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Electronic Supplementary Information (ESI)

An efficient polymer moist-electric generator

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The PDF file includes:

Supplementary Information and Methods (including materials preparation and testing)

Fig. S1. The testing setup of the PSSA membrane based polymer moist-electric generator (PMEG).

Fig. S2 The voltage output of the PSSA membrane moisturized from two sides of a membrane.

Fig. S3 The voltage output of the PSSA membrane with different electrode materials.

Fig. S4 The voltage of the PMEG with epoxy fully covered the wire and the connection part of the electrode.

Fig. S5 Experimental setup of the influence of relative humidity and temperature to the power generation process.

Fig. S6 Influence of temperatureb and the relative humidity to the power generation process.

Fig. S7 Voltage output of PMEG under wetting and dewetting process.

Fig. S8 The voltage output of the PMEG when liquid water is used to realize the power generation process.

Fig. S9. Short-circuit-current density of the PMEG $(1 \times 1 \text{ cm}^2)$.

Fig. S10. Repeatability of the power generation process.

Fig. S11. Electric output of PMEG with the different electrical resistance as load.

Fig. S12. Configuration of the flexible polymer moist-electric generator (f-PMEG).

Fig. S13. The discharging profile of a capacitor charged by one f-PMEG unit using vapor from boiling water.

Fig. S14. The setup of a mist-powered light.

Fig. S15. Short circuit current of PMEG under constant moisture feeding for a long term.

Fig. S16 Voltage output of PMEG stimulated by non-protonic DMF solvent.

Fig. S17. The potential acquired from KPFM of the side moisturized.

Fig. S18. Photo of the comparison experiment of the pH indicator in different situation.

Fig. S19. The dynamic voltage change between two sides of the PSSA membrane.

Fig. S20. Modeling, simulated proton movement induced potential distribution on a PSSA membrane.

Fig. S21. The stimulated voltage output by the PSSA membrane.

Supplementary Table. Summary of recent rising power generation methods.

Other Supplementary Material for this manuscript includes the following:

Movie S1. Electronic calculator powered by two PMEG units.

Movie S2. Voltage output by a wearable f-PMEG under bending and twisting.

Movie S3. A mist-powered light.

Supplementary Information and Methods

1. Preparation of polyelectrolyte membrane

Poly(4-styrensulfonic acid) (PSSA, Mw ~75,000, 18 wt.% in H₂O) was purchased from Sigma-Aldrich (CAS No. 28210-41-5). And the solution was casted into a plastic petri dish and dried over-night in oven set at 40 °C and the relative humidity was set to be 60°C. The other chemicals were all brought from Aladdin (China). The preparation of the Nafion film, polyvinyl alcohol (PVA) film, polyacrylic acid (PAA) film, hydroxyethyl cellulose film and natural polysaccharide like guar gum film, chitosan film, and alginate sodium film followed the same protocol as PSSA membrane.

2. Preparation of the electrodes

High purity gold (99.999%) was sputtered onto glass slices and stainless steel for 20 mins at a constant current at 20 mA. 1×1 cm², 1×2 cm², 2×2 cm² top electrodes with manufactured holes for ventilation are used. The diameter of the hole is 1.2 mm. The effective electrode area of the top electrode was calculated to be ca. 0.4 cm², 0.8 cm² and 1.5 cm², respectively. All the necessary parts were water-proof treated for any possible corrosion.

PET films (100 micron in thickness) are used as substrates for the fabrication of the flexible PMEG. Conductive carbon paste (CH-8, Jelcon corp., Japan) was printed onto the PET films by a screen print method. And the printed PET films were dried at 80°C for 6 hour. High power laser direct writing technique was used to fabricate ventilation holes onto the film.

3. Signal measurement

All the voltage and current signals were recorded in real time using a Keithley 2612 multimeter, which was controlled by a LabView-based data acquisition system. The bias voltage for testing short-circuit current was about 1 μ V and the bias current for testing open-

circuit voltage was set to be about 1×10^{-11} A. To avoid any inference from the static electricity, all the samples were short circuited before testing. The energy stored in capacitor was measured and calculated by discharging the capacitor with a galvanostatic technique using electrochemical workstation (CHI 660D, China).

