

Supporting Information

Hybridizing Energy Conversion and Storage in a Mechanical-to-Electrochemical Process for Self-Charging Power Cell

Xinyu Xue[†], Sihong Wang[†], Wenxi Guo, Yan Zhang, Zhong Lin Wang*

A. Piezoelectric output of the polarized PVDF films

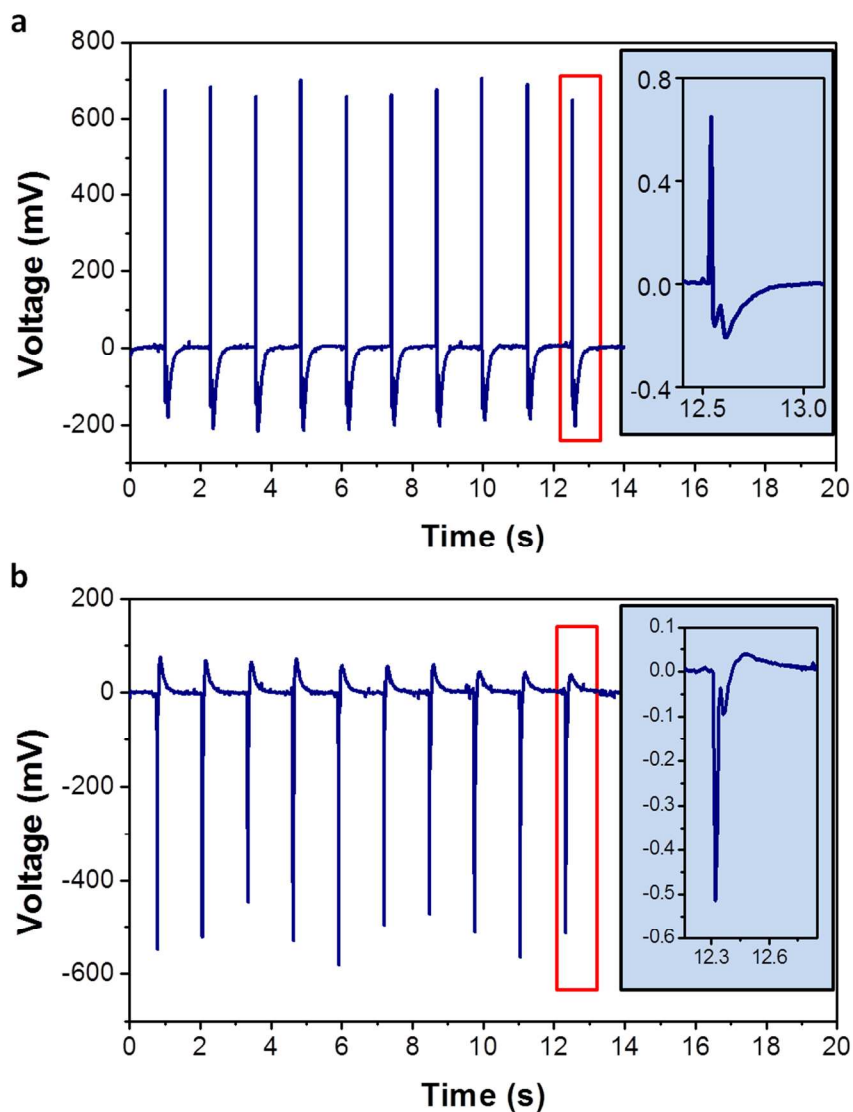


Figure S1. Study of the piezoelectric performance of PVDF film as for nanogenerator prior to fabrication of a self-charging power cell. The piezoelectric performance of PVDF separator film was investigated by sealing Pt-PVDF-Pt sandwich structures in a stainless-steel 2016-coin-

type cell without electrolyte injection, similar to the structure of piezoelectric nanogenerator. **(a)** & **(b)** are the voltage output profiles of PVDF separator films with two opposite polarizations under a periodic mechanical compressive straining. The output signal is reversed by reversing the polarity of the PVDF film **(b)**. When the PVDF film is subjected to a compressive strain, a piezoelectric field is created inside the film, which results in a transient flow of free electrons in the external load to screen the piezopotential. When the strain is released, the piezopotential diminishes and the accumulated electrons are released. The applied stress drives the electrons to flow back and forth in the external circuit, resulting in an alternating output. The difference in the magnitude of the output voltage is due to the difference in straining rates of the PVDF film when be compressed and released.

