

A flexible lithium-ion battery with quasi-solid gel electrolyte for storing pulsed energy generated by triboelectric nanogenerator

Shaoqing Li^{a,d,1}, Dan Zhang^{c,1}, Xiaoyi Meng^{a,d}, Qiu-An Huang^c, Chunwen Sun^{a,b,*},
Zhong Lin Wang^{a,b,e,*}

^a Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, PR China

^b CAS Center for Excellence in Nanoscience, National Center for Nanoscience and Technology (NCNST), Beijing 100190, PR China

^c School of Computer Science and Information Engineering, Hubei University, Wuhan, Hubei 430062, PR China

^d University of Chinese Academy of Sciences, Beijing 100049, PR China

^e School of Material Science and Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

ARTICLE INFO

Keywords:

Flexible lithium-ion batteries
Gel electrolyte
Triboelectric nanogenerators
Power management unit

ABSTRACT

Sustainable operation of flexible and wearable electronic devices is possible with energy harvested from environment, but such power could be in the form of pulses with varying amplitude and frequency. In this work, we prepared quasi-solid lithium-ion batteries (LIBs) for storing the energy generated by a triboelectric nanogenerator (TENG). The lithium-ion batteries composed of a gel electrolyte, LiFePO₄ cathode and metallic lithium anode can deliver a capacity of ~ 140 mA h g⁻¹ at 0.2 C rate and ~ 120 mA h g⁻¹ at 1 C rate. A flexible pouch cell was further fabricated with this quasi-solid electrolyte, which shows good flexibility, high mechanical strength and excellent safety against the nail puncture. The flexible LIB was used to store the pulse form energy harvested by a TENG to provide more stable power output sustainably. The quasi-solid LIB can be charged by TENG directly for three times with a capacity loss of 17%. Importantly, a power management unit (PMU) was designed to make the output of TENG to be more suitable for charging the flexible LIBs. Our results show that this PMU is beneficial for decreasing the output voltage of TENGs, thus improving the cyclability of the cell, which may be utilized in various systems consisting of different batteries and TENGs.

1. Introduction

Flexible and wearable electronic devices are changing our life due to their distinct characteristics of superior performance, light weight and flexibility, etc. [1]. However, it remains a big challenge for developing suitable energy power systems for their continuous operation. The flexible power sources are also desirable [2,3]. Nowadays, lithium-ion batteries (LIBs) have been widely used in various portable electronics [4]. To meet the requirements of next-generation flexible and wearable electronic devices, flexible LIBs and supercapacitors (SCs) that can achieve reversible deformation and work properly in those conditions are greatly desired [5–7]. Unfortunately, although LIBs have high specific capacity and high theoretical energy density, they suffer from safety issues [8]. Solid-state batteries are believed to be safer, and to have longer cycle life, high energy density, and less requirements on packaging [9,10].

Triboelectric nanogenerators (TENGs) have been developed for harvesting energy from our living environment, with a characteristic of

varying voltage/current and frequency. The TENG is based on coupling mechanism between the triboelectric effect and electrostatic induction for harvesting various kinds of mechanical energy, such as human walking, body motion and vibration [11–13]. Direct charging of a LIB by TENG remains to be investigated with considering the typical characteristics of the power form, which is distinct from charging a battery with a continuous DC power.

Herein, we report a sheet-like flexible LIB fabricated with a quasi-solid gel electrolyte, which shows good flexibility to withstand various deformations including being bent, twisted and even squeezed into a ball without degrading the performance. Furthermore, this flexible LIB was used to store the energy harvested by a TENG to provide more stable power output sustainably. To further improve the performance of this energy harvesting and storage system, we designed a power management unit (PMU) which can make the output of TENG much more suitable for LIBs. Results show that this PMU can greatly enhance stability of our TENG-LIB energy system.

* Corresponding authors at: Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, PR China.

E-mail addresses: sunchunwen@binn.cas.cn (C. Sun), zhong.wang@mse.gatech.edu (Z.L. Wang).

¹ These authors contributed equally to this work.

