A wafer scale fabrication of 3D Si based nanocomposite arrays as anodes for on chip micro-LIBs has been performed in the Microenergy Group of A/P Dr. Jing Li and Prof. Junyong Kang at Xiamen University.

Title: Fabrication of 3D hexagonal bottle-like Si–SnO2 core–shell nanorod arrays as anode material in on chip micro-lithium-ion-batteries

This work introduces the fabrication of 3D Si–SnO2 arrays as anode in micro-LIBs with the volume expansion and electrochemical kinetic issues addressed, which will facilitate the configuration of solid state micro-batteries for power supply in micro-electronic devices.
Tunable electrochemical properties of fluorinated graphene†‡

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The structural and electrochemical properties of fluorinated graphene have been investigated by using a series of graphene fluorides (CFₓ, x = 0.47, 0.66, 0.89). Fluorinated graphene exhibited high capacity retentions of 75–81% of theoretical capacity at moderate rates as cathode materials for primary lithium batteries. Specifically, CF₀.₄₇ maintained a capacity of 356 mA h g⁻¹ at a 5 C rate, superior to that of traditional fluorinated graphite. The discharged graphene fluorides also provide an electrochemical tool to probe the chemical bonding on the parent graphene substrate.

Introduction

Functionalized graphene sheets (FGSs) with extraordinary properties such as lightweight, high in-plane conductivity and mechanical strength are an ideal material for various applications.¹⁻⁴ Halogenation of graphene with chlorine, bromine, or iodine by thermal exfoliation in gaseous halogen atmospheres has been recently reported by Pumera et al.⁵ The halogen atoms were successfully anchored to the graphene surface that functions as building blocks for potential applications in electronic and electrochemical devices.⁶ Fluorination of graphene has also been studied to improve the graphene properties for optics and electronics.⁶⁻⁷ For example, Şahin et al.⁸ studied structural properties of CₓF using theoretical calculations and Raman analysis. The discrepancy between experiments and calculations was attributed to the use of weighted average data for CₓF structures in experiments. However, changes in properties of CₓF materials at various n values have not been thoroughly investigated which may lead to the identification of more interesting CₓF materials for electronics and energy storage applications. So far, there is no experimental report on the electrochemical performance of graphene fluorides, which may also provide new critical information on the structure of fluorinated graphene. In fact, fluorinated carbon (CFₓ) is a high capacity cathode for primary lithium batteries. Li/CFₓ batteries have the highest theoretical specific capacity (864 mA h g⁻¹; x = 1.0) of the primary battery systems. Therefore, it is important to explore the relationship between the fluorine content on graphene and the final electrochemical performances of graphene fluorides.

In general, the synthesis route for CFₓ materials is the fluorination of a carbon source, in which the C/F ratio is controlled by the reaction temperature, carbon source and the partial pressure of fluorine.⁹⁻¹¹ Most of the studies that synthesize CFₓ are carried out at high temperatures for a high fluorine content material (x > 0.5), which leads to the formation of covalent sp³ bonding between carbon and fluorine and thus poor performance of these materials at high discharge rates.¹²⁻¹³ The formation of fluorine rich surface groups (CFₓ, CFₓetc.) with insulating properties usually leads to significant initial voltage delay. Despite the inherent challenges, high temperature (HT) treated materials show high discharge capacity at low to moderate rates upon chemical/thermal treatment or by reduction of fluorine content (sub-fluorinated carbons).¹⁴⁻¹⁷ The earlier work from our group demonstrated that a hybrid configuration of carbon monofluoride with silver vanadium oxide and graphene further effectively improved the high rate performance of CFₓ.¹⁸ Synthesis of carbon fluorides at low temperatures (<350 °C) leads to the formation of a mixture of semi-ionic and covalent C–F bonds. At temperatures below 100 °C, CFₓ materials (x < 0.25) exhibit ionic C–F bonds further enhancing material conductivity.¹⁹,²⁰