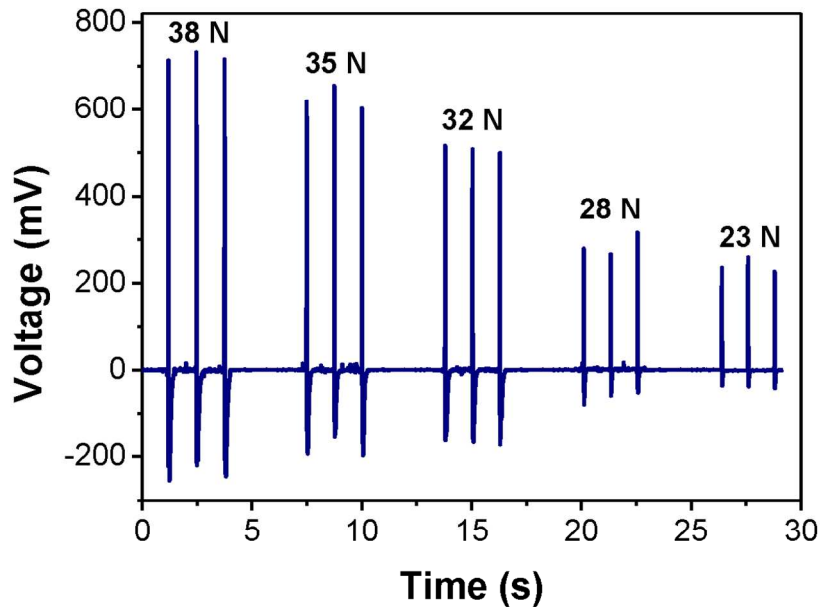


Figure S2. As we solely increase the mechanical force applied to PVDF film, the piezopotential is increased because of the increased strain. This study is important to prove that PVDF is effective for converting mechanical energy into electricity.

B. Crystal structure of as-synthesized TiO₂ nanotubes

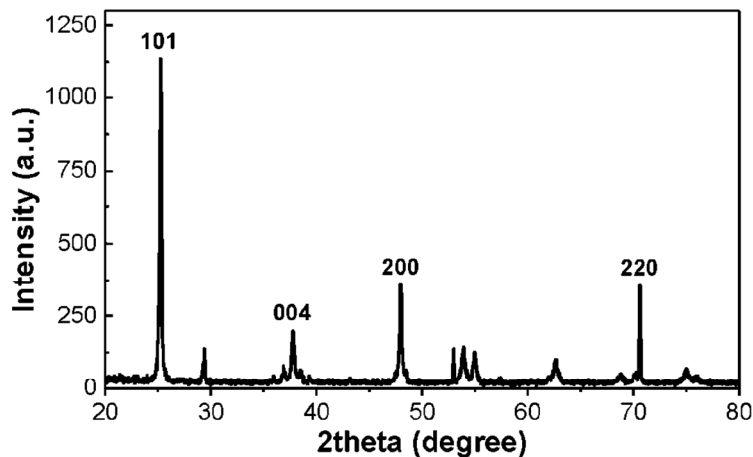


Figure S3. XRD pattern of as-synthesized TiO₂ nanotubes to define their phase. All of the main peaks can be indexed to anatase TiO₂ crystal (JCPDS File No. 21-1272).

C. Phase composition of PVDF film

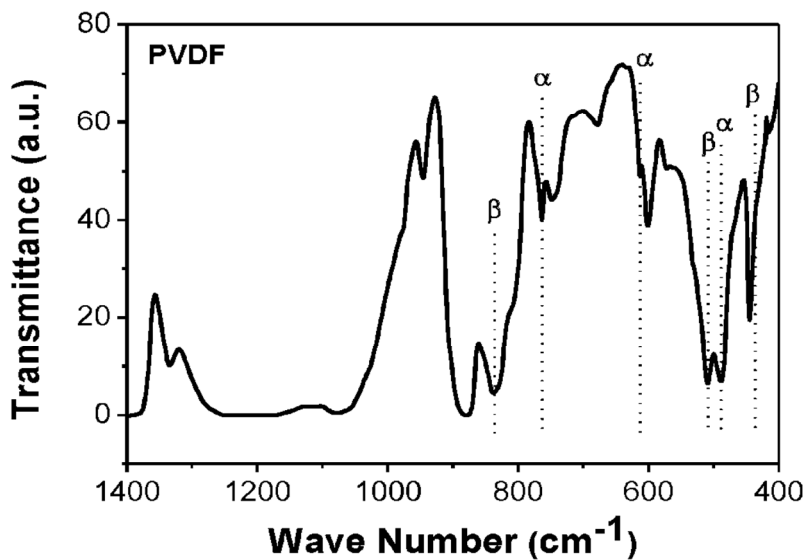


Figure S4. FTIR spectrum of PVDF separator film. Fourier transform infrared spectroscopy (FTIR) was used to characterize the phase of PVDF separator film. The mixture of the polar β phase and the non-polar α phase is indexed.

