Lithium-Ion Batteries

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Flexible Aqueous Lithium-Ion Battery with High Safety and Large Volumetric Energy Density

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Abstract: *A flexible and wearable aqueous lithium-ion battery is introduced based on spinel $Li_{1.1}Mn_2O_4$ cathode and a carbon-coated NASICON-type $LiTi_2(PO_4)_3$ anode (NASICON = sodium-ion super ionic conductor). Energy densities of 63 Wh kg^{-1} or 124 mWh cm^{-3} and power densities of 3275 W kg^{-1} or 11.1 W cm^{-3} can be obtained, which are seven times larger than the largest reported till now. The full cell can keep its capacity without significant loss under different bending states, which shows excellent flexibility. Furthermore, two such flexible cells in series with an operation voltage of 4 V can be compatible with current nonaqueous Li-ion batteries. Therefore, such a flexible cell can potentially be put into practical applications for wearable electronics. In addition, a self-chargeable unit is realized by integrating a single flexible aqueous Li-ion battery with a commercial flexible solar cell, which may facilitate the long-time outdoor operation of flexible and wearable electronic devices.*

Flexible, portable and wearable electronic devices have found a wide variety of promising applications such as smart clothes, rollup displays, wireless sensors, wearable devices and implantable medical devices and gained increasing interests in recent years.[1,2] As a result, it is desperately required to develop corresponding energy-storage systems, such as supercapacitors and lithium-ion batteries (LIBs), to power them. However, commercially available supercapacitors and LIBs are typically rigid and heavy due to the thick electrode stack and their packaging,[3,4] which unfortunately cannot satisfy the requirement of flexibility, portability, convenience and design for flexible electronic devices. Numerous attempts have been made to fabricate flexible supercapacitors and great advances have been achieved.[5–17] Nevertheless, inferior performances, including low energy densities, have prevented them from appearing in the market. Instead, lithium-ion batteries with much higher energy densities are believed to become a leading candidate to power flexible and wearable devices.[18–27] Recently, a lot of efforts have been made to develop flexible and lightweight LIBs while maintaining their high capacity.[28–31] However, all reported flexible Li-ion batteries are based on highly toxic and flammable organic electrolyte, which can cause safety hazards. Especially, the safety issues may be much enlarged for flexible and wearable LIBs, when they are stretched and distorted repeatedly during use. An attractive approach to circumvent this problem is to use an aqueous electrolyte for LIBs, which adopt a "rocking-chair" concept similar to the organic LIBs.[32,33] Unfortunately, up to present, flexible and wearable aqueous LIBs have never been reported. On the other hand, most reports about electrode preparation were through directly printing, coating, spraying or weaving active materials on/in the carbon substrates, where the carbon materials play the role of current collector.[2,4,9,16–19,21–23,25,27,31] This approach can efficiently utilize the characteristic of carbon substrates, including high flexibility, porous structure and high electronic conductivity, and thus ensure the electrochemical and mechanical properties of electrode at deformed states. However, the key disadvantage is that the mass loading of electrode materials is quite low,[20] which much limited the practical energy density, especially in volumetric energy density. For example, in most of the previous reports, the mass loading of electrode active materials is generally lower than 1.5 mg cm^{-2}.[9,22–25,28] To the best of our knowledge, the largest reported energy density about wearable and flexible LIBs is only 17 mWh cm^{-3}.[31]

