High-Performance Triboelectric Nanogenerators Based on Solid Polymer Electrolytes with Asymmetric Pairing of Ions

Hanjun Ryu, Ju-Hyuck Lee, Tae-Yun Kim, Usman Khan, Jeong Hwan Lee, Sung Soo Kwak, Hong-Joon Yoon, and Sang-Woo Kim

In general, various kinds of surface modifications are utilized to enhance the power output performance of triboelectric nanogenerators (TENGs), but they typically have limited stability. Here, a new strategy of adding electrolytes with asymmetric ion pairing to polymer friction layers of TENGs is introduced in order to enhance their triboelectric property. Indeed, Kelvin probe force microscopy (KPFM) measurements show that an addition of phosphoric acid ($\text{H}_3\text{PO}_4$), an electrolyte with more cations than anions, to polyvinyl alcohol (PVA) can make it one of the most negative triboelectric materials; whereas, an addition of calcium chloride (CaCl$_2$), an electrolyte with more anions than cations, to PVA can make it one of the most positive triboelectric materials. Furthermore, the TENGs based on such solid polymer electrolytes (SPEs) produce significantly higher power output than typical metal-polymer TENGs. Due to these unique features, SPEs are a promising triboelectric material for realizing high-performance TENGs for self-powered small electronics.

1. Introduction

Multifunctional sensor nodes distributed in the form of wireless sensor networks (WSNs) can greatly benefit our daily life, in terms of health care, environmental and structural monitoring, safety and security, nanorobotics, etc.[3,4] Though the capacity of batteries has greatly increased over the years, they have a limited life time and therefore replacement of a huge numbers of batteries can be an almost impossible task.[4–7] TENGs have been introduced for harvesting the abundantly available mechanical energy in the environment for the sustainable, self-powered operation of WSNs.[5] They make an excellent choice for self-powered smart technologies and can adapt well to various mechanical energy types by different modes of operation such as vertical contact-separation mode,[8,9] lateral sliding mode,[10,11] single electrode mode,[12,13] and freestanding mode,[14,15] respectively.

The power output of TENGs strongly depends on the selection of the contact materials.[16] For high output, the two contact layers of a TENG should preferably be on opposite sides of the triboelectric series.[17] Due to the highest electron affinity, fluoroplastics such as polytetrafluoroethylene (PTFE) are the most suitable for the negative contact layer for TENGs.[18] On the other hand, though some dielectric materials such as nylon are relatively more positive than metals like gold (Au) and aluminum (Al), metals are the best candidates for the positive contact layer as they have sufficient free electrons to transfer during contact electrification.[19] For this reason, metal-polymer pairs, specifically metal-PTFE pairs, are mostly utilized for TENGs. In addition, in order to enhance the output performance of the TENGs, various approaches are proposed. Surface functionalization is carried out in order to enhance the charge transfer ability of the contact layer by treating with materials such as poly-$\alpha$-lysine,[19] $\text{F}_3\text{C}-\text{RCS}$ silane,[19] or fluorine plasma ($\text{CF}_4$, $\text{C}_4\text{F}_8$).[20] Surface morphology is generally carried out in order to increase the area of triboelectrification by incorporating various micropatterns on the surface.[8] Nevertheless, surface morphology requires extra fabrication steps,[8,21] and both the surface functionalization and the surface morphology control suffer from poor durability.[8] Although importance of controlling the workfunction of triboelectric material is already emphasized,[22] there are still lack of material itself improvement. Due to all these reasons, it is necessary to improve the triboelectric property of the material itself in order to have durable, high output TENGs.

