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LETTER

Wearable Bipolar Rechargeable Aluminum Battery

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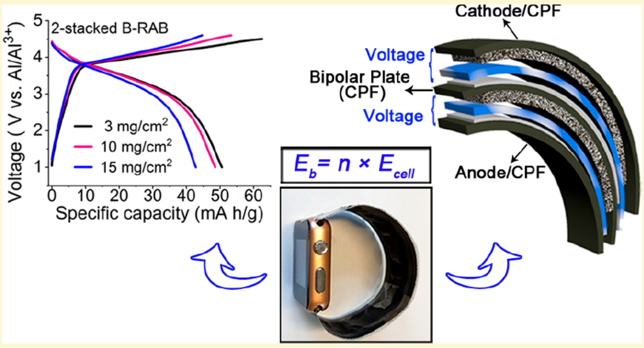
ABSTRACT: Structural design plays an essential role in the energy density of wearable batteries. Although various flexible materials have been developed to substitute traditional rigid components, current wearable batteries struggle to achieve high energy density because of the excessive inactive components in the traditional monopolar structure. Herein, an all-in-one bipolar Al system is designed as wearable batteries, in which multifunctional carbon/polyethylene film (CPF) serves as the bipolar plate, cell package, and encapsulant. Our designed bipolar Al battery can be designed as a flexible watch strap with a working voltage of 3.21 V and exhibits good capacity retention of 80% under high bending angles (120°), high current densities (960 mA/g), high mass loading (15 mg/cm^2), and low temperature (−20 °C). Additionally, as the stack number of cells increasing to five, the volume of traditional serial batteries can nearly halve through bipolar design. It is anticipated that our bipolar configuration concept would offer a new solution for the development of advanced wearable batteries and stimulate the surge of wearable electronics.



The upcoming commercialization of wearable smart electronics and flexible displays has prompted ongoing research on advanced power sources.[1,2] Ideally, to satisfy the deformability and portability of these electronics, a flexible battery requires simultaneous incorporation of excellent flexibility, high energy density, and high safety both in materials and structure designs.[3,4] Although great progress has been achieved on developing extremely flexible components in various battery systems, most attempts mainly focus on the traditional monopolar structure of the single-cell level, in which excessive inactive components are unavoidably employed to maintain flexibility, conductivity, and connection, significantly compromising overall energy density.[5−14] Given difficulties in improving energy densities of current intercalation chemistry, the innovation in the design of battery construction appears to be particularly pivotal.

Bipolar technology changes the traditional serial structure and the current flowing path through the sandwich-like stacking and shared current collectors between adjacent cells, effectively reducing the internal resistance and inactive segments of the package, current collector, and external conductor. It has been long used in conventional rigid batteries to achieve both high energy and power densities.[15,16] However, because of the lack of flexible, conductive, and stable bipolar plates and related sealing issues, this bipolar configuration can hardly be applied to flexible batteries.[17−19] Recently, diverse bipolar plates of graphite, metal, carbon, and polymer composites have been investigated in fuel cells to enhance the electrical and thermal conductivity, electrochemical stability, and mechanical properties.[20,21] Among them, the carbon/polyethylene composite film has been reported to have superior flexibility, heat sealing property, and electrical conductivity,[22] which inspires us to introduce it as bipolar plates for wearable batteries.

Despite the wide application of traditional Li-ion batteries in wearable electronics, they are not the optimal options for the future due to the safety issues and the limited lithium sources. Rechargeable Al battery (RAB) show significant potential as wearable batteries owing to the high theoretical volumetric capacity of 8040 mAh/cm^3 (vs Li metal 2062 mAh/cm^3), excellent flexibility, high safety, and natural abundance.[23−27]

Herein, we proposed an all-in-one wearable bipolar prototype by employing flexible carbon/polyethylene film