D. Viability of the self-charging power cell as a battery system

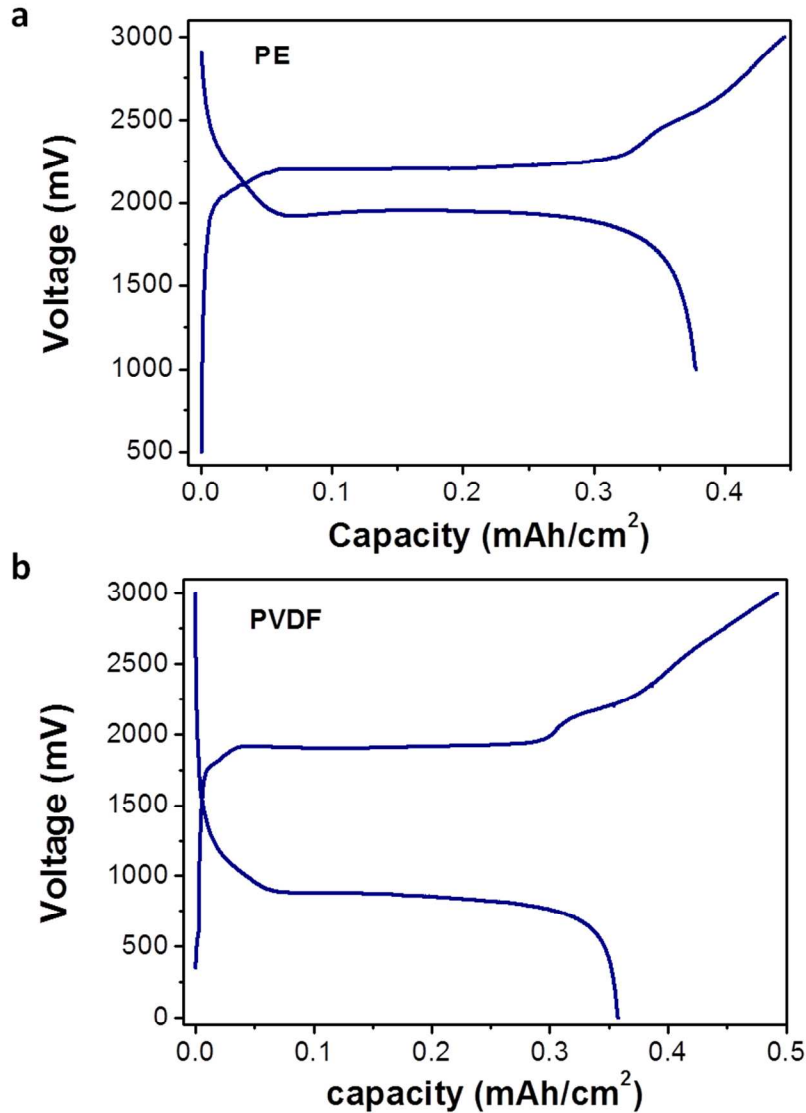


Figure S5. Galvanostatic charge-discharge voltage profiles to prove the viability of SCPC as a battery system. Initial charging and discharging cycle of (a) Conventional lithium ion battery with PE as the separator, and (b) SCPC with poled PVDF at C/10 rate (10 hours per half cycle). SCPC possess almost the same capacity of 0.36 mAh/cm² as that of traditional Li-ion battery, which confirms that the proposed structure of SCPC is fully eligible as a battery system. The only thing needed to be noted is that the discharge plateau of SCPC is lower than that of conventional lithium ion battery because the PVDF film is thicker and with less ionic conduction paths, thus the internal resistance of SCPC is higher.