Here, we investigate the reliable ionic doping effect on the triboelectric property of polymer contact layers for high-performance TENGs for the first time. We successfully demonstrate through KPFM measurements that electrolytes with asymmetric pairing of ions can significantly enhance the triboelectric property of polymers. The addition of CaCl$_2$, which has more anions than cations, can make PVA one of the most positive triboelectric materials. Likewise, $\text{H}_3\text{PO}_4$, which has more cations than anions, can make PVA one of the most negative triboelectric materials. In order to observe the corresponding enhancement in output power, we realized a contact mode TENG with CaCl$_2$-PVA-based SPE and PTFE as the contact layers and found that the SPE-based TENG provides dramatically higher output.
power than an Al-PTFE-based TENG. Furthermore, stable operation over 30,000 cycles confirms that SPE-based TENGs are highly durable ionic doping effect. Thus we suggest that the enhancement of triboelectric property of polymers on the basis of ionic effects could be a major breakthrough in the pursuit of durable, high output TENGs.

2. Results and Discussion

The triboelectric property of materials is generally characterized as a function of the surface atoms.[22] However, the effect of ions on the triboelectric property of a material has not yet been studied. In fact, cations, with a net positive charge, and anions, with a net negative charge, have the potential to significantly modify the triboelectric property of a material. As a consequence, SPEs, which are polymers containing electrolytes, can have a very different triboelectric property than their base polymer.

Figure 1a shows a schematic image of the PVA-based SPE TENG. Figure 1b is schematically describes the possible triboelectric property of SPEs with respect to its base material, i.e., either more positive, more negative, or the same, where PVA is considered as the base material of the SPE. In order to investigate the ionic effect on the triboelectric property of a polymer, we used KPFM measurements to analyze variations in the surface potential of PVA due to CaCl₂, H₃PO₄, and HCl electrolytes. The concentration of CaCl₂ in CaCl₂-PVA-based SPE was varied from 0.25 to 0.75 m; the concentration of H₃PO₄ in H₃PO₄-PVA-based SPE was varied from 0.5 to 1.5 m; and the concentration of HCl in HCl-PVA-based SPE was 1 m. The cation to anion ratios for HCl, CaCl₂, and H₃PO₄ are 1:1, 1:2, and 1:0.99, respectively.[23–25] Figure 1c and Figure S1 (Supporting Information) shows the corresponding results for the variation in the surface potential of a PVA-based SPE due to the electrolytes. H₃PO₄ that has more cations than anions reduces the surface potential of PVA from +247 to −285 mV, which more negative than pristine PVA. In contrast, CaCl₂ that has more anions than cations enhances the surface potential of PVA from +247 to +705 mV, which more positive than pristine PVA. However, HCl-PVA-based SPE that has symmetric pairing of cations and anions shows almost no change in surface potential, and so the triboelectric property of the HCl-PVA-based SPE in comparison to pristine PVA remains almost unchanged.

In order to confirm the triboelectric property change due to electrolytes, we also characterized the surface potential variation in CaCl₂-PVA, HCl-PVA, and H₃PO₄-PVA based SPEs before and after contact electrification with pristine PVA.[26] The contact of CaCl₂-PVA 0.75 m SPE with PVA reduces its surface potential from +705 to +435 mV (see Figure 1d), which shows that CaCl₂-PVA-based SPE is more positive than pristine PVA. On the other hand, the surface potential during contact between HCl-PVA 1 m SPE and PVA is almost unchanged (see Figure 1e). This is similar to the case of contact electrification between PVA and PVA (see Figure S2, Supporting Information). However, the contact between H₃PO₄-PVA 1.5 m SPE and PVA results in an increase of the surface potential from −285 to +75 mV which shows that H₃PO₄-PVA-based SPE is more negative than pristine PVA (see Figure 1f). In addition, the surface potential of PVA before and after contact electrification with CaCl₂-PVA 0.75 m SPE, HCl-PVA 1 m SPE and H₃PO₄-PVA 1.5 m SPE shows opposite change which result in triboelectrification (see Figure S2, Supporting Information). Supporting Information 1 describes in detail the relationship between the change in surface potential and charge transfer during contact electrification. Contact electrification of the SPEs with one of the most positive material of nylon and one of the most negative material of PTFE shows the same trend (see Figure S3, Supporting Information). The results in Figure 1d–f
and Figure S3 (Supporting Information) demonstrate that the electrolytes with asymmetric ion pairing can enhance the triboelectric property of a polymer to the degree that they can even make it the more positive or more negative triboelectric material.