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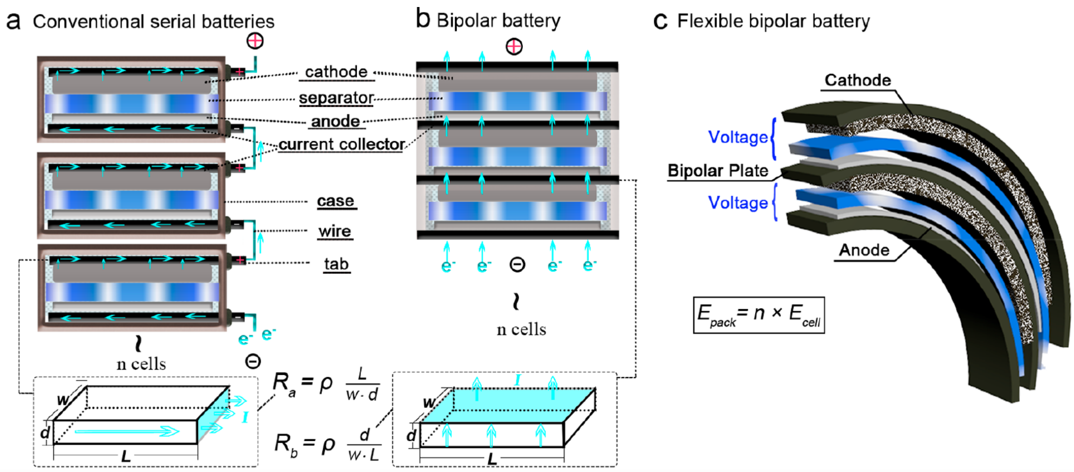

Figure 1. Proof-of-concept of the flexible bipolar battery. Schematic illustration of (a) conventional serial batteries, (b) a stacked bipolar battery, and (c) a stacked flexible bipolar battery.