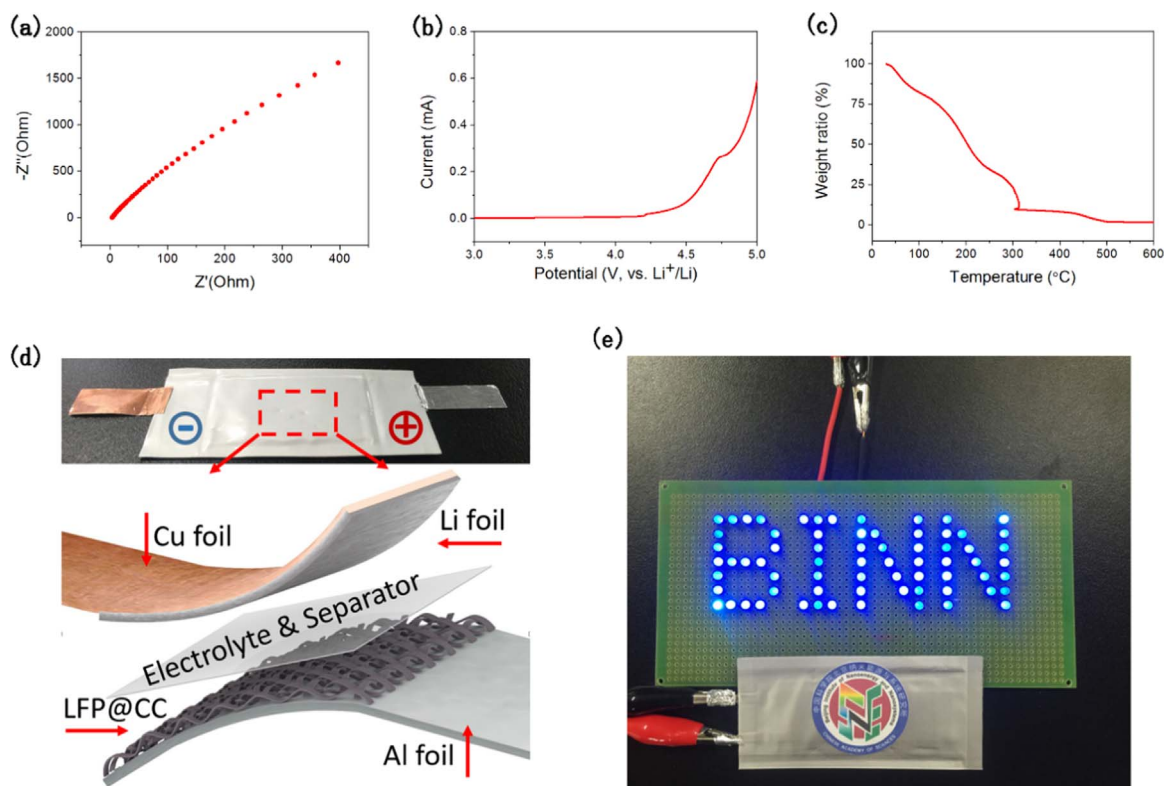


Fig. 1. Characterization of the gel electrolyte and illustration of the quasi-solid flexible LIB. (a) Nyquist plots of the gel electrolyte with the SSS symmetric cell (stainless steel sheets/ electrolyte/SSS). (b) LSV curve of the gel electrolyte in the potential window of from 3.0 V to 5.0 V at a sweep rate of 1 mV s^{-1} . (c) TGA result of the gel electrolyte. (d) Photograph and structural schematic of the cell. (e) Demonstration of a LED screen showing the letters of BINN, the abbreviation of Beijing Institute of Nanoenergy and Nanosystems, powered by the flexible cell.