4. Material characterization

The morphology and corresponding chemical composition analysis was conducted on a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS) (Zeiss SUPRA TM 55 SAPPHIRE, Germany). Fourier Transform infrared spectroscopic (FTIR) test was conducted on a Thermo IS5 machine. Kelvin probe force microscopy (KPFM) was conducted on a Bruker Dimension Icon machine.

5. KPFM test

One single piece of PSSA membrane (200 μ m in thickness) was stored in an incubator with a constant Δ RH at 60% for 2 days to ensure the homogeneous distribution of water molecular in the membrane. And the potential of the two sides of the membrane was tested on a KPFM machine. One side of the membrane was moisturized by 100 s and 200 s (named Moist-side) and the other side was covered without moisturizing named nonM-side. The potential change of Moist-side and nonM-side was measured by KPFM after moisturizing, respectively.

6. Numerical simulation

The proton migration process and the corresponding induced electric field under constant moisture feeding was simulated by a theoretical model based on Nernst-Planck-Poisson equations with proper boundary conditions¹:

$$\nabla^2 \varphi = -\frac{F}{\varepsilon} \sum z_i c_i \tag{S1}$$

$$j_{i} = -D_{i} \left(\nabla c_{i} + \frac{z_{i}Fc_{i}}{RT} \nabla \varphi \right)$$
(S2)
$$\nabla \cdot j_{i} = \frac{\partial c}{\partial t}$$
(S3)

where φ , *F*, ε , *z*, *c*, *D*, *j*, *R* and *T* represented the electrical potential, Faraday constant, dielectric constant of material, valence of ionic species, ion concentration, diffusion coefficient, ionic flux, ideal gas constant and temperature, respectively. A diffusion coefficient and dielectric constant from the previous report.² In this case, the diffusion coefficient is 5×10^{-15} m²/s and the dielectric constant is 20. The initial ion concentration is set to be 6×10^{-6} mol/m³ and 1×10^{-15} mol/m³ at the top and bottom side of the PSSA membrane, respectively. The boundary condition for induced potential on the film surface was described by:

$$\vec{\mathbf{n}} \cdot \nabla \varphi = -\frac{\sigma}{\varepsilon} \tag{S4}$$

where σ is the surface charge density, which depends on the ionic concentration. To simulate a steady state of the electrical field, the ion flux had the zero normal components at the boundaries

$$\vec{n} \cdot j=0$$
 (S5)

The calculations for the ionic migration process were performed by commercial software Comsol Multiphysics (version 4.4).

Supplementary Figure



Fig. S1 The testing setup of the PSSA membrane based polymer moist-electric generator (PMEG). PSSA membrane was cut into (a) 1×1 cm², (b) 1×2 cm², (c) 2×2 cm² sized rectangular shape and sandwiched between two electrodes of gold. The upper electrode was manufactured with holes for efficient moisture access. (d) Scheme illustrating the experimental setup. The effective electrode area for the upper electrode was 0.4 cm², 0.8 cm² and 1.5 cm², respectively.



Fig. S2 The voltage output of the PSSA membrane moisturized from two sides of a membrane.

To make sure the homogeneous distribution of water molecules in the membrane, the PSSA membrane is stored in the incubator for over 3 days before the test. The voltage output of the PSSA membrane moisturized from two sides is shown in Fig. S2, respectively. From which it can be found that there is no preference of which side of the membrane to be moisturized.



Fig. S3 The voltage output of the PSSA membrane with different electrode materials, from left to right: gold, CH-8 carbon paste, platinum, graphite paper, carbon cloth, active carbon and polyaniline.

The voltage outputs of other inert electrodes are summarized in Fig. S3. From which we could conclude that the voltage outputs are similar when inert electrodes are adopted. The lower voltage output of active carbon and polyaniline system could be attribute to the supercapacitance of these two electrodes.



Fig. S4 The voltage of the PMEG with epoxy fully covered the wire and the connection part of the electrode.

The following setup for investigating the influence of the relative humidity (RH) and the temperature to the power generation process (Fig. S5). Briefly, Δ RH is controlled by mixing dry and wet nitrogen gas with different ratios and monitored by commercial humidity sensor. A heater is used to control the temperature of the PSSA membrane.

It can be found that the voltage output increases with the raise of the temperature (Fig. S6a). The voltage gradually increases from ~0.4 V at 10° C to ~1.2 V at 60° C. And when the temperature reaches 80° C, the voltage decreases to ~0.8 V, which can be attributed to the loss of water content in the PSSA membrane, leading to the less effective transport of ions.

