

Solvothermal exfoliation of fluorographene by the intercalation of organic solvents for lithium primary batteries

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Abstract

Fluorographene (FG), a kind of graphene derivatives, is considered as one of important candidate materials for advanced technological applications because of its distinctive magnetic, electrical and electronic properties. Generally, FG nanosheets can be synthesized by severely fluoridizing graphene using many fluoride reagents or laser irradiation. Recently, a solvothermal-assisted exfoliation shows a great potential for the preparation of high-quality single- or few-layer nanomaterials. High temperature and pressure reduce the free energy, weaken van der Waals attraction between adjacent layers and promote the intercalation of solvent molecules into interlayers, resulting in the efficient exfoliation. Furthermore, F-graphite shows a wide lamellar space of 0.71 nm and a weak bonding energy of 9.36 kJ mol^{-1} ^[1], which favor the intercalation of molecules. In this paper, high-quality FG was prepared by the solvothermal exfoliation of F-graphite through the intercalation of acetonitrile and chloroform, which was demonstrated by wrinkled few-layered microstructures and the poor regularity along the stacking direction. The electrochemical performance of FG nanosheets was tested as the cathode material of Li-battery at different current densities. Compared with F-graphite, FG cathode displayed an excellent electrochemical performance with an improved discharge voltage, specific capacities and rate capability.

Figure 1 illustrates the preparation of FG nanosheets by the intercalation and exfoliation. FG-1 (intercalated by acetonitrile (ACN)) and FG-2 (intercalated by chloroform) prepared by the solvothermal intercalation exhibit a high yield of production up to 15%, which is almost three-fold higher than that of FG prepared only by ultrasonication. Elemental composition and the nature of chemical bonds of FG nanosheets were studied by C1s XPS spectra (Figure 2) deconvoluted to several symmetrical peaks. Compared with FG-1 with five peaks at 285.3, 284.5, 289.0, 291.0 and 292.0 eV, FG-2 exfoliated by chloroform exhibits a new peak at 288.4 eV in C1s spectra corresponding to semi-ionic C–F bonds^[2]. This bond is also confirmed by F1s spectra with two peaks at 688.4 and 690.0 eV associated with semi-ionic C–F bonds and covalent C–F bonds, respectively^[3]. Meanwhile, a minor shift of the peak from 689.0 eV to 688.6 eV also reflects the partial transformation of covalent C–F bonds to semi-ionic C–F bonds. It is probably due to the formation of C–H•••F hydrogen bonds (H-bonds) between chloroform molecules and F atoms of F-graphite.

Figure 3a displays specific capacities of FG nanosheets at different current densities. A remarkable increase specific capacities of FG cathode is obtained due to the improved Li^+ diffusion rate into interlayers of FG with a large space. FG-2 with semi-ionic C–F bonds shows a high specific capacity of 520 mAh g^{-1} at 1C, which is 2.5-fold higher than that of FG-1. Moreover, FG-2 also shows a specific capacity of 413 mAh g^{-1} at 2C and 228 mAh g^{-1} at 3C. FG-1 fails to discharge at 3C. The discharge capacity of FG-2 at current densities from 0.1C to 2C outperforms that of FG nanosheets synthesized using F_2/He in previous studies^[4]. Figure 3b indicates that all samples show high energy densities and low power densities at low discharge rates ($\leq 0.1 \text{ C}$) while the average power density of Li-battery using FG nanosheets is enhanced at high discharge rates. The increase in discharge rates leads to decreased energy densities due to the drop of the output potential as well as the discharge capacity. FG-2 shows a dramatic increase in energy density and power density compared with FG-1 and F-graphite. A maximum power density value of 4038 W kg^{-1} is obtained for Li-battery using FG-2 nanosheets, which is almost four times higher than F-graphite (1136 W kg^{-1}).

