

Introduction

Many wearable and portable electronic devices require efficient, compliant power sources that can fully function when bent, folded, or compressed. Lithium-ion batteries (LIBs) dominate the portable power-source market due to their high energy density, high output voltage, long-term stability and environmentally friendly operation. High performance flexible LIBs are considered to be one of the most promising candidates of power sources for the next generation flexible electronic devices. LIBs typically consist of several functional layers. When battery flexibility is desired, all of the battery components should be flexible. Among the various functional layers, the current collectors affect critically the battery performance, and their flexibility is typically difficult to achieve together with a high conductivity.

In this paper, we report a flexible lithium-ion battery using graphite-paper (GP) with enhanced conductivity as current collector. The enhancement of conductivity of GP was achieved by depositing a sub-micron thick metal layer onto a commercial graphite paper by physical vapor deposition (PVD). Particularly, we use an Al-deposited GP as the current collector for cathode and a bare GP or a copper-deposited GP as the current collector for anode. In this LIB, LiFePO₄ (LFP) and Li₄Ti₅O₁₂ (LTO) are used as cathode and anode active materials, and a polyethylene (PE) nanostructured membrane is used as a separator [1].

Fabrication of LIB based on GP current collector

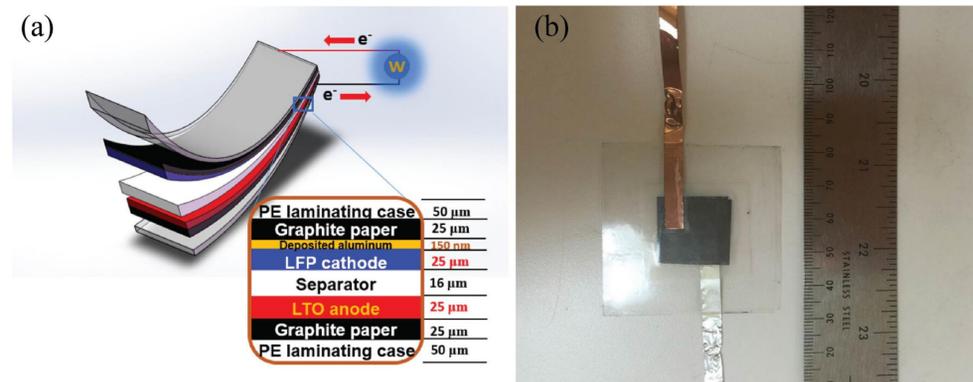


Fig.1 (a) Schematic of the thin, flexible lithium-ion battery; (b) A lithium-ion battery sample;

A highly conductive and flexible current collector was fabricated by depositing a sub-micron thick aluminum or copper layer onto a graphite sheet by PVD. The PVD was performed under a high vacuum condition ($\sim 10^{-7}$ mbar) with a deposition rate of 0.2 nm/s. Then, the graphite sheet with a metallic coating was directly stored in N₂-filled glove box for subsequent procedures. The obtained conductivity-enhanced GP (abbreviated as Al@GP in the following) current collector can be then used as substrates for deposition of LFP/PVDF to make LFP-Al@GP electrodes.

To synthesize the anode and cathode, LFP and LTO were first pre-mixed with MWCNT in a mortar, respectively. Then mixture was then dispersed in polyvinylidene fluoride (PVDF)/1-methyl-2-pyrrolidone solution using a magnetic stirrer for 4 h. The optimal weight ratio of LFP (or LTO), MWCNT and PVDF was found to be 8:1:1. The obtained slurry was then poured onto the current collector and made into a uniform wet-film using a Micrometer Adjustable Film Applicator. The composites were dried in a vacuum furnace at 80 °C for 3 h, and then cut into 2*2 cm² square-shaped electrodes. These electrodes were then further dried at 110 °C for 12 h to ensure that the solvent (1-methyl-2-pyrrolidone) in slurry was completely evaporated.

The lithium-ion batteries were finally assembled by stacking the as-prepared electrodes together with a PE separator layer. 3 droplets (~ 0.15 mL) of electrolyte (1.0 M LiPF₆) dissolved in ethylene carbonate/dimethyl carbonate (EC/DEC) = 50/50 (v/v) were added to the battery during the stacking process. Note that the battery assembly process was completed in a N₂-filled glove box to avoid oxidation of electrolyte. Finally, the battery was encapsulated with PE films using a lamination machine before it was taken out for characterization.

Characterization

The image of the cross section of the battery sample was taken by an optical microscope (Fig. 2(a)). The tomography of the Al coating on graphite paper substrate was investigated by scanning electron microscopy (SEM), and an energy dispersive spectrum (EDS) of the Al@GP was measured (Fig. 2(b)). The charge/discharge tests and EIS measurements were performed by an Electrochemical Work Station. All of the capacities and C-rate currents in this work were calculated based on the mass of LFP active materials (1 C corresponding to 170 mAh/g).

