



Short communication

Anticorrosive flexible pyrolytic polyimide graphite film as a cathode current collector in lithium bis(trifluoromethane sulfonyl) imide electrolyte

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ABSTRACT

Flexible pyrolytic polyimide graphite film (PGF) is explored as a cathode current collector in lithium ion batteries using lithium bis(trifluoromethane sulfonyl) imide (LiTFSI) based electrolyte. It is demonstrated that no obvious anodic current is observed up to 4.5 V versus Li^+/Li for PGF, while significant corrosion current is found from 3.6 V for aluminum, indicative of better electrochemical stability of PGF than that of aluminum in LiTFSI based electrolyte. LiMn_2O_4 on aluminum and PGF has been used as model electrode for testing. There is hardly any capacity retained after 10 cycles at room temperature for the LiMn_2O_4 /aluminum electrode. With regard to the LiMn_2O_4 /PGF electrode, the capacity retention ratio remained 89% after 1000 cycles. Moreover, at an elevated temperature of 55 °C, the capacity retention ratio kept at 81% after 300 cycles. Since LiTFSI-based electrolyte shows advantages in safety, stability and conductivity but could not be used due to Al-corrosion, the application of the PGF current collector could overcome this barrier.

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1. Introduction

Lithium ion batteries (LIBs) can efficiently store and deliver energy on demand in consumer electronics and electric cars [1–3]. Improved battery performance is closely related to the development of materials for various battery components. Except for numerous achievements on high-density positive materials [4–8], the enhancement in energy density is also closed related to the application of novel electrolytes with high potential windows and stability. Lithium hexafluorophosphate (LiPF_6) is commonly used as electrolyte salt in commercial LIBs. However, LiPF_6 is thermally unstable and moisture sensitive. It can trigger detrimental side reactions with residual trace water in organic solvent and generate HF that is detrimental to cell performance [9].

It is generally considered that lithium imide salts are the most promising alternatives to LiPF_6 salt [10]. Typically, lithium bis(trifluoromethane sulfonyl)imide (LiTFSI) salt possesses excellent thermal stability, better conductivity and electrochemical stability in comparison with LiPF_6 salt, while it shows severe corrosive behaviors toward an aluminum current collector, especially at high oxidizing potentials (above 3.5 V versus Li^+/Li) [11,12]. It is a great challenge to inhibit the aluminum corrosion in LiTFSI based electrolytes. To tackle the challenge, much effort has been made. A general approach is to adjust the solution composition of the LiTFSI based electrolyte, such as the addition of defined amount of

LiPF_6 [13], the use of room temperature ionic liquid solvent [14], and so on. According to our knowledge, all these efforts are still unsatisfactory. Actually, minor attention has been paid to develop a novel alternative current collector with powerful tolerance toward corrosion in LiTFSI systems.

Usually, graphite materials are used as current collectors in fuel cells and vanadium redox flow batteries, because of their good electrical conductivity and excellent corrosion resistance [15]. However, the above-mentioned graphite materials lack enough flexibility and electrochemical stability. It is reported that a flexible pyrolytic polyimide graphite film (PGF) possesses a highly in-plane oriented structure, which endows the PGF with an excellent electrochemical corrosion resistance [16,17]. The PGF are also mechanically strong and flexible and therefore, could facilitate the cell fabrication. Herein, flexible PGF is first explored as LIB cathode current collector using LiTFSI salt electrolyte. It could be expected that PGFs may bring all of these advantages into play and exhibit a much better electrochemical stability than aluminum.

2. Experimental

2.1. Preparation of PGF

The Kapton-type polyimide films of 50 μm in thickness (Dupont Co., Ltd.) were used as starting materials. The films were cut into squares

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with dimensions of 25 cm × 25 cm and sandwiched between polished high-density graphite plates in order to avoid sticking of the film during carbonization, and then carbonized at 600, 1800 and 2200 °C in an argon atmosphere, respectively. Finally, they were graphitized at 2800 °C for 8 h in an argon atmosphere.

2.2. Sample characterization

Morphological and structural information was obtained from field emission scanning electron microscopy (SEM, HITACHI S-4800) and high-resolution transmission electron microscopy (HRTEM, JEOL 2100F). X-ray diffraction (XRD) patterns were recorded in a Bruker-AXS Micro-diffractometer (D8 ADVANCE) with Cu K α radiation ($\lambda = 1.5406$ nm).

