------------------|-------|
|                    | 1     | 2     | 3     | 4     | 5     | 6     | 7     | 8     | 9     | 10 |
| **A** 1            | 214   | 214   | 211   | 209   | 215   | 209   | 214   | 215   | 215   | 216 |
| **2**              | 208   | 214   | 208   | 216   | 214   | 214   | 216   | 216   | 207   | 216 |
| **3**              | 212   | 206   | 216   | 216   | 208   | 215   | 215   | 216   | 214   | 213 |
| **B** 1            | 210   | 215   | 213   | 215   | 215   | 215   | 214   | 214   | 214   | 214 |
| **2**              | 214   | 212   | 209   | 215   | 207   | 211   | 213   | 208   | 207   | 216 |
| **3**              | 211   | 208   | 208   | 207   | 207   | 214   | 209   | 214   | 211   | 216 |
| **C** 1            | 203   | 210   | 203   | 207   | 212   | 204   | 206   | 204   | 205   | 203 |
| **2**              | 206   | 213   | 204   | 203   | 203   | 205   | 204   | 206   | 205   | 203 |
| **3**              | 203   | 215   | 212   | 214   | 203   | 206   | 217   | 205   | 212   | 203 |

The study revealed that the repeatability, the reproducibility, and the repeatability and reproducibility (R&R) based on total tolerance were 17.48%, 16.86%, and 24.29%. According to quality control principles [22], if R&R is below 10%, the process is acceptable. If R&R is between 10 and 30%, the process is then acceptable based on the importance of the application and associated costs. If R&R is more than 30%, then the process is considered unacceptable and therefore cannot be made in mass production. Thereby, the NGs demonstrated the greater repeatability (16.86%) than the reproducibility (24.29%). Based on total tolerance, the effect of the equipment, particularly an electrospinning machine to produce uniform NGs was bigger than that of the operators. The electrospinning machine produced random fibres [13] attracted by the electrostatic field generated by the high voltage source. The forming process of fibres followed the direction of electrons movement from the needle tip to the collector. The greater the difference in the electrostatic field between the tip of the needle and the particular area of the collector, the thicker fibres were formed in the collector region. The collector area that has been met with thicker fibres caused the decrease of electrostatic field differences, and the following fibres moved to a different area of the collector having the larger electrostatic field. This process was difficult to control for a large enough area of the collector (5 x 5 cm). In addition, polymer jets coming out of the needle tip moving toward the collector was usually in a chaotic oscillating motion. The wider the collector caused the greater the chaotic oscillating motion leading to the more non-uniform distribution of fibers on the wide collector. Reducing the size of the collector might obtain the more uniform distribution of fibers on the collector. Thus, to study further to
avoid this, it can be done by (1) creating a smaller collector area or (2) creating a moving or rotating collector so that the flatness of the fibres on the surface of the collector can be better.

Furthermore, the percentage of appraiser variation of 16.86% was acceptable [22]. Reproducibility was determined from the variability created by several operators measuring each part several times, effectively quantifying the variation in a measurement system resulted from the operators and environmental factors such as time [22]. The repeatability of 17.48% that was higher than the reproducibility of 16.86% indicated that the effect of part variation was greater than that of operator variation.

However, the performance of the first operator and the second operator was almost the same, but the performance of the third operator was still below the first operator and second operator as shown in Figure 4. The differences in the output voltage of the NGs produced had a wide range approximately 14 mV. The maximum voltage of NGs resulted was not stable when repeated by different operators. The existence of the operator factors caused the uniformity of ZnO fibres-based NGs have a relatively low value. For further study, the number of variables affecting the quality of the fibres-based NGs need to be trained to the operators, including what and how the influence of these variables on the quality of the fibres. The checklist of each variable and measuring the magnitude of each variable should be made easier and simpler so that the processing time is shorter. Furthermore, the inconsistency because of the operators can be minimized.

![Figure 4. A control chart influenced by operators](image)

4. Conclusion
ZnO fibres-based NGs have been successfully produced by electrospinning machine. The output voltages of NGs when subjected to the load of 0.5 kg were between 203 mV and 217 mV and suited to be developed as an electric charger. Over time, the voltage generated from ZnO fibres-based NGs declined caused by the damage to the fibrous structure. The R&R value of NGs at 24.29% was still acceptable so that NGs can be mass-produced. Furthermore, bringing down the value of the R&R of NGs can be done by (1) creating a smaller collector or (2) creating a rotating collector so that the thickness of the fibres can be arranged better. The relatively low reproducibility was due to the operators, therefore the checklist needed to be made easier and simpler for all the variables affecting to the quality of the fibres.

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