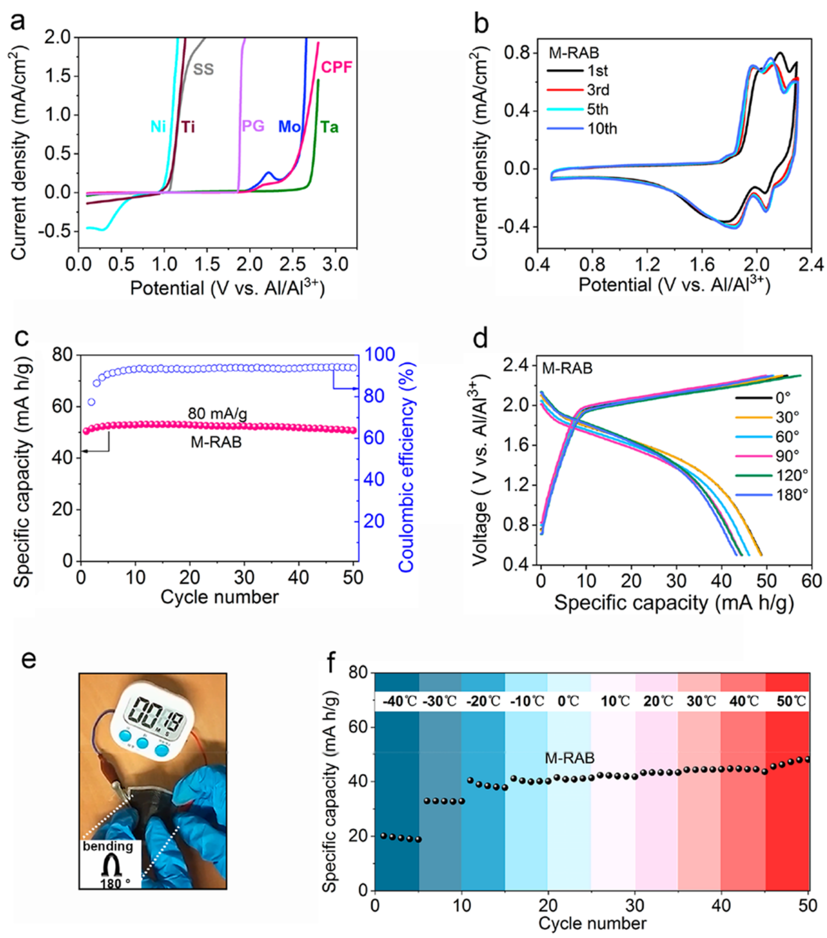

Figure 2. Single monopolar flexible RAB (M-RAB). (a) Anti-corrosive ability of optional bipolar plates (Ni, Ti, stainless steel (SS), pyrolytic graphite (PG), Mo, CPF and Ta) in $AlCl_3$: [EMIm]Cl electrolyte. (b) CV curves at 0.5 mV/s. (c) Cycling stability and (d) galvanostatic charge−discharge curves at different bending angles of M-RAB. (e) Illustration of flexible M-RAB running a timer under a 180° bend. (f) Temperature tolerance of M-RAB from −40 °C to +50 °C.

(CPF) as the bipolar plate, cell package, and encapsulant, and applied it to the rechargeable aluminum battery (RAB). Benefiting from the flexibility of CPF and low ohmic resistance of the bipolar construction, our bipolar rechargeable aluminum battery (B-RAB) exhibits excellent flexibility, high energy and power density, and good low-temperature durability. The concept provides a new solution to promote the rapid development of advanced wearable batteries.

The simplified construction of our flexible bipolar battery is illustrated in Figure 1. Generally, most batteries are assembled based on traditional "monopolar" technology that uses two current collectors on each cell for cathode and anode

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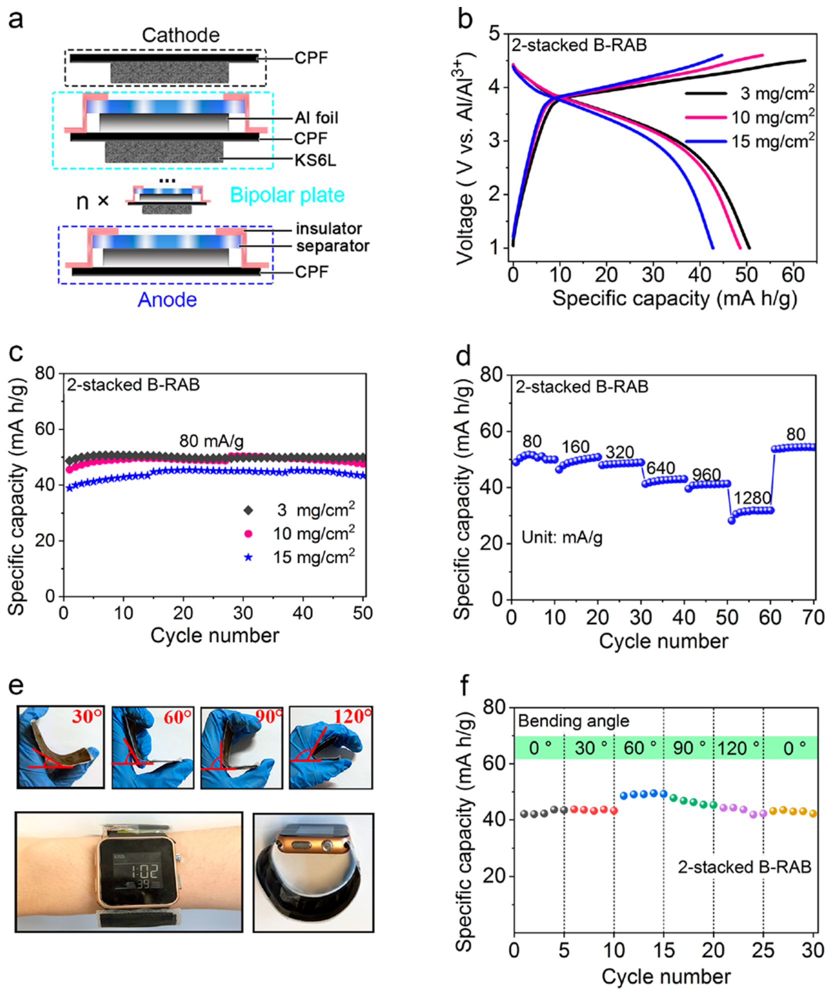