FG nanosheets were prepared by the solvothermal-assisted exfoliation of F-graphite based on the intercalation of low-boiling-point organic solvents (ACN, chloroform) without any stabilizer or modifier. This exfoliation shows a high-yield production of FG nanosheets up to 15 wt.%. The partial transformation from covalent C–F bonds to semi-ionic C–F bonds in FG nanosheets exfoliated by chloroform was studied. Compared with FG-1, significant improvement of rate capability was obtained for FG-2 with semi-ionic C–F bonds. FG-2 nanosheets exhibited a high specific capacity of 520 mAh g^{-1} at 1C, which is 2.5-fold higher than that of FG-1 and 5 times as much as that of F-graphite. Moreover, high-quality exfoliated FG nanosheets can be utilized for Li-battery with high rate capability and discharge voltage. FG-2 showed a maximum power density of 4038 W kg^{-1} at 3C. Results indicate that

the solvothermal exfoliation by low-boiling-point solvents is a facile and high-yield approach to prepare high-purity FG nanosheets.

References

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Figures

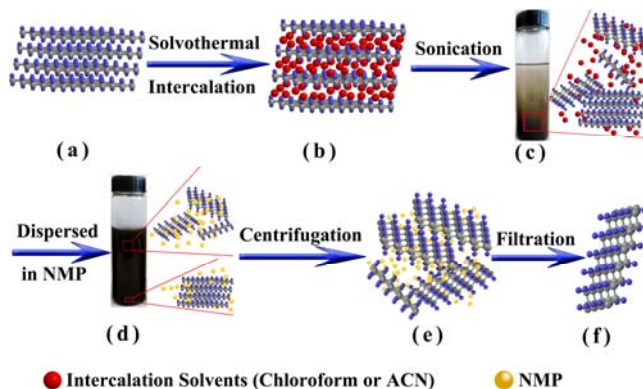


Figure 1 A schematic illustration of the preparation of FG nanosheets by the intercalation and exfoliation.

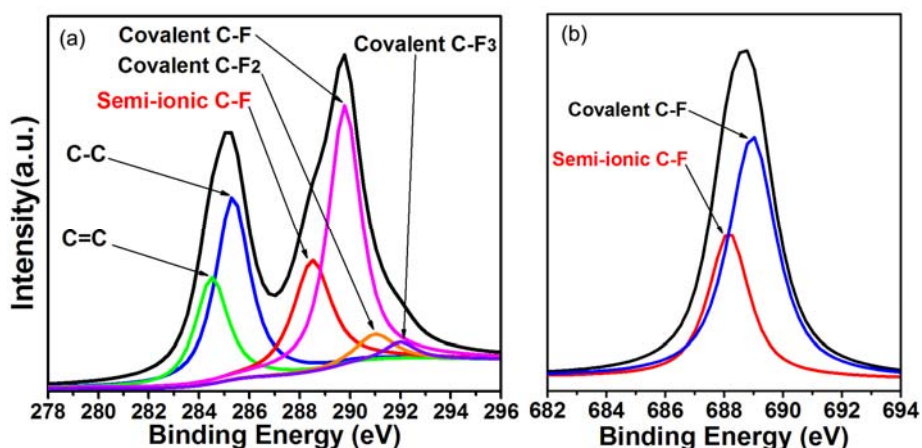


Figure 2 High-resolution XPS spectra of (a) C1s and (b) F1s of FG-2.

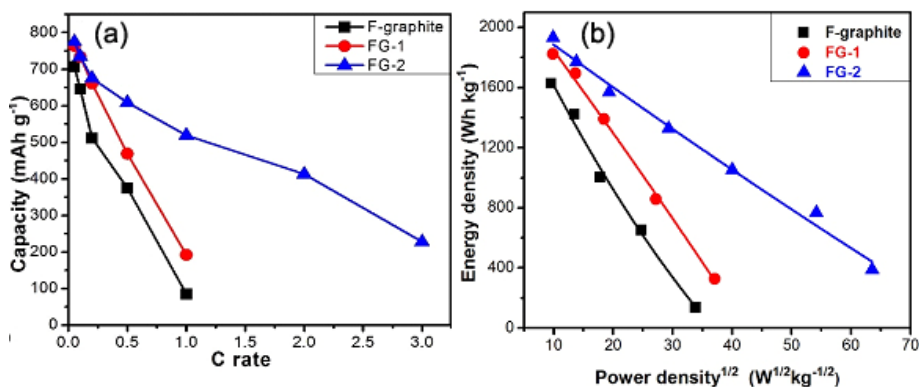


Figure 3 (a) specific capacities and (b) the Ragone plots giving the variation of energy density vs. power density of Li-battery at different current densities