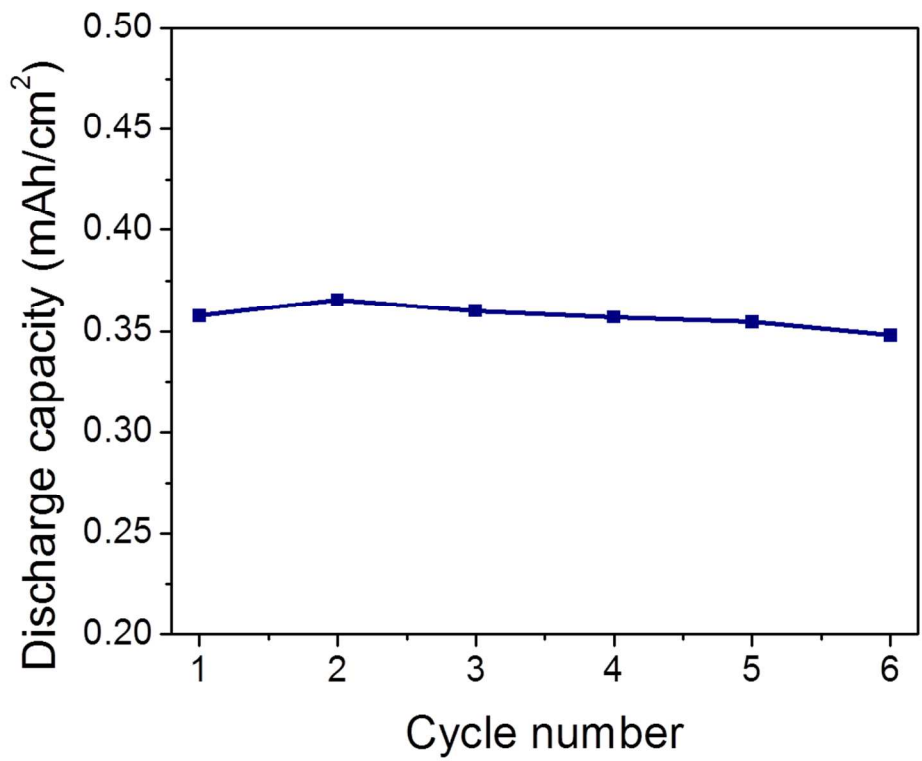


Figure S6. Dependence of the reversible discharge capacity of a SCPC on number of operation cycles at a C/10 rate if it is taken solely as a battery.

E. The Young's modulus of PVDF after immersing in electrolyte

It is generally known that the elastic modulus of PVDF may change after absorbing liquid. In order to get an accurate value of the elastic modulus of the PVDF film for our calculation, we experimentally compared the young's modulus of the PVDF film before and after absorbed with electrolyte. Our measurement was based on quantifying the maximum deflection at the tip of a PVDF cantilever under a transverse deflection force of f_y , which is given by:

$$v_{\max} = \frac{f_y l^3}{3EI_{xx}}$$

where the cantilever length is l and I_{xx} is its moment of inertia related to the geometrical shape of the cantilever. Therefore, the deflection is inversely proportional to the Young's modulus. Since the Young's modulus of the dry PVDF film is known, which is 2 GPa, by measuring the relative change in deflection distance, the Young's modulus of the PVDF after absorbing the electrolyte was determined to be 1.2 ± 0.1 GPa. This is the value we used for quantifying the efficiency of the SCPC.

F. The origin of piezoelectricity and charge distribution in polarized PVDF films

The piezoelectricity of the PVDF originates from the spontaneous electric polarization in its polar β phase, where the center of positive charges and center of negative charges do not coincide in every molecule. After the PVDF film is polarized, all of the electric dipole moments align along the direction of the electric field during poling process. All of the dipole moments in the same direction will add up, so that the two surface of PVDF film will have bonded charges. For a strain free PVDF film in electric equilibrium, the bond charges are compensated by the opposite space charges (Fig. S7a). When a compressive (or tensile) strain is applied onto the PVDF film along the poling direction, the distance (d) between the positive charge center and the negative charge center is changed, so that the dipole moment ($p=q \cdot d$) is changed. This will result in the change of the bond charge density at the two surfaces, so that the opposite signed space charge will no longer be in equilibrium to balance the bonded charges, thus there will be a voltage drop across the surfaces, which is the piezo-potential referred in the text (Fig. S7b).

The mechanism of the mechanical-to-electrochemical process we proposed in this paper applies not only for all of the piezoelectric materials, such as PVDF and PZT and so on, but also for other type of piezoelectric materials which do not have spontaneous electric polarization, like wurtzite structure, such as ZnO and GaN. For simplicity and clarity, because the piezo-potential works the same for all of the piezoelectric materials, we just present it using the very basic definition of piezoelectricity in the mechanism as illustrated in Fig. 2.