Figure 3. Demonstration of a 4 V class B-RAB. (a) Schematic illustration of assembled B-RAB. (b) Typical charge−discharge curves. (c) Cycling stability with different KS6L mass loading and (d) rate capability of the 2-stacked B-RAB. (e) Demonstration of the flexibility of B-RAB by bending from 0° to 120° and photographs of a commercial watch powered by a 2-stacked B-RAB. (f) Cycling stability of the flexible 2-stacked B-RAB at different bending angles.

separately and then connects these cells in a series of metallic connectors outside of the cells (Figure 1a). While in bipolar construction (Figure 1b), adjacent unit cells share one current collector, eliminating unnecessary components for connecting and packaging. More importantly, in a bipolar configuration, current flows through the thickness of the current collector (d) instead of across the length of the entire current collector (L) with less internal resistance, more symmetrical current distribution, and less voltage polarization. According to the calculation in Figure S1, the minimum requirement for the conductivity of the current collector in the bipolar pack is seven orders of magnitude lower than that required in the traditional serial pack. Therefore, the flexible carbon/polyethylene film (CPF) with a resistivity of 1.8×10^{-2} Ω·m could be introduced, which inherits the flexibility of polyethylene, the good electrical conductivity of carbon, and the lightweight, corrosion resistance of both (Table S1). Additionally, benefiting from the thermoplastic property of CPF, the sealing process could be simplified. By combining other flexible components of the cathode, separator, and the aluminum foil anode (Figure S2), a prototype of the flexible bipolar rechargeable aluminum battery (B-RAB) can be fabricated (Figure 1c).

In addition, the specifications, cost, and electrochemical stability were evaluated to demonstrate the applicability of CPF as current collectors in wearable RAB (Figures 2 and S3–S11). The estimation of areal cost and weight of the optical current collectors (Figure S3) indicates that CPF (2.9 \$/m^2 and 10.6 mg/cm^2) is much cheaper and lighter than the commonly used Ta (255 \$/m^2 and 41.5 mg/cm^2) and Mo (49 \$/m^2 and 25.5 mg/cm^2) current collectors in RAB. To verify the compatibility of CPF with corrosive $AlCl_3$: [EMIm]Cl electrolyte in RAB, linear sweep voltammetry (LSV) was conducted at 5 mV/s. CPF exhibits high electrochemical stability within 0.1-2.4 V (vs. Al^{3+}/Al), illustrating the good corrosion resistance (Figure 2a). The aluminum deposition/striping test was also conducted on the prepared ionic electrolyte (Figure S4). To further evaluate the electrochemical stability of CPF in the wearable battery, a single layer of monopolar rechargeable aluminum battery (M-RAB) was assembled by employing CPF as the current collector, cell case, and encapsulant (Figure S5). The reported graphite (KS6L) cathode with a comprehensive understanding of mechanism was used here to verify the feasibility of our configuration design for the wearable battery.[28] The blank CPF of M-RAB was also tested and found to be favorably electrochemically inactive in the corrosive electrolyte (Figure