Tomography and EDS of Al@GP

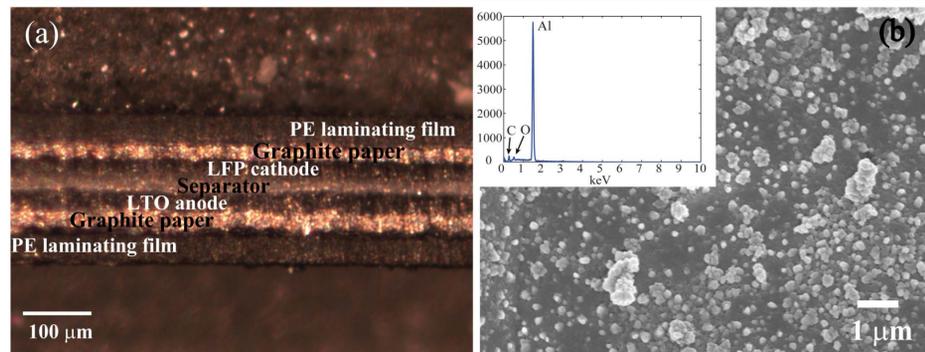


Fig. 2 (a) Cross section of the lithium-ion battery sample taken by an optical microscope; (b) SEM image of the Al coating on the graphite substrate and the inset is an energy dispersive spectrum (EDS) of the Al coating on the graphite paper.

Al particles could aggregate to form clusters with the size ranging from tens to hundreds of microns, thus leading to a high aspect ratio and large activated surface area of the electrode. The EDS result suggests a good purity of the Al coating. The existence of oxygen is due to the passivation of the Al coating.

Electrochemical performance of the LFP/Al@GP electrode

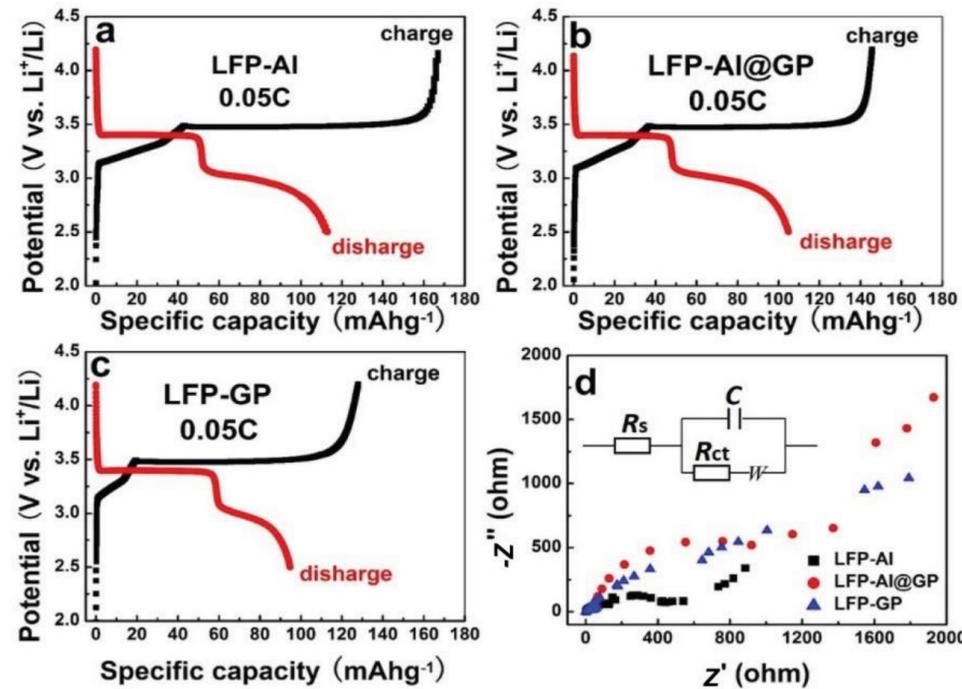


Fig. 3. charge/discharge voltage curves of the half cells with the rate of 0.05 C. (a) LFP-Al (foil), (b) LFP-Al@GP (Al enhanced GP), and (c) LFP-GP (pure GP). (d) Equivalent circuit and electrochemical impedance spectra of the LFP-Al@GP electrode, LFP-Al@GP electrode and a reference LFP-Al current collector.