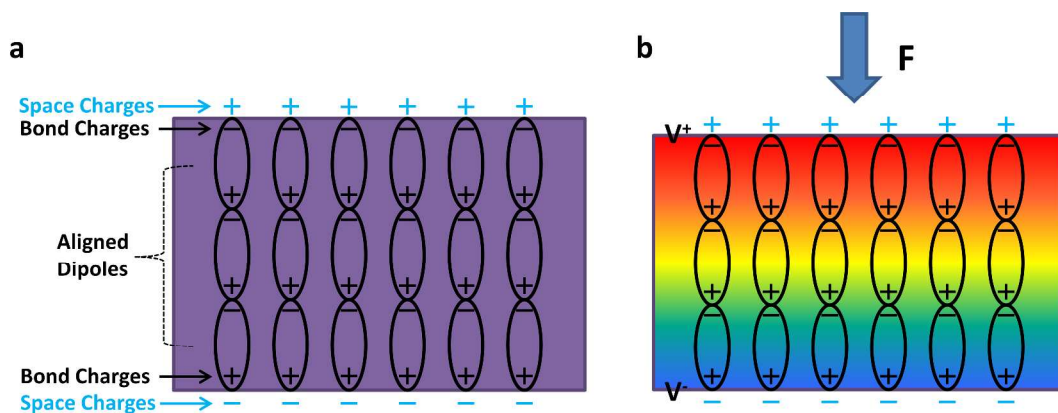


Figure S7. The origin of electricity and charge distribution in polarized PVDF film . (a) Strain-free state with zero macroscopic piezopotential. **(b)** Under compressive strain with measurable macroscopic piezopotential.

G. Intercalation and deintercalation of Li ions across the interfaces between electrolyte and the two electrodes in the SCPC

During the self-charging process of SCPC, the Li ions will deintercalate from and intercalate into the cathode and anode electrodes, respectively, in the same manner as in traditional Li ion batteries, without being affected by the presence of piezopotential, which is mostly confined inside of the PVDF film, because the positive piezo-charges at the top of the film and the negative piezo-charges at its bottom act like a parallel plate “capacitor” with little leakage of field outside of the film, so that it will not repel the Li ions to move in an opposite direction for charging. In addition, the intercalation/deintercalation process is the result of the shifting of the chemical equilibriums around the two electrodes, which will not be influenced by the piezoelectric field. The chemical equilibrium at the electrodes is likely to be broken by the change of the Li ion concentration in the electrolyte (inside the pores of the PVDF film) around the two electrodes under the drive of the piezoelectric field. In order to establish a new chemical equilibrium, the Li ions will deintercalate from and intercalate into the cathode and anode, respectively. Finally, as for the devices sealed in the coin cells, both of the electrodes have intimate contacts with the PVDF separator, so that the electrodes will have equal potential with the PVDF in contact and the ambient electrolyte.

H. The transfer of electrons across the electrodes during the self-charging process.

The migration of Li^+ under the driving of piezopotential will break the local chemical equilibrium around the two electrodes, so that cathode will release Li^+ and electrons while the anode will combine Li^+ with electrons, leaving positive charges. The redundancy of electrons at the cathode and the lack of electrons at anode will give them the tendency to transfer from cathode to anode.

There are generally two ways for the electrons to transfer from cathode to anode: either inside the battery system in some manner, or through the leakage of the external circuitry (that is the electrochemical workstation connected across the two electrodes of the device for the monitor of open-circuit voltage during the self-charging process). If the electrons is mainly transferred through the leakage current of the electrochemical workstation, when we disconnect the device with the electrochemical workstation, which means that there will be no external circuitry, then either of these two cases will happen: both the extra electrons at the cathode and the positive charges at the anode will preserve at the current collectors during the electrochemical reactions, or the self-charging process cannot move forward continuously. Out of this consideration, we compared the self-charging behavior of SCPC with and without the parallel connection of the electrochemical workstation. After the periodic deformation for 1 hour in both cases, we connected the devices across the two ends of a resistor ($\sim 30\text{k}\Omega$) with a current amplifier in series, to measure the discharge current. As shown in Fig. S8a for self-charging without connection to the electrochemical workstation and Fig. S8b with the connection, the discharge behavior is similar: at the very moment that the device was connected to the resistor, the discharge current abruptly went to several μA , then started to decay gradually in a relaxation manner (the reason that the initial discharge current is different is because the resistors used are different). From this comparison, we can see that the SCPC can be self-charged independently under the repeated deformation no matter there is an out circuitry or not, and charges are transferred from one electrode to the other inside the device, so that the energy is successfully stored through harvesting the mechanical energy.

Thus, we intend to suggest that the electrons move inside the battery system during the self-charging process. Although theoretically the medium—electrolyte and PVDF separator—between the two electrodes are electronic insulators, there still exists some leakage of electrons insides the battery, which is the reason for the self-discharge phenomena universally presented in all the batteries^{31, 32}. We can name a few possible leakage mechanisms according to previous investigation on the self-discharge, such as the resistive leakage of electrons due to the actual

finite resistance of electrolyte, and some side redox reactions with the participation of electrolyte, which can transfer the electrons indirectly from one electrode to another. Upon the subjection of periodic piezoelectric field, these approaches for electron leakage could be possibly enhanced. Although so far it is still difficult to nail down to certain exact electronic conducting mechanisms, it is very likely that the charges are transferred and stored through the electrochemical reactions under the effect of piezoelectric field.