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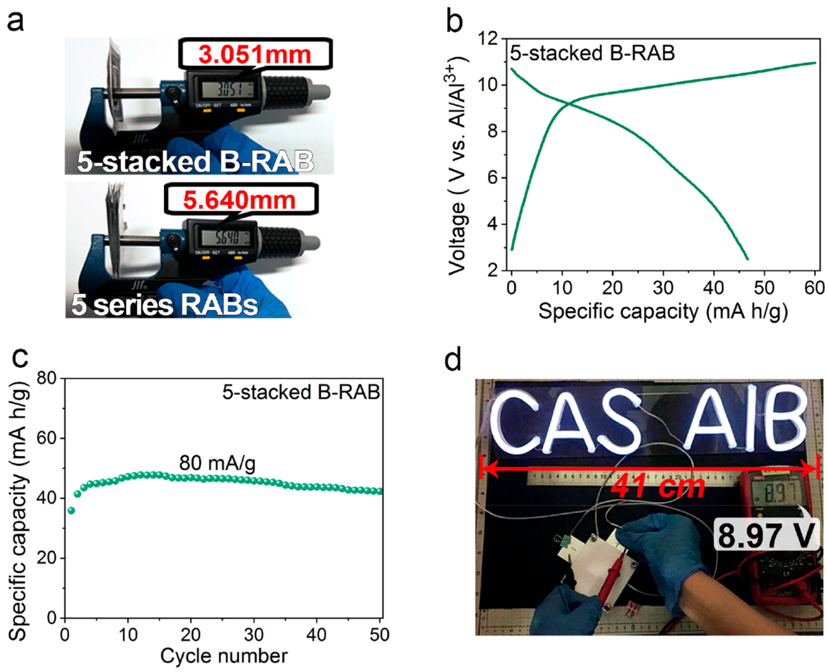

Figure 4. Demonstration of a 10 V class B-RAB. (a) Comparison of total thickness of a 5-stacked B-RAB and that of five conventional serial RABs. (b) Typical charge−discharge curves and (c) cycling stability of the 5-stacked B-RAB at 80 mA/g. (d) Illustration of the 5-stacked B-RAB lighting commercial LEDs with a working voltage of 9 V.

S6). Cyclic voltammetry (CV) was conducted to test the stability of M-RAB (Figure 2b). The oxidation peaks at 1.97 and 2.12 V corresponds to the intercalation of $AlCl_4^-$ into graphite, while the reduction peaks at 1.84 and 2.07 V represent the deintercalation process. The CV curves almost overlap each other without additional corrosion peak after 10 cycles, illustrating the high stability of CPF in RAB. To further evaluate the cycling stability, galvanostatic charge/discharge tests were performed. Consistent with our CV results and the literature,[28] the graphite cathode in M-RAB has an average discharge voltage of 1.58 V (Figure S7) with a steady specific capacity of 52 mAh/g and a Coulombic efficiency of approximately 95% at a mass loading of 5 mg/cm^2 (Figure 2c), demonstrating the feasibility of our configuration. After 50 cycles, the morphology of cycled CPF is quite similar to its pristine state (Figure S8) with a robust connection to cathode materials (Figure S9), reflecting the excellent tolerance of CPF to repeated electrochemical cycling. Meanwhile, the superior flexibility of CPF endows the M-RAB with freely bending ability. Under varying bending angles, M-RAB displays similar charge−discharge curves (Figure 2d) and powers a timer to run continuously (Figure 2e and Video S1). In addition, the thermostability of CPF was further analyzed in the thermogravimetric-differential scanning calorimetry (TG-DSC) test (Figure S10), and the real-time influence of temperature on M-RAB was examined in Figure 2f. As the test temperature varied from −20 °C to 50 °C, though the electrolyte solidified at −20 °C (Figure S11), a capacity of 40 mAh/g could be maintained owing to the stability and reversibility of $AlCl_4^-$/graphite intercalation compound and ionic conductivity of the electrolyte,[29,30] thus almost meeting the temperature requirements of wearable devices.