In fact, for practical applications, the energy/power ratio of the battery needed for a specific application may vary largely but can be tuned by the fluorine content in CFₓ. Although the theoretical capacity decreases with decreasing fluorine content, the rate capability and initial voltage delay are improved. Lam and Yazami²¹ have synthesized CFₓ materials (0.33 < x < 0.66) by direct fluorination of natural graphite at temperatures of 375–400 °C and demonstrated good rate performance of ~400 mA h
g$^{-1}$ at rates as high as 2.5 C. Mechanochemical synthesis of CF$_x$ materials with F content as high as 0.8 has been reported to show a capacity retention of <500 mA h g$^{-1}$ at low rates of C/35 and C/17.$^{22}$

FGSs with a C/O ratio of 14 (supplied by Vorbeck Materials Corp.) were used to prepare graphene fluorides,$^{23,24}$ which were then tested as the cathode material for primary batteries. The synthesis–structure–performance relationship in fluorinated FGSs, particularly the influence of functional groups and fluorine atoms on the structural and electrochemical properties of CF$_x$ (x = 0.47, 0.66 and 0.89), has been systematically discussed in this work.

**Experimental methods**

Fluorination of FGSs (Vorbeck Materials) was carried out in 7% v/v of fluorine (F$_2$)/helium (He) for a day followed by gradual rise of F$_2$ in ∼1 to 2 hours to 100% with no helium. CF$_{0.89}$, CF$_{0.66}$ and CF$_{0.47}$ were synthesized at temperatures of 150 °C, 75 °C and 25 °C, respectively. The reactor was weighed before and after fluorination to obtain the C/F ratio. It was assumed that there is no weight loss due to volatile products and that all the weight gain resulted from fluorine addition.

The structure of fluorinated graphene samples was determined by X-ray diffraction (XRD) using a Philips X’Pert X-ray diffractometer and a Cu Kα sealed tube (λ = 1.54178 Å) in 0–2θ scan mode at 0.5’’ min$^{-1}$ spanning over a range of 5–80°. A JEOL JEM 2010 microscope fitted with a LaB6 filament (200 kV) was used for the transmission electron microscopy imaging (TEM). The slurry comprised of 85 wt% active material, 10 wt% conductive Super P carbon and 5 wt% polyvinylidene fluoride (PVDF) with N-methyl-2-pyrrolidone as the solvent. The slurry was cast on to an aluminum foil on a Hohsen Corporation MC10 coater in the form of a thin film which is ∼20 microns thick with a loading of ∼1 to 1.5 mg cm$^{-2}$. Electrodes were vacuum dried at 70 °C overnight to remove any excess solvent and moisture. Coin cell assembly was carried out in an argon environment glove box (MBRAUN, Inc.) with 1 M LiPF$_6$ in 1:2 (v/v) of ethylene carbonate (EC) and dimethyl carbonate (DMC) as the electrolyte. An Arbin BT-2000 battery tester was used to obtain the charge/discharge characteristics and a CH Instruments 6005D potentiostat/galvanostat was used for impedance measurements in a frequency range of 100 kHz to 5 MHz with an amplitude of 10 mV.

**Results and discussion**

To investigate the chemical bonding between C and F, graphene fluorides were synthesized with a fluorine content of 0.47, 0.66 and 0.89 (atomic ratio between F and C). It is well documented that fluorination of graphite leads to the formation of puckered rings with a loss in conductivity.$^{25}$ However, fluorinated FGSs retain their original lamellar architecture upon fluorination as indicated by the TEM image in Fig. 1a and ESI Fig. S1.$^\dagger$ The physical structure of the as-synthesized CF$_x$ samples characterized using TEM is similar to the FGS precursors despite fluorination. This can lead to faster diffusion of solvated Li$^+$ ion compared to its transport in fluorinated carbon and will be further discussed in the electrochemical analysis section.