2.3. Electrochemical measurements

Electrochemical evaluations were carried out in coin cells (CR2032). Firstly, slurries were formed by mixing LiMn₂O₄, conductive carbon black (super P) and polyvinylidene fluoride dissolved in N-methyl-2-pyrrolidone in the mass ratio of 85:10:5. Then the slurries were coated

onto aluminum and PGF current collectors, pressed and dried under vacuum at 120 °C for 12 h, respectively. Finally, disks of 12 mm diameter were punched and used as cathode. Moreover, fresh electrodes made by bare aluminum or PGF without coating slurries were also obtained for a fair comparison.

Coin cells were finally assembled in an argon-filled glovebox with electrode, metallic lithium as the counter/reference electrode, 1 M LiTFSI in EC and DMC (EC/DMC, 1:1 vol) as electrolyte, and Celgard 2400 polypropylene as a separator. Charge/discharge measurements were carried out galvanostatically at various current densities over a voltage range of 3.3–4.3 V versus Li⁺/Li using a battery test system (LAND CT2001A, Wuhan Jinnuo Electronics, Ltd.). Cyclic voltammograms (CVs) were tested using electrochemical workstation (ZAHNER-Elektrok GmbH & Co. KG, Germany) at a scanning rate of 10 mV s^{−1} between 1.5 and 5.5 V. All the tests were performed at room temperature.

3. Results and discussion

Fig. 1a shows the XRD pattern of the PGF. The sharp and intensive peak located at 26.55° is indexed to be (002) peak of typical graphite, which indicates a highly c-axis oriented structure with an interlayer