2. Results and discussion

The ionic conductivity of the gel electrolyte is determined by electrochemical impedance spectroscopy (EIS). Fig. 1a shows the Nyquist plot of the gel electrolyte. The calculated ionic conductivity of this gel electrolyte is $5.67 \times 10^{-4} \text{ S cm}^{-1}$ by the equation $\sigma = l/(R_b/A)$, where l is the average thickness of the separator where the gel electrolyte was uniformly encapsulated in it; A is the contact area between separator and the stainless steel sheets; R_b is bulk electrolyte resistance. With this relatively high ionic conductivity (which generally varies from 10^{-7} to $10^{-3} \text{ S cm}^{-1}$ for gel polymer electrolytes [14]), lithium ions can transfer rapidly during charging/discharging process. The comparison of the conductivity of this gel electrolyte with previous literatures is listed in Table S1. Moreover, linear sweep voltammogram (LSV) was performed to evaluate the electrochemical stability of the gel electrolyte at 1 mV s^{-1} sweep rate (Fig. 1b). The electrolyte begins to decompose at $\sim 4.5 \text{ V}$ (vs. Li^+/Li) and accelerates quickly with voltage increasing. A decomposition voltage of 4.5 V is sufficient for LIBs with most of cathodes. To further investigate the thermal stability of the gel electrolyte, thermogravimetric analysis (TGA) was conducted. As shown in Fig. 1c, the gel electrolyte shows a low volatility ($\sim 96\%$) and high thermal stability below $50 \text{ }^{\circ}\text{C}$, however, the weight loss of gel electrolyte reaches $\sim 80\%$ when temperature increases to $300 \text{ }^{\circ}\text{C}$, which can be mainly ascribed to volatilization and vaporization of the succinonitrile and solvents. After that the weight loss can be attributed to the decomposition of PEO, PVdF-HFP and LiClO_4 .

To further evaluate cycling stability against the growth of Li dendrites, lithium plating/stripping cycling experiment was performed. In this test, symmetric $\text{Li}|\text{Li}$ cells with gel and liquid electrolyte respectively are discharged and charged at a current density of 0.05 mA cm^{-2} for 6 h respectively. As shown in Fig. S1, the cell with gel electrolyte shows more stable voltage profiles than that with traditional liquid electrolyte for about 2000 h. This result shows the

gel electrolyte has an excellent mechanical stability, which can circumvent the Li dendrites issues associated with metallic lithium batteries [4]. To examine the fire resistance of the electrolytes, three identical PE separators with different electrolytes were exposed to fire, as shown in Fig. S2. The bare PE separator was the first to collapse due to its poor thermal stability. The separator with liquid electrolyte began to burn quickly within 1–2 s, while the separator with the gel electrolyte still remained stable. These results demonstrate the gel electrolyte has higher burning point under air atmosphere than traditional liquid electrolyte, which can prevent explosion and combustion issues of the conventional liquid electrolyte based LIBs. Considering good physical and chemical properties provided by the gel electrolyte, such as high viscosity and chemical stability in air atmosphere, a sheet-like flexible cell was fabricated. Fig. 1d shows the photograph and structural schematic of the cell. As shown in Fig. 1e, it can power a LED screen continuously.

The electrochemical performance of the as-fabricated flexible LIB battery is shown in Fig. 2. The rate performance of the flexible pouch cell is comparable to that of a coin cell (Fig. S3). The capacity at 0.5 C rate can still remain 89.6% of that at 0.1 C . Fig. 2b shows the long-term cycling performance of the flexible cell. The decay of the discharge capacity is only 3.0% for 40 cycles. Even at the 60th cycle, the discharge capacity still remains 84.6% of the initial capacity for 60 cycles. The performance of our flexible cells is better than those reported in the literatures [15–19] for flexible non-liquid LIBs (Table 1). For flexibility testing, as shown in Fig. 2c, a flexible cell was bent for 30 times before tests, and the bending degree was set to 60° . Then the cell was charged and discharged at 0.2 C rate for 5 cycles. After that, this cell was bent for 15 times and tested at 0.2 C for another 5 cycles. This procedure was repeated for three times. After a combined test including 75 bending cycles and 20 charge/discharge cycles between them, the cell still shows a capacity retention of $\sim 80\%$. In Fig. 2d, it shows that a cell is firstly charged and discharge at 0.2 C rate for 10 cycles in its flat