On the basis of the above preliminarily verifications, a two-cell stacked bipolar rechargeable aluminum battery (2-stacked B-RAB) was assembled via an all-in-one bipolar design by employing the lightweight CPF as bipolar plates, current collectors, cell packages, and encapsulants (Figure 3a). It has a high voltage of 3.21 V (double voltage of M-RAB) and similar electrochemical characteristics to the M-RAB (Figure 3b), confirming the reliability of CPF as the bipolar plate. Notably, as the mass loading increased from 3 to 15 mg/cm^2, the 2-stacked B-RAB still retained a discharge specific capacity of 40 mAh/g with a mass utilization greater than 80% and superior cycling stability (Figure 3c). Besides, B-RAB also exhibits excellent rate capability (Figure 3d). As the current density increased from 80 to 960 mA/g, the capacity retention of 2-stacked B-RAB remained over 80% with the small over-potential (Figure S12), demonstrating the advantage of the bipolar structure in diminishing internal ohmic polarization. Additionally, the electrochemical stability of the 2-stacked B-RAB with a bending variation from 0° to 120° is depicted in Figure 3e. It always maintains a capacity of more than 40 mAh/g under different bending angles, further reflecting the excellent flexibility (Figures 3f and S13). Furthermore, benefiting from the simple heat-sealed fabrication and good processability of CPF, the shape of the battery can be freely designed according to the requirements of different applications. The 2-stacked B-RAB can be skillfully designed as a 14 cm wearable watch strap to power an electronic watch that works at above 3 V (Figures 3e and S14 and Video S2).

To fully display the advantages of the bipolar structure in enhancing energy density and output voltage, a multilayered bipolar pack comprising a stack of five cells (5-stacked B-RAB) was constructed. As shown in Figure 4a, the thickness of this compact B-RAB is only about 3.051 mm, which is approximately 54 % of the total thickness (~5.640 mm) of five conventional serial monopolar RABs with the commercial Al plastic film package and metal foil current collectors, indicating the great potential of bipolar architecture in improving the energy density of the battery. More impressively, the 5-stacked B-RAB outputs a voltage approaching 10 V (Figure 4b) and delivers a steady discharge capacity of

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approximately 45 mAh/g during cycling (Figure 4c), demonstrating another advantage of bipolar construction in enhancing the output voltage of the battery. It was further illustrated that, after charging to 11 V (Figure S15), the 5-stacked B-RAB could light a series of 9 V-LEDs (a length of 41 cm), which are widely used in commercial advertising signs (Figure 4d and Video S3). This flexible bipolar design on cells can be extended to other advanced electronics, which require flexibility, high energy density, and high working voltage, such as robots and drones.

In summary, we proposed a novel concept of flexible bipolar construction for wearable batteries, designed an all-in-one wearable bipolar configuration by using flexible CPF as the bipolar plates, cell packages and encapsulants, and applied it in rechargeable aluminum batteries. The wearable B-RAB has multiple promising advantages: (1) enhancing the energy and power densities by reducing inactive components and internal resistance, (2) exhibiting excellent flexibility through using flexible polymer composite film, (3) simplifying the fabrication process of the wearable battery via all-in-one design, and (4) maintaining good safety by employing the air-stable aluminum anode and non-flammable ionic liquid electrolyte. Therefore, it displays excellent flexibility, high energy, and power density, and wide temperature durability. The version of B-RAB would be further updated with the improvement of carbon/polymer film on electrical and thermal conductivity, thermal and mechanical stability, weight, and thickness. Therefore, it is anticipated that our flexible bipolar construction concept will provide a new way to develop advanced high-energy-density flexible battery.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.0c00145.

Experimental procedures, calculation, assembly process, photographs, SEM images, charge and discharge curves, open circuit voltage of M-RAB and B-RAB, TG and DSC curves of CPF, cost and weight evaluation of current collectors, and one comparison table (PDF)

Flexibility tests on M-RAB (AVI)

Flexibility test and application of B-RAB (AVI)

Application of B-RABs (AVI)

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Notes

The authors declare no competing financial interest.

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