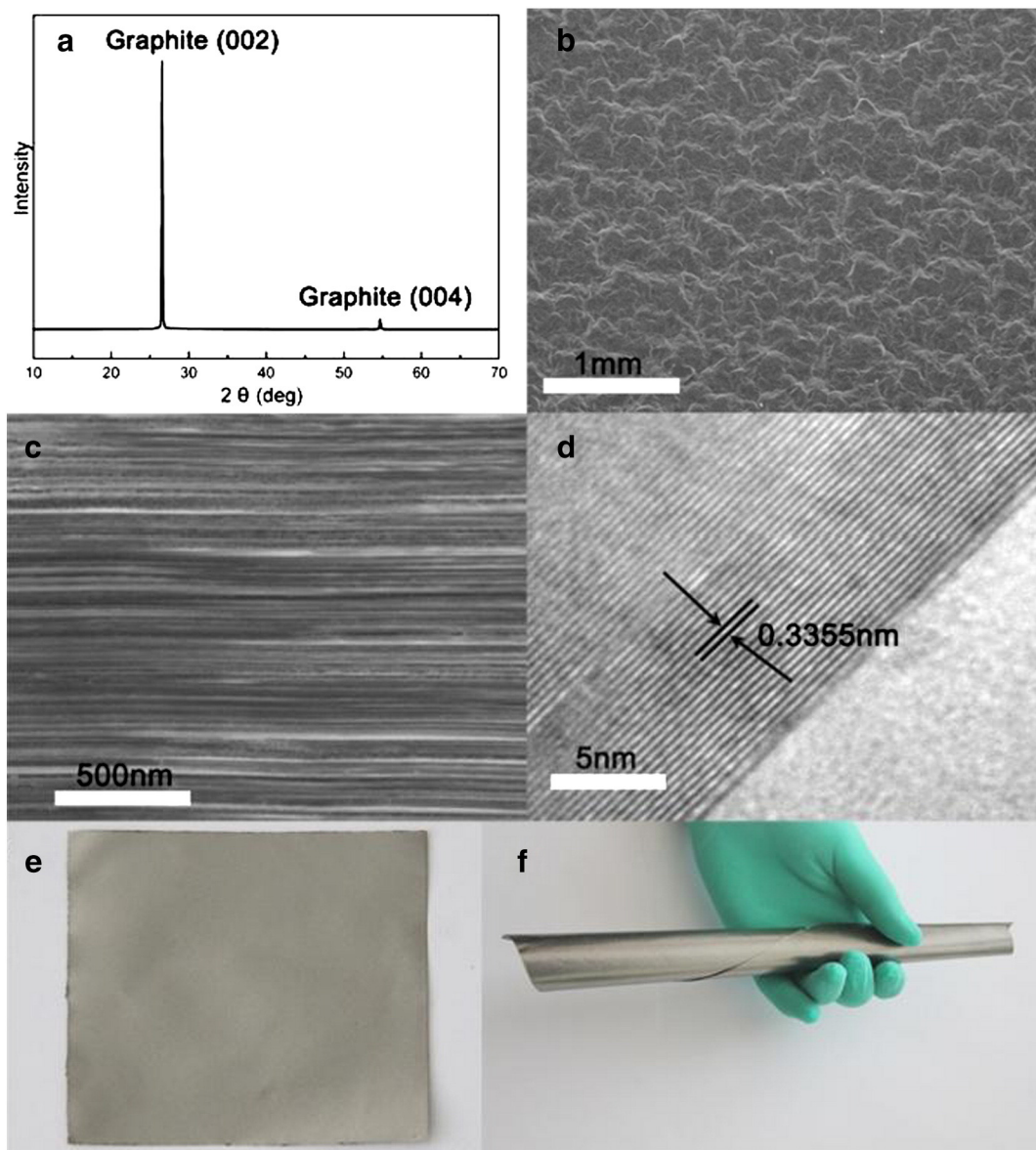


Fig. 1. (a) XRD pattern, SEM images of (b) the surface, (c) the cross-section and (d) HRTEM image of the PGF, typical photograph of (e) the prepared PGF and (f) the rolled one.

spacing of 0.3355 nm, corresponding to a graphitization degree of 98.8%. It has been proposed that carbon materials containing more graphitic components exhibit a better corrosion resistance [18]. The morphology and nanostructure of the PGF were characterized by SEM and HRTEM. Fig. 1b shows that the surface appears to be rough in microscale. Fig. 1c depicts the cross-section SEM image of the PGF. It presents a typical stacking structure of graphite layers, reflecting a highly in-plane oriented structure and alignment of aromatic segments parallel to the basal plane, which is in accordance with the presence of typical (002) and (004) peaks in XRD pattern [19]. Such a texture is reported to be more resistant to electrochemical oxidation [17]. The HRTEM image gives a more direct evidence of the highly in-plane oriented structure (Fig. 1d). The parallel basal planes are well stacked with an average distance of 0.3355 nm. As shown in Fig. 1e and f, a piece of PGF can be rolled up facilely, indicating that the PGF could be fabricated into a variety of shapes and sizes enabling cell design flexibility.

The electrochemical performance of the bare aluminum and PGF electrodes in 1 M LiTFSI in EC/DMC (1:1 vol) was investigated by CV, as shown in Fig. 2a and b. Much higher anodic currents are observed on aluminum electrode, compared with those on PGF electrode. The electrolyte solution begins to corrode the aluminum electrode at a potential of 3.6 V versus Li^+/Li , while the electrolyte decomposition starts at 4.5 V versus Li^+/Li for the PGF electrode [11]. This suggests that PGF as a cathode current collector in LiTFSI salt based electrolyte shows a much more excellent corrosion resistance and electrochemical stability than aluminum. Fig. 2c and d shows the SEM images of aluminum and PGF electrodes after three CV cycles. Apparently, the surface of the aluminum foil is full of micropores, indicating that the corrosion and destruction of the aluminum electrode takes place in LiTFSI/(EC + DMC) electrolyte. However, the surface of the PGF electrode shows no corrosion, suggesting that the PGF electrode is stable and free of corrosion in such electrolyte system.

Coin cells were assembled with a Li metal anode, LiMn_2O_4 on aluminum or PGF current collectors as cathode in 1 M LiTFSI in EC/DMC (1:1 vol) electrolyte. As shown in Fig. 3a, the initial charge/discharge

specific capacities of LiMn_2O_4 /aluminum electrode are 133 and 117 mAh g^{-1} at 0.2 C ($1 \text{ C} = 148 \text{ mA g}^{-1}$), corresponding to an initial coulombic efficiency of 88%. Because of the destructive corrosion of the aluminum current collector, the active materials are peeled off from the collector. Consequently, there is hardly any capacity retained after 10 cycles. The coulombic efficiencies also severely fluctuate during the cycling. When PGF is applied, the first charge/discharge specific capacities are 135 and 125 mAh g^{-1} at 0.2 C, corresponding to an initial coulombic efficiency of 92% (Fig. 3b). After 1000 cycles at 0.5 C, the discharge capacity retention ratio remains 89%, delivering exceptionally good capacity retention and excellent coulombic efficiency. Moreover, even after 300 cycles at 55°C (Fig. 3c), the discharge capacity retention ratio is still 81%, exhibiting superior thermal stability.