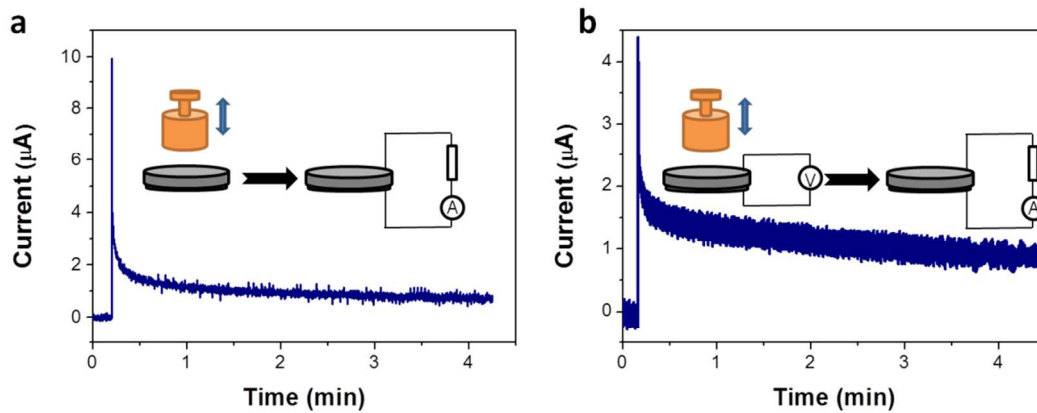


Figure S8. The discharge current of SCPC after self-charging in two conditions through cycled deformation: (a) without and (b) with the connection to an electrochemical workstation (symbolized by a volt meter in the figure).

I. Self-charging effect of SCPC in relatively high voltage range.

In Fig.3 and Fig.4, the self-charging behavior of SCPC under the effect of piezoelectric field are demonstrated from the as-fabricated initial voltage of the battery structure without any previous electrical charging or discharging, which is in the low voltage regime. In order to validate the mechanism we proposed in wider voltage range, and to show the potential of fully charging the SCPC under the mechanism, we performed similar experiments in relative higher voltage range on the SCPC, the similar structure with PVDF separator in opposite poling direction, and the one with unpolarized PVDF separator. We firstly charged the battery-type storage units to higher voltage. After the charging process was over and enough time for the voltage to stabilize, we started applying the periodic deformation (the same magnitude and frequency with Fig. 3a) to examine the change of the open-circuit voltage.

As shown in Fig. S9a, the SCPC still can be self-charged starting from 1.445V with the voltage increased by 55mV in 7000s. Although the self-charging process is much slower at higher voltage for a number of reasons, the mechanism still works. Thus, through the future improvement of device structure and fabrication techniques, the SCPC could be fully charged based on the as-proposed mechanical-to-electrochemical process.

The device with the PVDF film in the opposite poling direction is firstly fully charged. Upon periodic deformation, the voltage decreased from 2.1V to 0.4V in 1 day's time, passing by the discharge plateau (Fig. S9b), which normally takes months of time for ordinary battery. Thus, we can see that the self-discharging rate is largely increased by the piezopotential in the opposite direction. Moreover, this fully discharge process confirms that the mechanical-to-electrochemical process we proposed can continuously drive the progress of electrochemical reactions to accomplish the entire charging or discharging process.

Though the similar experiment on the device with unpolarized PVDF film as the separator (Fig. S9c), which is just a conventional battery, we can find that the voltage will slightly decrease in the higher voltage range (from 1.46V) when the battery is subjected to periodic deformation. Thus, with the current device structure and packaging technique using the coin cell, the battery will suffer a more severe leakage problem because of deformation, which hinders the higher efficiency and stability of the current self-charging power cell.