Herein, we designed a wearable and flexible aqueous LIB that is based on a spinel $Li_{1.1}Mn_2O_4$ (LMO) cathode and a carbon-coated NASICON-type $LiTi_2(PO_4)_3$ (LTPO) anode (Figure 1). The electrode was prepared by directly rolling a mixture of LMO (or LTPO) as active material, acetylene black (AB) as conductive agent and polytetrafluorethylene (PTFE) as binder into a film (Figure 1 a), which was then pressed onto a flexible and lightweight stainless steel mesh (see Figure S1 in the Supporting Information) to form a flexible electrode. As shown in Figure 1 b and 1 c, the electrode active material (LMO or LTPO) and the conductive carbon material of AB are well mixed in the electrode film, which results in enhanced electrical conductivity of the electrode. Additionally, the line-shaped polymer binder of PTFE further improves the interfacial contact between electrode active materials (LMO or LTPO) and AB, which ensures the flexibility of electrode film. Therefore, the resulting electrode can be freely folded, rolled and twisted without mechanical damage, exhibiting a perfect flexibility (Figure S2). This simple electrode fabrication method makes the mass loading of active material (LMO or LTPO) as high as 10 mg cm^{-2}, which is much higher than previous reports.[9,22–25,28] Then, the as-prepared electrodes and the microporous polyacrylonitrile (PAN) nonwoven separator wetted by aqueous electrolyte (2 M $LiNO_3$) were used to fabricate a 2 V aqueous LIB device (Figure 1 d), which exhibits typical flexibility (Figure 1 e and 1 f). Electrochem-

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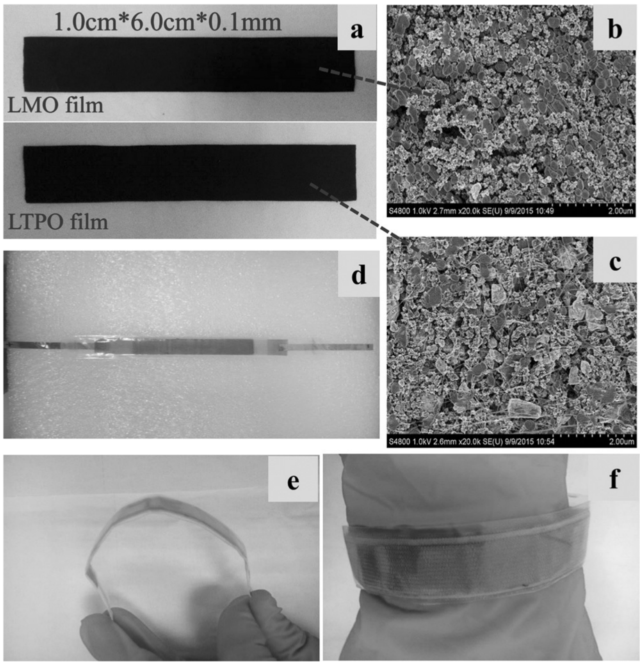

Figure 1. Preparation of flexible aqueous belt-shaped Li-ion battery. a) The images of electrode films and corresponding SEM images (b and c). d) Fabricated flexible belt-shaped full cell and its mechanical flexibility with different shapes (e and f).

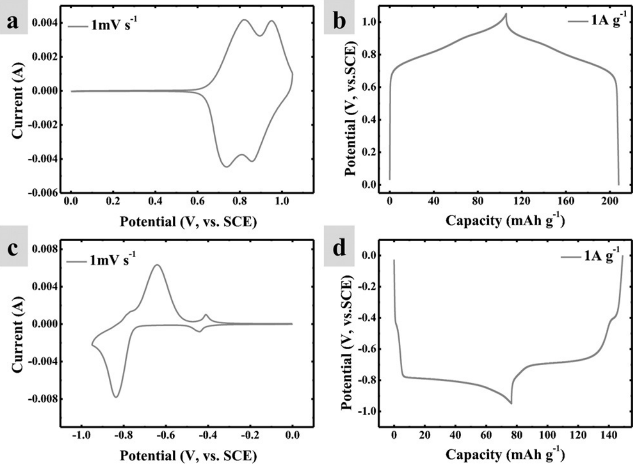

Figure 2. The electrochemical performance of LMO and LTPO in 2 M $LiNO_3$ electrolyte with a three-electrode system where active carbon and saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. a) CV profile within the potential window of 0–+1.05 V (vs. SCE) at the sweep rate of 1 mVs^{-1} and b) galvanostatic charge/discharge measurements for LMO; c) CV investigation with the potential window from 0 to −0.95 V (vs. SCE) at the sweep rate of 1 mVs^{-1} and d) galvanostatic charge/discharge measurement for LTPO.

ical performance of the LIB and its flexibility were investigated in detail. In addition, two such wearable and flexible cells connected in series with an operating voltage of 4 V were also fabricated and investigated.