The energy band diagrams in Figure 2 schematically describe the additional electron unoccupied states in an SPE and the electrons transfer between an SPE and its base polymer during contact electrification. Typically, insulators have large band gaps, which contain partially localized electron trap states between the lowest unoccupied molecular orbital and highest occupied molecular orbital.[27] Also, electron charged states at relatively higher energy levels than electron unoccupied states describe the additional electron unoccupied states in an SPE and the electrons transfer between an SPE and its base polymer during contact electrification. Typically, insulators have large band gaps, which contain partially localized electron trap states between the lowest unoccupied molecular orbital and highest occupied molecular orbital.[27]

Figure 2. a) Energy band diagram for PVA and CaCl₂-PVA SPE before contact electrification. b) Energy band diagram at the moment of contact. c) Energy band diagram and flow back of some electrons after releasing.

Figure 3. a) Energy band diagram for PVA and H₃PO₄-PVA SPE before contact electrification. b) Energy band diagram at the moment of contact. c) Energy band diagram and flow back of some electrons after releasing.
mainly contribute to electron transfer in contact electrification between insulators. Therefore, additional the energy bands due to anions which have electron charged states or due to cations which have electron unoccupied states effect ionic doping in PVA.[27–33]

CaCl₂ electrolyte which has more anions, creates high-energy electron charged states in PVA (see Figure 2 and Figure S4, Supporting Information). The additional electron charged states in CaCl₂-PVA 0.75 m based SPE enhance the charge transferred potential of the SPEs in a contact electrification process. Figure 2a shows the energy band diagrams of CaCl₂-PVA-based SPE before the contact electrification. E_in is the surface potential of CaCl₂-PVA SPE and E₄CaCl₂ (0.458 eV, see Figure S1, Supporting Information) is the difference of surface potential between pristine PVA and CaCl₂-PVA SPE. At the moment of contact (see Figure 2b), electrons are transferred from the CaCl₂-PVA SPE to PVA until surface potential of both triboelectric layers are same. Figure 2c shows after the contact electrification. Hence some of the transferred electrons flow back to the CaCl₂-PVA SPE during separation, the potential of both triboelectric layers are same. Figure 2c shows the energy band diagrams of H₃PO₄-PVA-based SPE before the contact electrification. E_in is the surface potential of H₃PO₄-PVA SPE and E₄H₃PO₄ (0.270 eV, see Figure 1d), is decreasing than initial state due to electron transfer to pristine PVA.[34]

On the other hand, H₃PO₄ electrolyte, which has more cations, creates low-energy electron unoccupied states in PVA (see Figure 3 and Figure S4, Supporting Information). The additional electron unoccupied states in H₃PO₄-PVA 1.5 m based SPE enhance the charge received potential of the SPEs in a contact electrification process. Figure 3a shows the energy band diagrams of H₃PO₄-PVA-based SPE before the contact electrification. E_in is the surface potential of H₃PO₄-PVA SPE and E₄H₃PO₄ (0.532 eV, see Figure S1, Supporting Information) is the difference of surface potential between pristine PVA and H₃PO₄-PVA SPE. In Figure 3b, the energy band diagrams of H₃PO₄-PVA-based SPE are at the moment of contact electrification. PVA transfers electrons to H₃PO₄-PVA SPE until build same surface potential of both triboelectric layers. After releasing, some of the transferred electrons flow back to the PVA (see Figure 3c). Therefore the difference of surface potential between pristine PVA and H₃PO₄-PVA SPE, E₄H₃PO₄ (0.360 eV, see Figure 1f), is decreasing than initial state due to electron transfer from pristine PVA.[34]