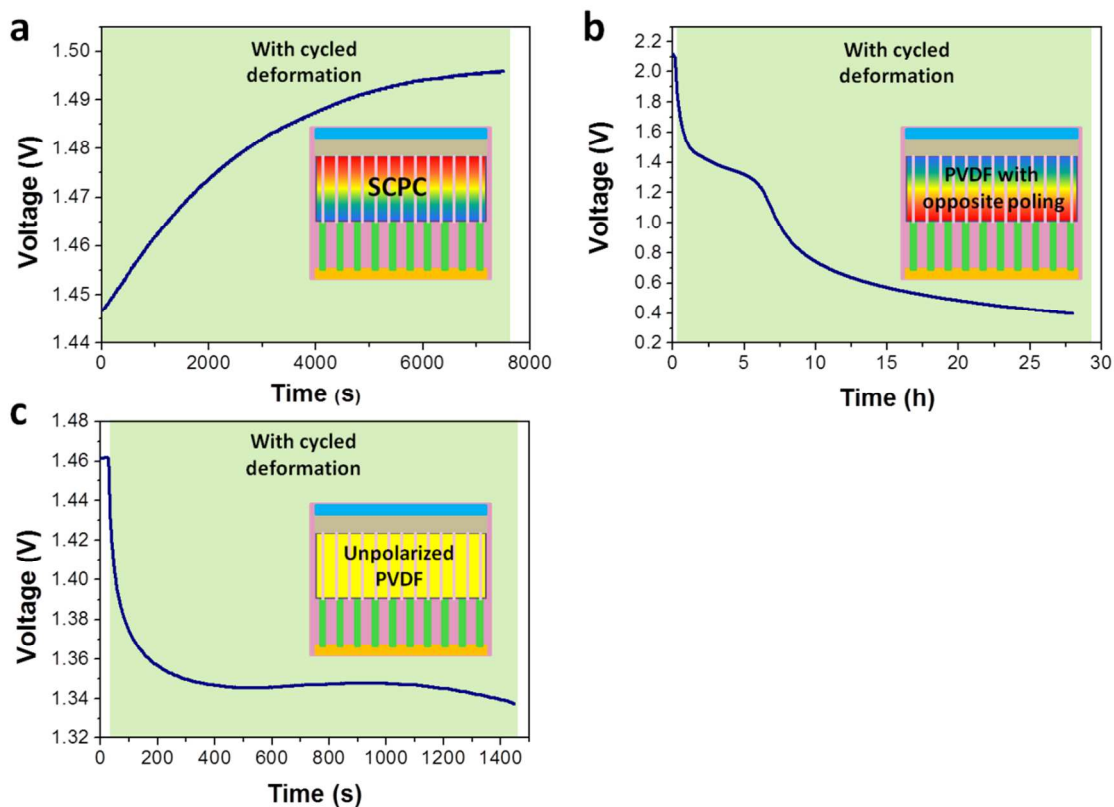


Figure S9. Reponse of devices to perodic deformation at relative high voltage range. (a) Self-charging behavior of SCPC starting from 1.445V. **(b)** Accelerated self-discharging for the device of the similar structure but with the PVDF film of the opposite poling direction. **(c)** Response of a conventional Li-ion battery with unpolarized PVDF film as separator.

J. The approximate determination of the self-charging current

When connecting the SCPC with a resistor parallelly, it will start to discharge through the resistor, and the discharge current will slowly decay, because the open circuit voltage gradually decreases with the discharging process. As the device discharged to only a small capacity left and a very small discharging current ($\sim 60\text{nA}$), we began to apply the cycled deformation onto the device, which will start the self-charging process, along with the discharge (Fig. S10). As we can find from Fig. S10, the discharge current started to increase, because the energy storage rate is higher than the energy dissipation rate. The discharge current will gradually saturate when these two rates got equal, where the discharge current became approximately the same with the self-charging current. Thus, through Fig. S10 we can find that the self-charging current is approximately 120nA .

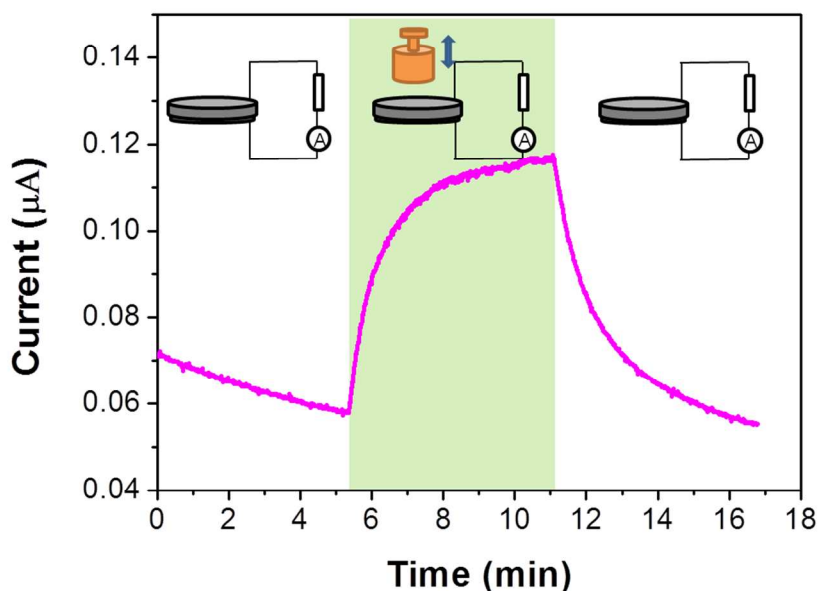


Figure S10. The discharge current when SCPC was connected to a resistor. In the green shadow region, the cycled deformation was applied onto the device when the discharge process went on.