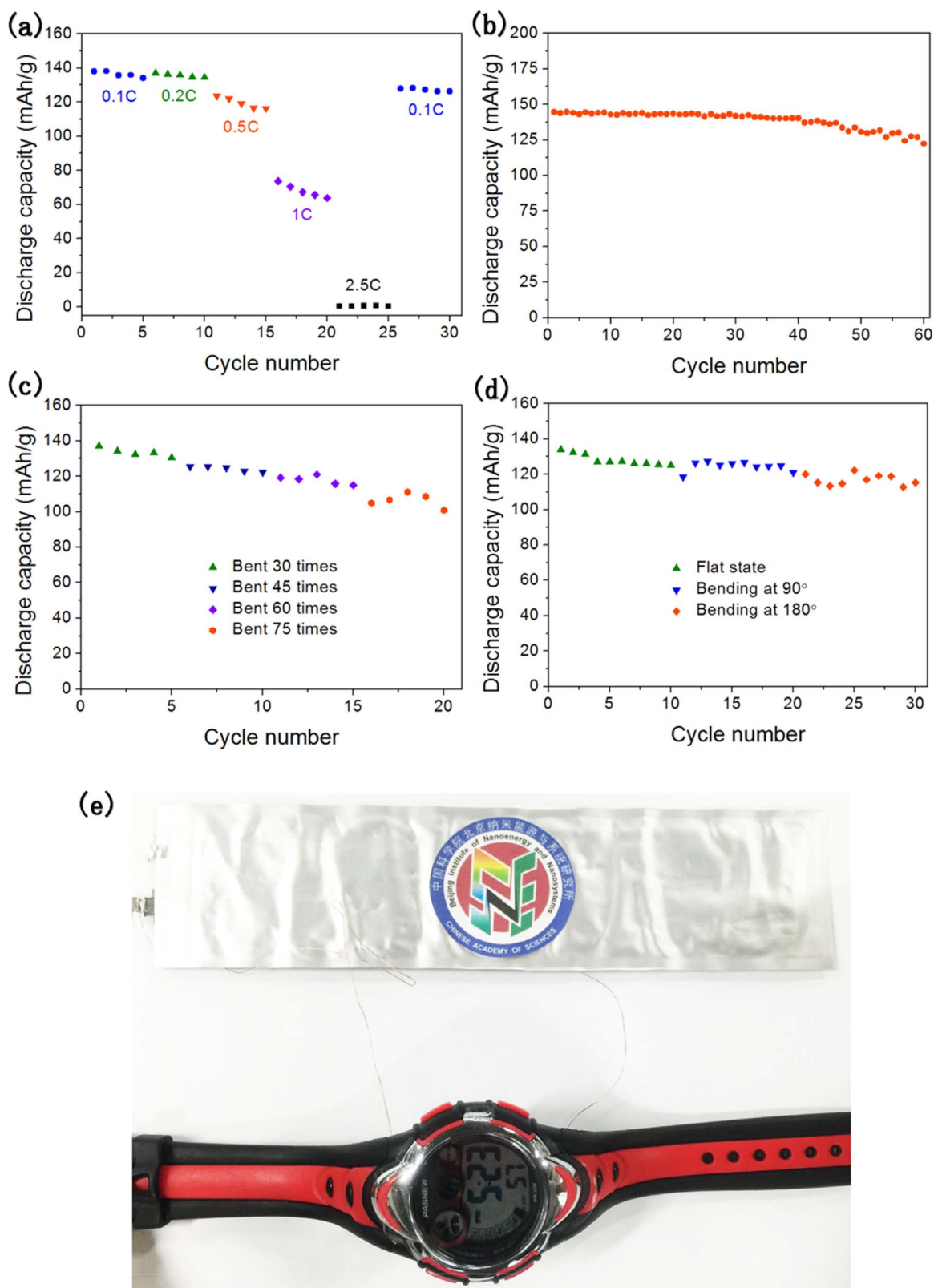


Fig. 2. Electrochemical performance of the quasi-solid flexible cell: (a) Rate performance of the flexible cell at different C rates. (b) Cycle performance of the flexible cell at a current density of 0.2 C Rate. (c) Performance of the flexible cell at different states. (d) Performance of the flexible cell bent at different states. (e) Photograph of a digital watch powered by the flexible LIB.

state. Then it was bent to certain degrees, and charged/discharged at the same rate for 10 cycles. Fig. 2e shows a photograph of a digital watch (bottom) powered by the flexible LIB (top) potential as a watch strap, which demonstrates its feasibility for practical applications.

To mimic extreme working situations, the cell was further squeezed into a ball-like state. As shown in Fig. S4a, it can still work well to light a light-emitting-diode (LED) lamp. Fig. S4c shows the cycle performance and the corresponding Coulombic efficiency. At this state, the

Table 1

The performance comparison of flexible batteries with different electrolytes and cathode materials.