Prior to the fabrication of the flexible full cell, electrochemical performance of the LMO and LTPO flexible electrode films in aqueous electrolyte were investigated by cyclic voltammetry (CV) and galvanostatic charge/discharge measurements with a three-electrode system, respectively. Preparation and characterization of both materials are given in Figure S3 and Figure S4. It can be detected from the CV profile of LMO that two pairs of redox peaks locate in the potential of +0.82 V/+0.75 V and +0.95 V/+0.88 V (vs. SCE; Figure 2 a), which corresponds to the Li^+-intercalation/de-intercalation.[34] As shown in Figure 2b, the specific capacity of LMO is 105 mAhg^{-1}. CV curve of LTPO is presented in Figure 2c, where the redox peak at −0.81 V/−0.65 V (vs. saturated calomel electrode = SCE) can be observed clearly. The small redox peaks located around −0.4 V (vs. SCE) should be attributed to the impurity of $TiPO_4$ in the LTPO sample (Figure S4). It can be detected that the specific capacity of LTPO is 80 mAhg^{-1} (Figure 2d). The cycle performance for both electrodes is given in Figures S5 and S6, respectively.

After the electrochemical investigation of single electrode, LMO and LTPO are then used as cathode and anode materials, respectively, to form a flexible belt-shaped aqueous Li-ion full cell with the lamination process. As shown in Figure 3a, the cell can be charged/discharged within the voltage window from 0 to 2.0 V, which is consistent with the potential difference of the cathode and the anode observed aforementioned. The mass loading of cathode material (LMO) and anode material (LTPO) is 10 mgcm^{-2} and 12 mgcm^{-2}, respectively. The current density (Ag^{-1}) and the specific capacity (mAhg^{-1}) are calculated based on the total mass of electrode materials (LMO + LTPO). The flexible cell delivers a discharge capacity of 40 mAhg^{-1} at the current density of 0.2 Ag^{-1}, indicating a cathode capacity of 88 mAh$g^{-1}{}_{LMO}$ based on the mass of LMO and an anode capacity of 72 mAh$g^{-1}{}_{LTPO}$ based on the mass of LTPO. The small plateau at about 1 V arises from the impurity of $TiPO_4$ in the anode LTPO electrode (Figure S4). When a current density of 1 Ag^{-1} is applied, the discharge capacity of 35 mAhg^{-1} can still be achieved. Even at a much higher current density of 2 Ag^{-1}, the flexible cell can still deliver a capacity of more than 25 mAhg^{-1}, suggesting a perfect rate capability. Ragone plot of the flexible cell is given in Figure 3b. It can be detected that the specific energy reaches 63 Whkg^{-1} at a specific power of 320 Wkg^{-1}, and still keeps 28 Whkg^{-1} at a power density of 3275 Wkg^{-1}. The volumetric energy density and power density were also calculated based on the total volume of cathode, anode and separator. The maximum volumetric energy density and power density are 124 mWhcm^{-3} and 11.1 Wcm^{-3}, respectively, which are about 7 times higher than the largest value (17.7 mWhcm^{-3} and 1.7 Wcm^{-3}) reported up to present (Table S1). The cycle performance given in Figure 3c indicates the cell can keep its columbic efficiency around 100% during 100 cycles with capacity retention of about 72% at the current density of 1 Ag^{-1}. Moreover, flexible aqueous Li-ion battery can still work well even with higher mass loading of active material (ca. 20 mgcm^{-2}) (Figure S7).