K. In the traditional charging methodology, the voltage output of the generator unit before and after the rectification.

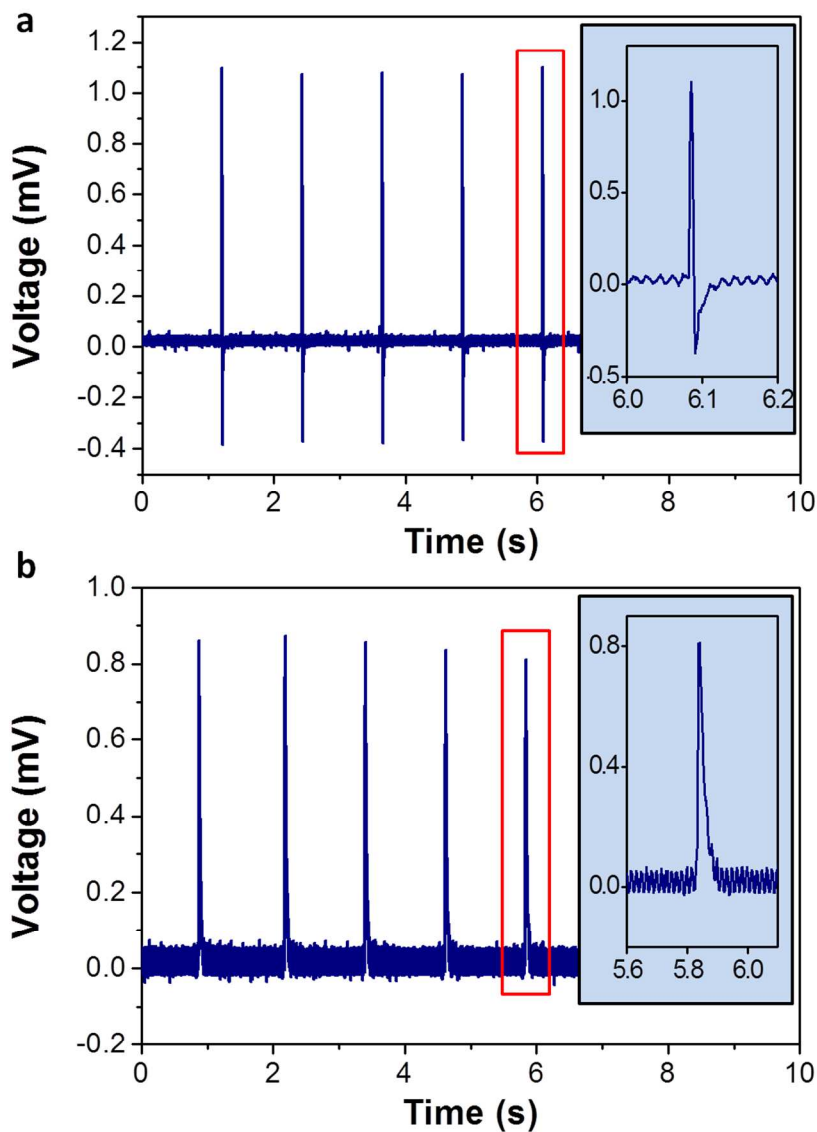


Figure S11. Output of the generator unit and rectification in traditional charging method. (a) Open circuit voltage of the generator unit fabricated by sealing a PVDF film in a stainless coin cell so that it will be subjected to the same straining condition as the one in the self-charging power cell. (b) Open circuit voltage of the generator unit after rectification, which shows that the positive signals are preserved with the amplitude a little bit smaller, while the negative ones are almost cut-off. So we can tell that a substation portion of energy is lost after rectification.

- 31 Blyr, A., Sigala, C., Amatucci, G., Guyamard, D., Chabre, Y., & Tarascon, J-M. Self-discharge of LiMn₂O₄/C Li-ion cells in their discharged state. *J. Electrochem. Soc.* **145**, 194-209 (1998).
- 32 Sloop, S. E., Kerr, J. B., Kinoshita, K. The role of Li-ion battery electrolyte reactivity in performance decline and self-discharge. *J. Power Sources* **119**, 330-337 (2003)