Electrolyte	Electrode materials	Capacity at low C rate (mA h g ⁻¹)	Capacity at 0.5 C (mA h g ⁻¹)	Capacity retention	Ref.
Gel	LFP	145 (0.2 C)	120	91% for 50 cycles	This work
Liquid	LFP	N/A	108	< 90% for 30 cycles	[15]
Non-liquid	LFP	~ 160 (0.05 C)	N/A	90% for 30 cycles	[16]
Liquid	TiO ₂ /rGO	168 (0.1 C)	89	< 90% for 50 cycles	[17]
Liquid	LMO	N/A	88 (0.2 A g ⁻¹)	~ 85% for 50 cycles	[18]
Liquid	Si/MWCNT	N/A	1670 (0.6 C)	58% for 50 cycles	[19]

Note: LFP = LiFePO₄, LMO = LiMn₂O₄, rGO = reduced graphene oxide, MWCNT = multi walled carbon nanotubes.

cell can deliver a reversible capacity of ~ 130 mA h g⁻¹ at 0.2 C rate with a Coulombic efficiency of higher than 90%. To examine the safety of the cell with the gel electrolyte, we have also conducted a nail puncture test. Nail puncture will cause short circuit in LIBs since the metal nail will connect cathode and anode. It usually causes fire or even explosion for LIBs with organic liquid electrolyte during nail puncture. As shown in Fig. S4b, the flexible cell with the gel electrolyte was punctured for several times with a nail. During the nail puncture process, the cell can still light up a LED even in its bent state (Fig. S2d). After the test, metal nail was removed and the voltage of the cell was measured by a universal meter. As shown in Fig. S4b, the open-circuit voltage (OCV) of the flexible cell was dropped to 1.55 V from 3.34 V right after the nail puncture, which means gel electrolyte may cause slight circuit shorting. However, due to the good thermal stability of the gel electrolyte, circuit shorting couldn't cause fire or other safety issues. After the nail was pulled out, the OCV of the cell can gradually recover to 3.15 V and 3.25 V after 1 h and 2 h, respectively, indicating a self-healing characteristic of the gel electrolyte. Even after 7 days, the cell can still work and light up a LED (Fig. S2e). These results indicate that the quasi-solid gel electrolyte has better fire resistance and safety performance.

To develop a self-charging power system, a radial-arrayed rotary TENG has been used to harvest mechanical energy, as shown schematically in Fig. 3. A radial-arrayed rotary TENG can provide an open-circuit voltage of 850 V and a short-circuit current of ~ 3 mA at 3 kHz frequency with high reliability [20]. To make it more suitable for charging LIBs, we fabricated a TENG with a low open-circuit voltage (~ 10 V). The short-circuit current and open-circuit voltage of the TENG are shown in Fig. S5. Lower voltage can cause less harm to the cell, which means this TENG can directly charge a LIB without fatally harming it. However, the output voltage of the TENG is still much higher than the decomposition voltage of a gel or liquid electrolyte (typically less than 5 V). It is found that the cell with a quasi-solid gel electrolyte can only work well for 3 cycles if it is charged directly by the TENG. In order to further improve cyclability of the LIBs, a power manage unit (PMU) with an output voltage of 3.6 V was developed for this energy system (Fig. S6). The working principle of the PMU is described as follows. This PMU uses a full bridge rectifier, which have a typical potential drop of 400 mV instead of 1400 mV as that of a commonly used rectifier. Thus, this PMU design is more energy efficient. After the energy output from TENG is rectified and filtered, a capacitor is used to store it temporarily. When the voltage of capacitor reached 5.4 V, a buck chopper is triggered to provide 3.6 V voltage output until the voltage of capacitor is decreased to 3.9 V. After that, the capacitor is recharged again.