In present case, the mass loading of electrode materials is as high as 10–12 mgcm^{-1}, which is about 10 times higher than

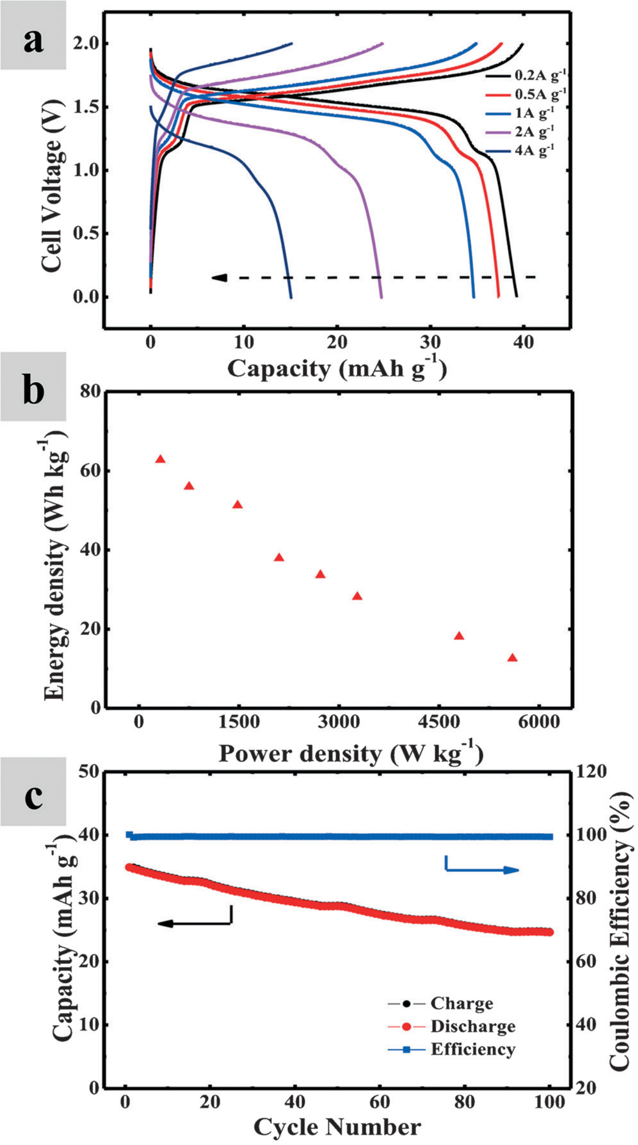

Figure 3. Electrochemical performance of the flexible belt-shaped Li-ion battery. a) Galvanostatic charge/discharge at different current densities. b) Ragone plot for the battery. c) Cycle life with the current density of 1 A g^{-1}. [The current densities and the capacity are calculated based on the total mass of electrode materials.]

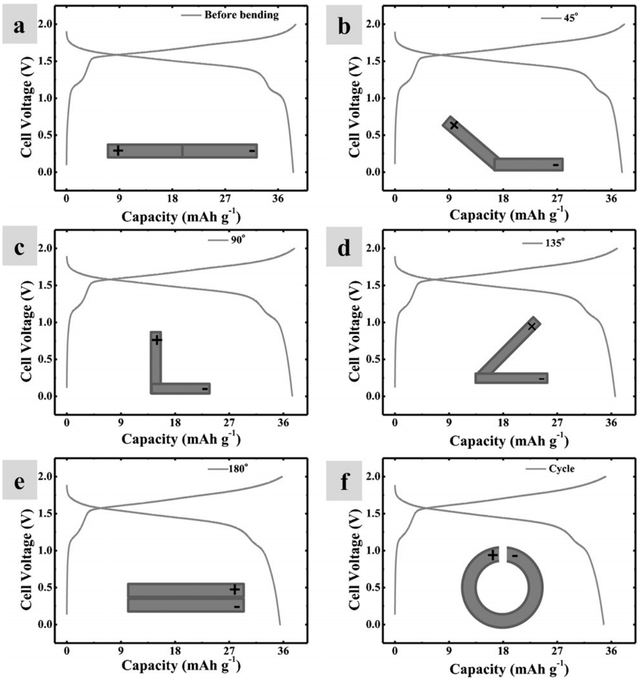

Figure 4. The performance of the flexible battery under different flexing angles. a) Flat state before bending; bended to (b) 45°; c) 90°; d) 135°; e) 180°and f) bended to a cycle.