X-ray diffraction analyses of pure CF$_2$ powders are presented in Fig. 1b. The peaks at 26.5° correspond to the (002) diffraction of graphitic carbon.$^{26–28}$ The appearance of a broad peak at 26.5° for all the three samples indicates that the FGSs are dispersed and randomly stacked. Higher fluorine content increases the peak intensity at 26.5°, which shows an improved tendency to graphitize or lead to stacking of sheets. Ideally, individual graphene sheets do not exhibit the (001) diffraction at ∼12°.$^{29,30}$ However, fluorinated graphene exhibits a peak at low angles of ∼10 to 12° corresponding to the (001) orientation$^{26–28}$ suggesting stacked architecture for these materials. An increase in the peak intensity at low angles with increased fluorine content also suggests higher sheet stacking. The low angle peak shifts to higher 2θ degrees with decreasing fluorine content are related to an inter-layer decrease of (CF)$_n$. This is because the fluorine atom with a covalent radius$^{31}$ of 0.72 Å is adsorbed in between the graphene layers in CF$_{0.89}$ forming stacked layers of graphene. In CF$_{0.47}$, fluorine interaction primarily occurs on the graphene surface instead of sticking to graphene sheets together along the (001) direction. Therefore, the observed inter-layer spacing formed by graphene restacking is reduced in graphene fluorides with relatively lower F content. In addition, the high fluorine content in both CF$_{0.89}$ and CF$_{0.66}$ also arises from the presence of insulating surface groups CF$_3$ and CF$_2$. Comparison of the physical appearance of the powders (ESI Fig. S2†) clearly indicates that CF$_{0.89}$ is a white powder with the color turning black with a decrease in the fluorine content indicating improved conductivity.$^{32}$

The electrochemical properties of fluorinated graphene, CF$_x$ (x = 0.47, 0.66, 0.89), were evaluated and are presented in Fig. 2a. The operational voltage varies significantly with the fluorine content in CF$_x$ (Fig. 2a) further indicating the strong correlation between the F coverage on FGSs and electrochemical performance. Higher discharge voltage (∼2.8 V) in CF$_{0.47}$ indicates faster solvated Li$^+$ diffusion due to high surface area graphene with expanded inter-layer spaces. For CF$_{0.89}$ and CF$_{0.66}$, an initial voltage delay and lower discharge voltages were seen. This is due to the fact that more sites on graphene are now occupied by insulating surface groups leading to slower
solvated Li\(^+\) diffusion and reduced in-plane conductivity. The specific capacities for CF\(_{0.89}\) and CF\(_{0.66}\) are \(\sim 670\) mA h g\(^{-1}\) and \(\sim 537\) mA h g\(^{-1}\) at a rate of C/10, respectively. All these materials deliver 75–81% of their theoretical capacities at low rates. Although CF\(_{0.47}\) exhibited a relatively low capacity of 462 mA h g\(^{-1}\) at C/10, it demonstrates superior rate capability than the other two. For example, at 5 C, a high capacity of 356 mA h g\(^{-1}\) is still obtainable while CF\(_{0.89}\) and CF\(_{0.66}\) cannot be discharged at all (Fig. 2b). Although the discharge plateau for CF\(_{0.47}\) decreases to \(\sim 1.9\) V at 2 C due to polarization, voltage does not drop further at 5 C current density, demonstrating the good in-plane conductivity of unreacted graphene as well as more open structures (increased inter-layer spacing) to promote the diffusion of solvated Li\(^+\) ions. In comparison to fluorinated carbon that does not show any discharge at rates above C/5, fluorinated graphene shows greatly improved rate performance.