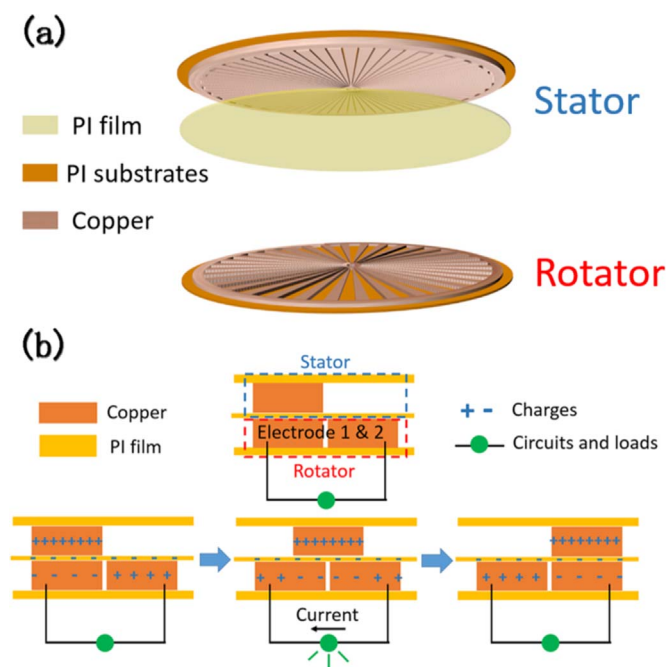


Fig. 3. Schematic of the rotary TENG (a) and its working principles (b).

Fig. 4a and d show the charging curves of the flexible cell charged by the TENG with and without a PMU respectively and discharging curves in a battery test system at a 0.2 C rate. The cell can deliver a capacity of more than 100 mA h g⁻¹ after directly charged by the TENG without any additional circuit or power management (Fig. 4d). It is noted that high voltage and pulse output characteristics of TENGs tend to accelerate the decomposition of the electrolyte, which can lead to performance degradation of the LIBs. So we designed a PMU that can reduce the TENG's output voltage from 10–20 V to 3.6 V without obvious energy loss. As shown in Fig. 4, compared with directly charging, better electrochemical performance is achieved with a PMU, such as smaller overpotential and more stable charging and discharging plateaus. After fully charged by the TENG with a PMU three times, the cell shows no obvious capacity loss or other degradation compared with the cell charged directly by the TENG. More specifically, compared with that in the first cycle, the cell charged by the TENG assisted with a PMU shows only 5% capacity loss and a drop of 9.9 mV for the potential at the capacity of 60 mA h g⁻¹ in the third discharging process while the cell charged by the TENG without a PMU shows a capacity loss of 17% and a potential drop of 26.1 mV. After the cell was charged by TENG and discharged, a galvanostatic charge/discharge test was performed in the battery test system to monitor the performance change of the cell. As shown in Fig. 4c and f, the cell with a PMU shows much smaller overpotential, higher Coulombic efficiency and better stability.

In order to figure out the effect of pulse charging the cell by a TENG, a galvanostatic charge/discharge test was performed (Fig. S7). The performance is compared with that of the cell charged by a TENG (Fig. 4f). It can be seen that the cell charged/discharged in a galvanostatic mode shows more stable and smooth charge/discharge profiles with a potential drop of only 18.9 mV after 200 cycles, while the cell charged by a TENG shows a potential drop of 26.1 mV after only 3 full cycles. These results clearly indicate that directly charging the cell by a TENG has a destructive effect on the cell performance due to the high voltage and pulse output characteristics of the TENG, which will lead to the decomposition of electrolyte and a bigger polarization of the battery. It further demonstrates that a PMU is necessary for achieving stable system performance. This raises a new challenge for the future application of TENG.