A half-cell battery with an active area of 2*2 cm² was fabricated using LFP-Al@GP as the cathode and pure GP as the anode. The performance of this half-cell battery was compared with its two counterparts in which the cathode was fabricated by coating LFP onto an Al foil current collector (abbreviated as LFP-Al) or by coating LFP onto a GP current collector (abbreviated as LFP-GP). The capacity of the LFP-Al@GP/GP cell at 0.05 C discharge rate was 104.8 mAh/g with a coulombic efficiency of 71% (Fig. 3(a)). This was comparable to the performance of the half-cell battery using LFP-Al cathode that had a capacity of 113 mAh/g and a coulombic efficiency of 67.7% (see Fig. 3(b)). These results indicated that the Al@GP could be an excellent current collector for the cathode as its electrochemical properties are virtually identical to pure Al foil electrodes.

Electrochemical performance of the LFP-Al@GP//LTO-GP Flexible full Battery

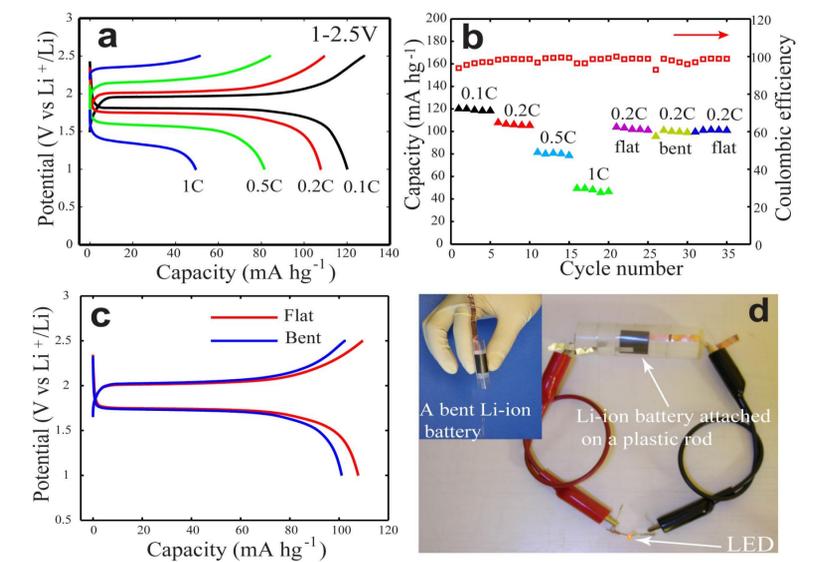


Fig. 4 Characterization of the LFP-Al@GP//LTO-GP full battery. (a) Charge/discharge voltage curves of the battery with different charge-discharge rates. (b) Capacity and coulombic efficiency of the battery with different charge-discharge rates for 35 cycles. (c) Voltage curves of the flat battery (red line) and a bent battery (blue line). The bending radius of the battery is ~ 1 cm. (d) A LED was lit up by a bent full battery. The inset demonstrates the excellent flexibility of the full battery.

The electrochemical properties of a full battery were investigated using charge /discharge cyclic analysis with different charge/discharge rates (from 0.1 C to 1 C). The LFP-Al@GP//LTO-GP battery had an excellent rate capacity, which was calculated to be 120.2, 107.8, 81.8 and 49.4 mAhg⁻¹ at 0.1, 0.2, 0.5, and 1 C, respectively (Fig. 4(a)). It can be clearly seen that the discharge capacities exhibit a tendency to decrease with the increment of current density; however, the voltage plateau still remained flat even when current density is up to 1 C, indicating an excellent charge/discharge performance. Moreover, after a series of tests under different charge/discharge rates, the discharge capacity of the battery was still as high as 103.8 mAhg⁻¹, when the rate turned back to 0.2 C. This suggests that the structure of each components of the full battery remained intact after subjecting to high current densities. The coulombic efficiencies of the full battery were > 94 % during the whole cycle.

Note that the full battery shows excellent flexibility. The effect of bending on the performance of the flexible battery was also investigated. Fig.4(c) shows the charge/discharge measurement of the bent battery at 0.2 C after 25 charge/discharge cycles under different rates. Compared with the flat state, only a slight overpotential was observed, and a 2% decrease in capacity was found. What's more, the flexible battery showed an excellent cyclic stability both under flat and bent states (Fig. 4(b) and (c)). The retention capacity of the bent battery was $\sim 92\%$ of that of the flat battery even after the battery undergoes 25 charge/discharge cycles. Furthermore, we note that even after bending the battery for another 5 charge/discharge cycles, more than 93% of the capacity could be still restored if the battery is released. In Fig. 4(d), we demonstrate that a LED could be lit up by the battery bent at a 1 cm radius.

Articles cited:

1. Qu, H., Hou, J., Tang, Y., Semenikhin, O. and Skorobogatiy, M., 2016. Thin flexible lithium-ion battery featuring graphite paper based current collectors with enhanced conductivity. Canadian Journal of Chemistry, 95(2), pp.169-173.