After cycling, the cells were disassembled. Compared with the fresh coin cell accessories (the first row in Fig. 3d), the LiMn_2O_4 /aluminum electrode is completely contaminated (the second row in Fig. 3d). A dark layer of impurities covers the cell caused by severe corrosion of aluminum and serious exfoliation of the active materials during charge/discharge cycles. With respect to the LiMn_2O_4 /PGF electrode, after 1000 cycles, the coin cell accessories keep a good appearance without contamination (the third row in Fig. 3d). The separator becomes slightly yellow which is a normal phenomenon after long time cycles. The exceptional anticorrosive property of the PGF in LiTFSI salt electrolyte endows the cell with good electrochemical performance.

4. Conclusions

The work demonstrated that a flexible pyrolytic PGF can serve as a more suitable cathode current collector than aluminum in EC + DMC electrolytes containing LiTFSI in LIBs. It was found that the PGF exhibited a much more stable electrochemical behavior toward electrolyte corrosion than aluminum. The highly in-plane oriented structure with almost entirely of basal planes of carbon crystallites endowed the PGF with an excellent electrochemical corrosion resistance. Charge/discharge tests performed with LiMn_2O_4 /PGF electrode either at room temperature or

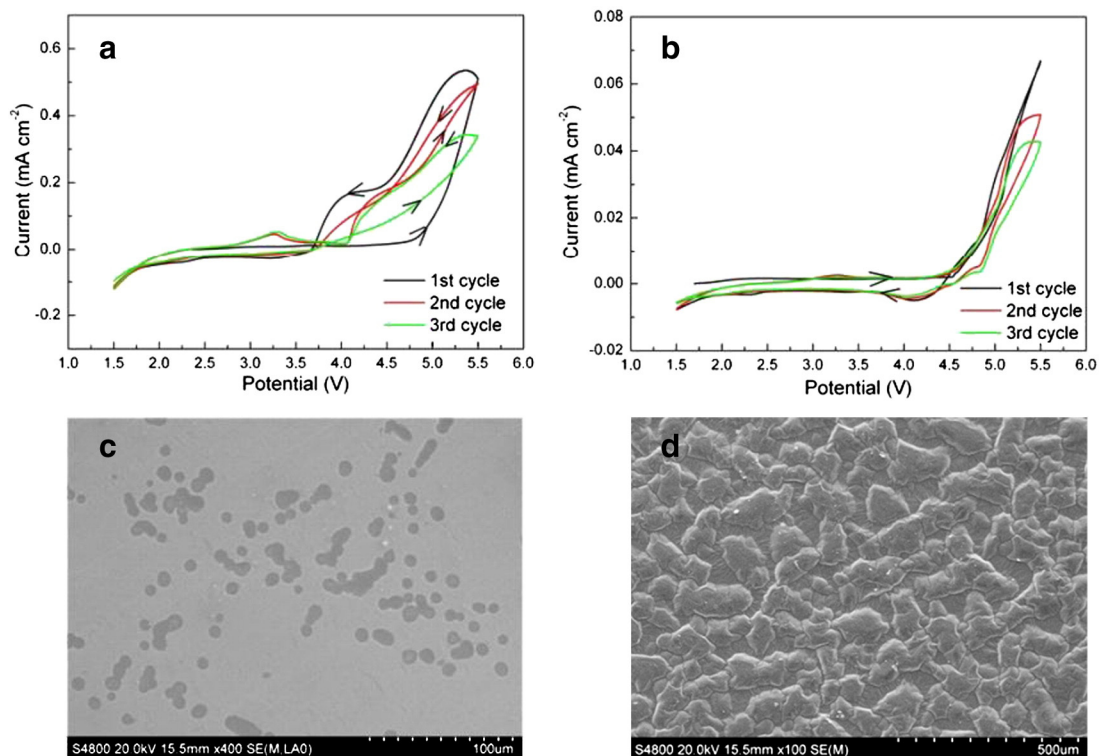


Fig. 2. CV curves of the bare (a) aluminum and (b) PGF in 1 M LiTFSI in EC/DMC (1:1 vol), SEM images of (c) aluminum and (d) PGF after three CV cycles.