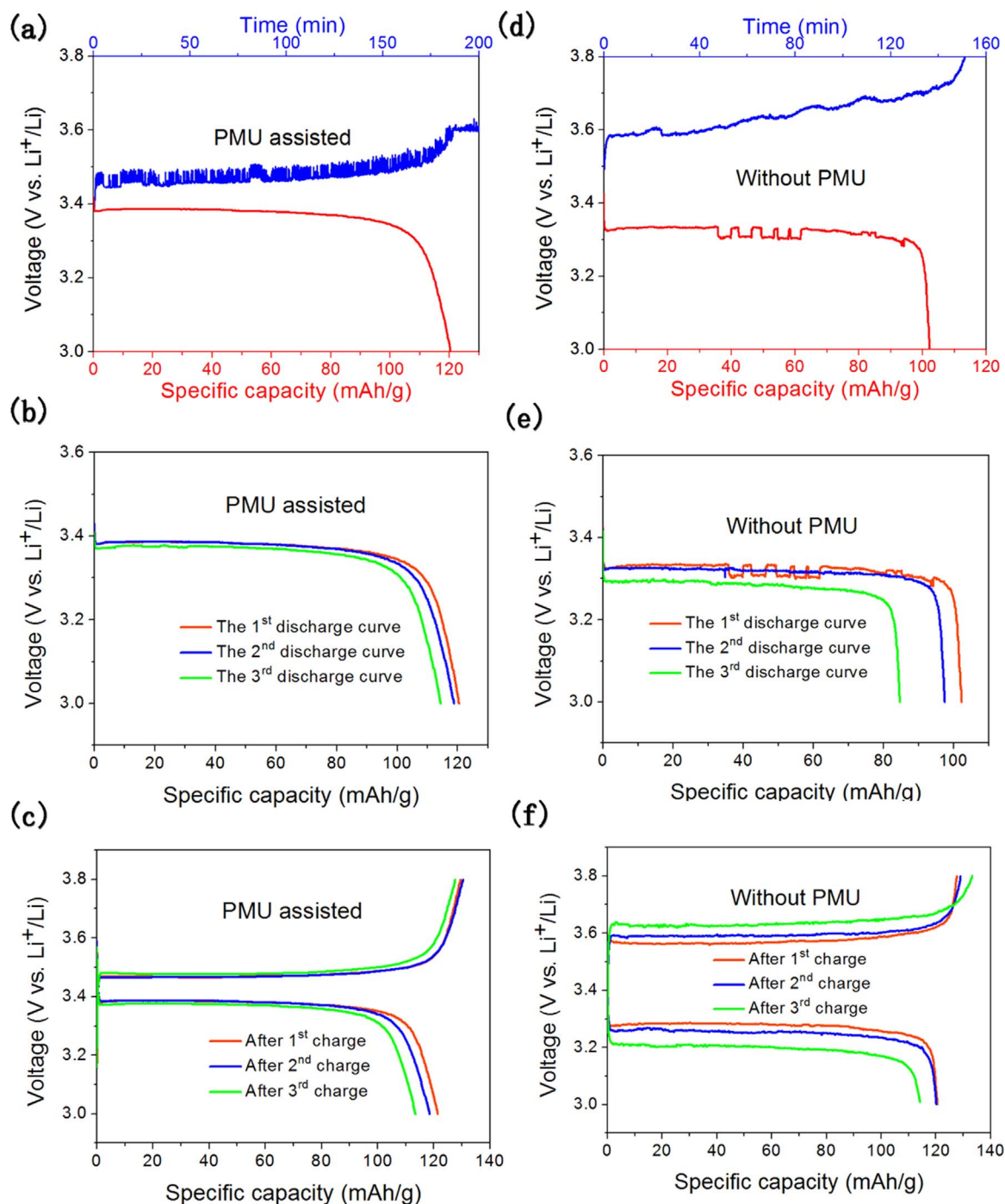


Fig. 4. Performance of the LIB charged by a TENG. (a) The charging and discharging curves of the flexible cell. The cell was charged by the TENG assisted with a PMU and discharged on cell testing system at 0.2 C rate. (b) The discharging curves of the cell at different cycles and 0.2 C rate after the cell was charged by the TENG assisted with a PMU. (c) Charging and discharging curves at 0.2 C rate after each time the cell was charged by the TENG assisted with a PMU. (d) Charging and discharging curves of the flexible cell charged directly by the TENG. (e) Discharging curves of the cell at different cycles and 0.2 C rate after the cell was charged directly by the TENG. (f) Charging and discharging curves at 0.2 C rate after each time the cell was charged directly by the TENG.

3. Conclusion

We report a sheet-like flexible LIB fabricated with a quasi-solid gel electrolyte for storing the energy harvested by a TENG to provide more stable power output sustainably. High voltage and pulse output characteristics of TENGs can lead to performance degradation of the flexible LIBs. The cell charged by the TENG directly shows a capacity loss of 17% and a potential drop of 26.1 mV. To improve the performance of this energy harvesting and storage system, we designed a PMU that can make the output of TENG more suitable for LIBs. This

PMU enables to effectively alleviate the destructive effect of pulse output and high-voltage characteristics of TENGs and stably charge a battery with various types of TENGs. It is possible to develop a self-power system by integrating our flexible battery with a flexible TENG.