We have used KPFM measurements to demonstrate that electrolytes with asymmetric ion pairing can greatly enhance the triboelectric property of a polymer. In order to investigate the corresponding enhancement in the triboelectric output performance, we realized several SPE TENGs. First, we fabricated 2 × 2 cm² sized TENGs with an SPE and PTFE or nylon as the contact layers and we applied a vertical force of 0.4 kgf to the TENGs (see Figure 4a,b and Figures S5 and S7, Supporting Information). HCl-PVA 1 m SPE, due to symmetric pairing of ions, was considered as a reference, in order to verify the effect of anions (Cl⁻) and cations (H⁺) on the triboelectric output performance of SPE-based TENGs (Figure S6, Supporting Information) shows that PVA and HCl-PVA 1 m SPE has a similar triboelectric property. The peak direction of the triboelectric output voltage and current show the relative triboelectric properties of the contact layers in a TENG (see Supporting Information 2 for details).[35]

The triboelectric property of HCl-PVA 1 m SPE is more negative than that of nylon, as a positive peak occurred first, as shown in Figure 4a and Figure S5a (Supporting Information). However, the triboelectric property of CaCl₂-PVA 0.25 m SPE, with a greater number of anions (Cl⁻), is more positive than that of nylon as a negative peak occurs first. This is due to the fact that CaCl₂-PVA SPE has higher electron charged states than nylon, and therefore transfers electrons to nylon during contact electrification. Furthermore, as the concentration of CaCl₂ electrolyte in PVA increases from 0.25 to 0.75 m, the peak value of the TENG output increases from 0.4 V and 50 nA to 2.5 V and 341 nA (see Figure 4a, Figure S5a, Supporting Information).

On the other hand, the triboelectric property of HCl-PVA 1 m SPE is more positive than that of PTFE, as a negative peak occurs first, as shown in Figure 4b and Figure S5b (Supporting Information). The triboelectric property of H₃PO₄-PVA 0.5 m SPE is more positive than that of PTFE, as a negative peak occurs first. However, as the concentration of H₃PO₄ electrolyte in PVA increases from 0.5 to 1 m, the peak direction reverses with a peak output performance of 0.69 V and 67 nA. With a further increase in concentration of H₃PO₄ electrolyte from 1 to 1.5 m, H₃PO₄-PVA 1.5 m SPE has even better peak output performance of 2.39 V and 266 nA (see Figure 4b, Figure S5b, Supporting Information). Therefore, the triboelectric property of H₃PO₄-PVA SPEs can be even more negative than that of PTFE, and therefore can receive electrons from PTFE during contact electrification. Likewise, the triboelectric property of H₂SO₄-PVA 1 m SPE is also more negative than that of PTFE (see Figure S8, Supporting Information).

In order to compare the output performance of polymer-polymer, metal-polymer, and SPE-polymer TENGs, we fabricated 4 × 4 cm² sized TENGs with PTFE and nylon/Al/SPE as the contact layers. Figure 4c,d and Figures S9 and S10 (Supporting Information) show the characterization results of the TENGs. The output performance of Al-PTFE TENG (86 V and 8.7 µA) is two times higher than that of nylon-PTFE TENG (40 V and 4 µA) because metals, due to the abundance of free electrons, can supply more electrons during contact electrification. Remarkably, with a peak output of 211 V and 27 µA, CaCl₂-PVA 0.75 m SPE-PTFE has much higher performance than Al-PTFE TENG (see Table 1). Besides, the SPE-based TENG has reliable ionic doping effect with a stable response over 30,000 cycles (see Figure 4e). Figure 4f shows the modified triboelectric series including the various ion doped PVA.