The voltage output enhances with the increasing of the Δ RH and gradually stabilizes at ~0.8 V (Fig.S6b). The enhancement of the voltage output can be understood by the higher water uptake endows the membrane higher water diffusion coefficient and the conductivity of ions, which facilitate the power generation process.



Fig. S5 Experimental setup of the influence of relative humidity and temperature to the power generation process.



Fig. S6 Influence of temperature (a) and the relative humidity (b) to the power generation process.



Fig. S7 Voltage output of PMEG under wetting and dewetting process.



Fig. S8 The voltage output of the PMEG when liquid water is used to realize the power generation process.



Fig. S9 Short circuit current density of the PMEG ($1 \times 1 \text{ cm}^2$). The membrane was moisturized under a constant moisture feeding with a variation of relative humidity (ΔRH) of 80%. The current density was calculated by the short circuit current normalized to the effective electrode area of the upper electrode. In this case, the effective electrode area was 0.4 cm².



Fig. S10 Repeatability of the power generation process. (a) Long-term cycling test of the power generation process on PSSA membrane. PSSA membrane was dried for 30 min in 50 °C after every cycle. (b) FTIR test of the sample before and after the cycling performance test show identical profile, indicating no functional group changing during the test before and after the test.



Fig. S11 Electric output of PMEG with the different electrical resistance as load. (a) Dependence of current density and voltage output on electrical resistance of the external circuit. (b) Dependence of power density on electrical resistance of the external circuit.

The test of the dependence of the voltage and current density on the electrical resistance of the external circuit is test by connect a PGD with a resistance box. The power output is calculate by the following equation:

Where the U is the voltage tested on the resistance box. I is current in the circuit calculated by Ohm' law.



Fig. S12 Configuration of the flexible polymer moist-electric generator (f-PMEG). (a) Photo of two f-PMEG units connected in series. (b) SEM image of the carbon electrode. The morphology of the carbon electrode is solid and smooth. The scale bar represents 2 μ m. (c) EDS analysis of the carbon electrode. The electrode are consisted of carbon and oxygen elements without any other impurities.



Fig. S13 The discharging profile of a capacitor charged by one f-PMEG unit using vapor from boiling water. One f-PMEG unit was hung over boiling water (90°C) for 3 seconds to harvest the energy from hot vapor. The capacitor could be charged to about 0.2 V.



Fig. S14 The setup of a mist-powered light. (a, b) Setup of the a mist-powered light. The powering units consisted of six f-PMEG units connected in series. LED bulb is connected into the circuit. The whole device is mounted on a commercial humidifier. The mist from the humidifier passed through the inlets and contacted with the f-PMEG.



Fig. S15 Short circuit current of PMEG under constant moisture feeding for a long term. A PMEG was put into a incubator with a constant temperature and Δ RH to be 25°C and 70%. The signal gradually increases to a maxium value at about 25000 s and then decreases back to zero at about 150000 s after which the signal keeps unchanged.

To further discern the originality of the proton from water molecules or the PSS membrane, N, N-dimethylformamide (DMF) is used to replace water to realize the EPG process, from which protons would not be released. When DMF (desiccated by molecular sieve) is bubbling through and carried by nitrogen gas to stimulate the PSSA membrane, EPG process could also be found which is similar to that of water (Fig. S16), indicating the moving proton is dissociated from the PSS membrane, instead of the solvent.



Fig. S16 Voltage output of PMEG stimulated by non-protonic DMF solvent.



Fig. S17 The potential acquired from KPFM of the side moisturized. The potential detection of the PSSA membrane acquired from KPFM data show that during the moisturizing, the potential of the moisturized side keeps almost unchanged (from left to right: original, moisturizing for 100 s and 200 s, respectively).



Fig. S18 Photo of the comparison experiment of the pH indicator in different situation. From left to right: Bromophenol blue (BPB) in isopropanol (IPA), after water being added in to the BPB/IPA solution, PSSA membrane in BPB/IPA solution and after water being added in to the PSSA membrane in BPB/IPA solution. The result indicate that water dissociate the PSSA membrane is the main reason triggering the proton releasing.