Acknowledgment

The authors acknowledge the financial support of the National Key R&D Project from Ministry of Science and Technology, China (2016YFA0202702), National Natural Science Foundation of China

(Nos. 51372271 and 51672029). This work was also supported by and the *Thousands Talents Program* for the pioneer researcher and his innovation team in China.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ensm.2017.11.013.

References

- [1] D.Y. Khang, H.Q. Jiang, Y. Huang, J.A. Rogers, *Science* 311 (2006) 208–212.
- [2] M. Koo, K.I. Park, S.H. Lee, M. Suh, D.Y. Jeon, J.W. Choi, K. Kang, K.J. Lee, *Nano Lett.* 12 (2012) 4810–4816.
- [3] L. Wen, F. Li, H.M. Cheng, *Adv. Mater.* 28 (2016) 4306–4337.
- [4] J.M. Tarascon, M. Armand, *Nature* 414 (2001) 359–367.
- [5] X.F. Wang, X.H. Lu, B. Liu, D. Chen, Y.X. Tong, G.Z. Shen, *Adv. Mater.* 26 (2014) 4763–4782.
- [6] F. Meng, Q. Li, L. Zheng, *Energy Storage Mater.* 8 (2017) 85–109.
- [7] X. Guo, S. Zheng, G. Zhang, X. Xiao, X. Li, Y. Xu, H. Xue, H. Pang, *Energy Storage Mater.* 9 (2017) 150–169.
- [8] N. Li, Z.P. Chen, W.C. Ren, F. Li, H.M. Cheng, *Proc. Natl. Acad. Sci. USA* 109 (2012) 17360–17365.
- [9] C.W. Sun, J. Liu, Y.D. Gong, D.P. Wilkinson, J.J. Zhang, *Nano Energy* 33 (2017) 363–386.
- [10] H. Duan, Y.X. Yin, X.X. Zeng, J.Y. Li, J.L. Shi, Y. Shi, R. Wen, Y.G. Guo, L.J. Wan, *Energy Storage Mater.* 10 (2018) 85–91.
- [11] H.D. Hou, Q.K. Xu, Y.K. Pang, L. Li, J.L. Wang, C. Zhang, Z.L. Wang, *Adv. Sci.* 4 (2017) 1700072.
- [12] M.H. Yeh, L. Lin, P.K. Yang, Z.L. Wang, *ACS Nano* 9 (2015) 4757–4765.
- [13] X. Wang, S.H. Wang, Y. Yang, Z.L. Wang, *ACS Nano* 9 (2015) 4553–4562.
- [14] J.W. Fergus, *J. Power Sources* 195 (2010) 4554–4569.
- [15] S.W. Kim, J.H. Yun, B. Son, Y.G. Lee, K.M. Kim, Y.M. Lee, K.Y. Cho, *Adv. Mater.* 26 (2014) 2977–2982.
- [16] S.H. Kim, K.H. Choi, S.J. Cho, S. Choi, S. Park, S.Y. Lee, *Nano Lett.* 15 (2015) 5168–5177.
- [17] T. Hoshida, Y.C. Zheng, J.Y. Hou, Z.Q. Wane, Q.W. Li, Z.G. Zhao, R.Z. Ma, T. Sasaki, F.X. Geng, *Nano Lett.* 17 (2017) 3543–3549.
- [18] X. Dong, L. Chen, X. Su, Y. Wang, Y. Xia, *Angew. Chem. Int. Ed.* 55 (2016) 7474–7477.
- [19] H. Lin, W. Weng, J. Ren, L. Qiu, Z. Zhang, P. Chen, X. Chen, J. Deng, Y. Wang, H. Peng, *Adv. Mater.* 26 (2014) 1217–1222.
- [20] G. Zhu, J. Chen, T. Zhang, Q. Jing, Z.L. Wang, *Nat. Commun.* 5 (2014) 3426.