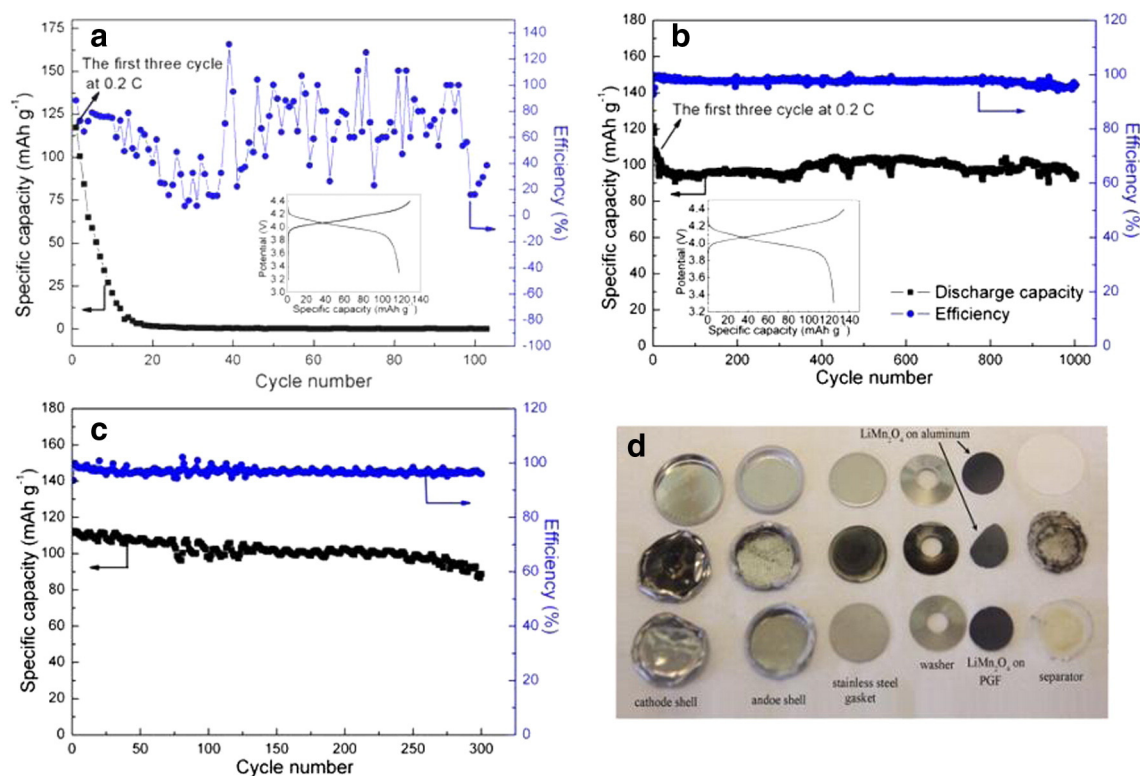


Fig. 3. Cycle performance of (a) LiMn₂O₄/aluminum and (b) LiMn₂O₄/PGF electrodes in 1 M LiTFSI in EC/DMC (1:1 vol), the first three cycles is at 0.2 C, the following cycles are at 0.5 C, the insets in (a) and (b) are their initial charge–discharge curves, respectively. (c) Cycle performance of LiMn₂O₄/PGF electrode at 55 °C at 0.5 C. (d) Comparison photograph of LiMn₂O₄/aluminum and (b) LiMn₂O₄/PGF electrodes after cycles. The first row is the fresh coin cell accessories; the second row is LiMn₂O₄/aluminum electrode; the third row is LiMn₂O₄/PGF electrode. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

at 55 °C also displayed significantly improved cyclability over LiMn₂O₄/aluminum electrode. The results indicated that PGF could be used as a cathode current collector and inhibit the corrosion in the electrolytes containing LiTFSI, which lead to the possibility for the application of LiTFSI salt with satisfactory performance and high safety in advanced LIBs.

Conflict of interest

There is no conflict of interest.

Acknowledgments

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