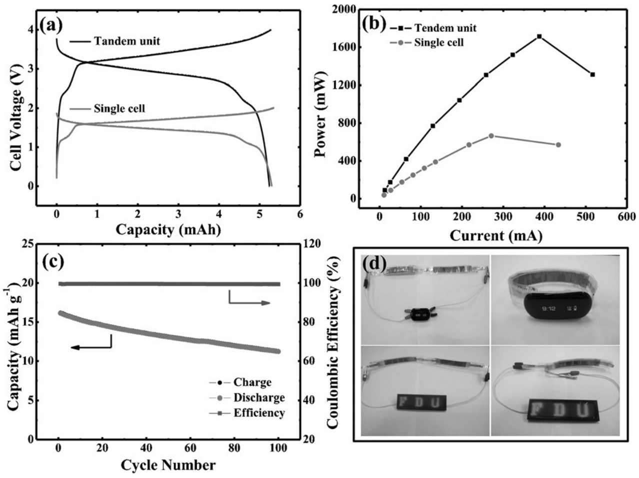

Figure 5. Electrochemical performance of the tandem unit with two present flexible belt-shaped Li-ion batteries in series. a) Comparison with single cell at the same current density. b) The output power plot compared with single cell. c) Cycle life with the current density of 1 A g^{-1} [The current density and the capacity are calculated based on the total mass of electrode materials in two flexible cells.]. d) To power miniaturized electronic devices (a wearable watch and a LED screen) under different bending states.

previous report (less than 1.5 mg cm^{-2}). Accordingly, it is necessary to investigate the flexibility of this cell. As shown in Figure 4, electrochemical performance of a same cell has been tested under various shapes, that is, before bending, bended to 45°, 90°, 135°, and 180°, last bended to a cycle. It can be detected that almost same capacity is achieved at different bending states, which confirms the excellent flexibility. Even after repeating the bending tests for 100 times, the cell shows negligible performance loss (Figure S8).

In order to explore the promising application of the presented flexible cell, two such belt-shaped cells were connected in series to achieve higher operation voltage. As shown in Figure 5 a, two such belt-shaped cells connected in series can be charged to as high as 4 V, which is comparable with current commercial nonaqueous batteries, such as graphite/$LiCoO_2$, graphite/$LiMn_2O_4$, and graphite/$LiFePO_4$ cells. The discharge voltage of the tandem unit is two times higher than single cell when operating under same current density, exhibiting highly consistent voltage efficiency. Accordingly, the output power of the series connection is twice higher than that of single cell (Figure 5 b). Cycling performance of the tandem unit given in Figure 5 c exhibits that the capacity retention of about 72 % over 100 cycles, which is similar with single cell. The data shown in Figure 5 a, 5 b, and 5 c well demonstrate the high uniformity of both cells in the tandem unit. After being charged to 4 V, the united flexible cells in series can light a commercialized wearable watch or a LED screen (Figure 5 d) that is generally powered by a nonaqueous LIBs with an operation voltage of 3.7 V (Figure S9). On the other hand, such a single flexible cell can be charged with a commercial 2 V flexible thin-film solar cell (Figure S10) by directly connecting them in parallel. Connected with the solar cell under sunshine for 1 000 seconds, the flexible aqueous cell can exhibit the discharge capacity of about 37 mAh g^{-1} at applied current density of 0.2 A g^{-1} (Figure S11). The obtained capacity (37 mAh g^{-1}) is only slightly smaller than that of direct charge–discharge (40 mAh g^{-1}), which means that the flexible Li-ion battery can be charged successfully with solar cell. As correctly pointed out by Dai et al,[35] the self-chargeable unit based on integrated flexible cell with solar cell should hold great promise for practical applications.

In summary, a flexible and wearable aqueous Li-ion battery with high safety has been successfully developed based on LMO and LTPO as cathode and anode material, respectively. Such a full cell delivers an energy density of 63 Wh kg^{-1} or 124 mWh cm^{-3} and a power density of 3 275 W kg^{-1} or 11.1 W cm^{-3}, which are seven times larger than the highest value reported up to present. The superior electrochemical properties and excellent flexibility make it appropriate for a wide range of applications in the field of flexible wearable electronics in the near future.

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