3. Conclusion

We have demonstrated a new strategy to control material itself surface potential using electrolytes with asymmetric pairing of cations and anions. Indeed, KPFM measurements have shown that H₃PO₄ can turn PVA into one of the most negative triboelectric materials; whereas, CaCl₂ can turn PVA into one of the most positive triboelectric materials. Through energy band diagrams, we have explained ionic doping effect that the anions and cations create additional electron charged and electron unoccupied states, respectively, in the SPEs, thereby enhancing their charge transfer ability in a contact electrification process. In order to quantify the enhancement in triboelectric output
performance, a TENG with PTFE and CaCl₂-PVA-based SPE as contact layers produced dramatically higher output than a TENG with PTFE and Al as contact layers with a stable operation over 30,000 cycles. Therefore, SPE-based TENGs potentially offer a strong alternative to typical metal-polymer-based TENGs. In brief, SPEs present an ideal opportunity to realize high-performance TENGs for application in self-powered smart technologies and WSNs.

4. Experimental Section

Preparation of SPEs: In order to prepare SPEs (either containing HCl, H₃PO₄, or CaCl₂), PVA powder (Mw 89,000–98,000, 99% purity, hydrolyzed, Sigma-Aldrich) in a quantity of 5 g and the electrolyte were first dissolved in 50 mL deionized water at 95 °C for 24 h; the concentration of HCl (35% m/m, Junsei) was 1 m; and the concentration of H₃PO₄ powder (Crystalline, ≥99.999% purity, Sigma-Aldrich) was from 0.5 to 1.5 m; the concentration of CaCl₂ powder (anhydrous, granular, ≥93.0% purity, Sigma-Aldrich) was from 0.25 to 0.75 m. Thereafter, the dissolved SPE was spin coated on Au deposited polyethylene naphthalate (PEN) substrate at 500 rpm for 30 s and was then dried for 12 h in a vacuum chamber at room temperature. The SPE thickness was 5 μm.

KPFM Measurements: KPFM measurements were carried out using a commercial atomic force microscopy (AFM) system (XE100, Park Systems). The analysis was performed in noncontact mode using a conductive probe (Multi75E-G, Budget Sensors) at 2 V signal of 17 kHz frequency. In order to know the prior condition of the AFM tip, the potential difference between the AFM tip and highly oriented pyrolytic graphite was measured before each analysis. The operating conditions during the KPFM analysis were: temperature = 21 °C and humidity = 17%.

TENG Fabrication and Characterization: The preparation of SPE-based contact layers of the TENGs is described in the “Preparation of SPEs” subsection of the “Experimental Section.” The Al-based contact layer was realized by an Al tape. Nylon- and PTFE-based contact layers were realized using commercially available nylon and PTFE sheets; back electrodes to PTFE and Nylon were realized by depositing 200 nm Au film. The contact layers of the TENGs were attached to acryl for support. A pushing tester (Labworks Inc., Model No. ET-126-4) was used to apply force to the TENGs. A Tektronix DPO 3052 digital phosphor oscilloscope and low-noise current preamplifier (Model No. SR570, Stanford Research Systems, Inc.) were used for electrical measurements.

Table 1. TENGs output performance for TENGs with PTFE and nylon/Al/CaCl₂-PVA 0.75 m SPE as contact layers.

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<th>Nylon</th>
<th>Al</th>
<th>CaCl₂-PVA 0.75 m SPE</th>
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</thead>
<tbody>
<tr>
<td>Peak Voltage [V]</td>
<td>40</td>
<td>86</td>
<td>211</td>
</tr>
<tr>
<td>Peak Current [μA]</td>
<td>4</td>
<td>8.7</td>
<td>27</td>
</tr>
<tr>
<td>Peak Power [mW]</td>
<td>0.16</td>
<td>0.74</td>
<td>4.45</td>
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Figure 4. TENGs output performance. a) Output voltage of CaCl₂-PVA SPEs and nylon-based TENG. b) Output voltage of H₃PO₄-PVA SPEs and PTFE-based TENG. c) Output voltage and d) current for TENGs with PTFE and nylon/Al/CaCl₂-PVA 0.75 m SPE as contact layers. e) Durability test of CaCl₂-PVA 0.75 m SPE based TENG. f) Modified triboelectric series consisting of SPEs.
Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

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