Fig. S19 The dynamic voltage change between two sides of the PSSA membrane. A piece of PSS membrane is sandwiched between two cylinders of bromophenol blue/isopropanol solution. 20 μ L of water was added into the upper cylinder. And the voltage output increases and reaches a maximum value at about 100 s and decreases back to zero after 300 s.



Fig. S20 Modeling, simulated proton movement induced potential distribution on a PSSA membrane. The proton migration process and the corresponding induced electric field was simulated by a theoretical model based on Nernst-Planck-Poisson equations with proper boundary conditions. The electric field within the PSSA membrane forms as the protons migration. And the electric field gradually increases to about 0.8 V at 750 s and reach a stable state at about 1000 s, which is consistent with the experimental data.



Fig. S21 The stimulated voltage output by the PSSA membrane. The simulated result of the voltage output, corresponding to the voltage difference between the two sides of the PSSA membrane gradually increases and reach a maximum value at about 0.8 V, perfectly fitting the experimental data.

No.	Material	Form of	Mechanism	Open circuit	Short circuit	Refencence
		water		Voltage	current	
1	Graphene oxide	Moisture	Proton movement guided by	0.45 V (pulse)	$2 \mu\text{A/cm}^2$ (pulse)	3
			moisture			
2	Carbon black film	Liquid	Evaporation induced flow	1 V	~100 nA	4
		water				
3	Graphene oxide with	Moisture	Proton movement guided by	26 mV (pulse)	5 μ A/cm ² (pulse)	5
	electrical treatment		oxygen concentration			
4	Printable carbon	Liquid	Evaporation induced flow	1 V	~700 nA	6
	membrane	water				
5	Porous carbon film	Moisture	Proton movement guided by	68 mV	3 nA	7
			oxygen concentration			
6	TiO ₂ nanowire	Moisture	Streaming potential	0.5 V (pulse)	50 μ A/cm ² (pulse)	8
7	3D Graphene oxide	Moisture	Proton movement guided by	300 mV (pulse)	3.5 mA/cm^2	9
	with electrical		oxygen concentration			
	treatment with Al					
	electrode					
8	PPy skeleton with	Moisture	Ion movement guided by ion	60 mV (pulse)	$10 \ \mu A/cm^2$ (pulse)	10
	ion gradient		concentration			

Supplementary Table 1. Summary of recent rising power generation methods.

9	PPy nanowire with	Moisture	Ion movement guided by ion	72 mV (pulse)	$0.14 \ \mu A/cm^2$	11
	ion gradient		concentration		(pulse)	
10	g-C ₃ N ₄ membrane	Salt	Ion transport based on the	76 mV	8.5 μΑ	12
		solution	concentration difference of ions			
11	Carbon nanotube	Salt	Streaming potential	0.341 V	8.5 µA	13
		solution				
12	Graphene oxide and	Moisture	Proton movement guided by	1.5 V (pulse)	100 nA (pulse)	14
	Laser treated		oxygen concentration			
	graphene oxide					
13	Single - walled	Liquid	Flow induced	0.38 mV	1.42 µA	15
	carbon nanotubes	water				
14	Reduced graphene	Salt	Pseudocapacitors charge and	84.76 μV	0.82 μΑ	16
	oxide on substrate	solution	discharge			
15	Nafion membrane	Salt	Ion transport based on the	84 mV	5.2 mA	17
	with carbon	solution	concentration difference of ions			
	nanotube paper					
16	Graphene on silicon	Liquid	Waving potential	0.1 V	11 µA	18
		water				
17	Graphene on silicon	Salt	Pseudocapacitors charge and	30 mV	1.7 μA	19
		solution	discharge			
18	Graphene on	Salt	Triboelectric effect	0.4 V	4.5 μΑ	20

	polyethylene	solution				
19	Graphene	Liquid	Streaming current		2.23 ± 0.26	21
	hydrogel membrane	water			nA	
20	Positively and	Salt	Osmotic power	152.8 mV		22
	negatively charged	solution				
	nanofluidic					
	membrane					
21	Carbon nanotubes	Liquid	Chemical energy converting into	~300 mV		23
		water	electricity			
22	3D graphene foam	Water	Charge coupling		20 µA	24
		with				
		ethanol				
23	Nanotube yarn twist	Liquid	Mechanical energy converting	~500 mV		25
		water	into electricity			
24	PSS membrane	Moisture	Proton movement guided by	0.8 V	0.15 mA/cm^2	THIS WORK
			moisture			

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