An impedance analysis at 10% depth of discharge was performed to eliminate the effect of initial voltage delay and better understand the reaction mechanism during discharge. The Nyquist plots for all the three materials are shown in Fig. 3. For all the materials, impedance due to physical cell construction including the contributions from current collectors, electrolyte and separator is quite low (3 \(\Omega\)). CF\(_{0.47}\) and CF\(_{0.66}\) materials are primarily made of individual graphene stacks with better accessibility for solvated Li\(^+\) diffusion before the reaction. In the case of CF\(_{0.89}\), higher fluorination leads to the formation of more undesired surface groups such as CF\(_2\)/CF\(_3\), which delay the transportation of solvated Li\(^+\) especially at high rates. The lithium ions diffuse into the interlayers of the stacked architectures and the reaction with CF\(_2\) proceeds gradually, which induces the sloping discharge profile for CF\(_{0.89}\) as shown in Fig. 2a. The total overall resistance is the highest for CF\(_{0.89}\) and the lowest for CF\(_{0.47}\) (Fig. 3). In an impedance spectrum, the onset between the semicircle and slope line is representative of the reaction kinetics with higher frequencies leading to faster kinetics and vice versa. The frequencies are the highest for CF\(_{0.47}\) and lowest for CF\(_{0.89}\) (Fig. 3), indicating the highest overall resistance for CF\(_{0.89}\)\(^{-1}\).

The samples after the discharge were investigated for the discharge products. The TEM image of CF\(_{0.47}\) after the discharge process presented in Fig. 4a shows crystalline domains which we infer are lithium fluoride (LiF) and are evenly spread out throughout the entirety of the sample. The figure in the inset shows a diffraction pattern indicating sample crystallinity. Most of the discharge product exhibited a spherical morphology within 20–30 nm without aggregation clearly mapping out the original distribution of C–F bonds. For CF\(_{0.89}\), LiF is also observed as shown in ESI Fig. S3\(^\dagger\) but are partially agglomerated unlike that for CF\(_{0.47}\). The formation of LiF after the discharge is further confirmed using XRD analysis. The peaks at 38.8\(^{\circ}\) and 44.9\(^{\circ}\) correspond to the (111) and (200) diffraction peaks\(^2\) of LiF (Fig. 4b). However, the broad peak at 21\(^{\circ}\) may be related to the layered nature of LiF as reported by Read et al.\(^3\)

**Conclusions**

In this study, graphene fluorides have been synthesized by partial fluorination of graphene. CF\(_x\) \((x = 0.47, 0.66\) and 0.89\) “grows” intrinsically on graphene as the substrate with the fluorine content affecting the structure and electrochemical properties. Close inspection revealed that CF\(_{0.89}\) with a relatively high fluorine content consists of stacked graphene layers with surface insulating groups such as CF\(_2\) and CF\(_3\). In contrast, CF\(_{0.47}\) is composed of fluorine primarily on the surface with small amounts of CF\(_2\) and CF\(_3\) groups leading to the lowest overall resistance. Compared to fluorinated graphite, the transport of solvated Li\(^+\) ions within fluorinated graphene is greatly improved benefitting the high rate performance. In addition, the large amounts of residual graphene domains

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**Fig. 2** (a) Low rate (C/10) performance of different fluorinated graphene materials (1 C current density for CF\(_{0.47}\) – 602 mA g\(^{-1}\); CF\(_{0.66}\) – 721 mA g\(^{-1}\); CF\(_{0.89}\) – 825 mA g\(^{-1}\)). (b) Rate performance of CF\(_{0.47}\) until 5 C rate.

**Fig. 3** Impedance spectra of all three fluorinated graphene materials at 10% DoD.

**Fig. 4** Characterization of the discharged sample: (a) TEM image of the CF\(_{0.47}\) material after the discharge cycle indicating crystalline domains of LiF (red circles). The inset shows a typical diffraction from one of the crystalline domains. (b) XRD profiles of all three fluorinated graphene materials showing the presence of LiF domains.
along with defective sites also contribute to the greatly improved performance of CF$_{0.47}$. The distribution of the discharge product LiF clearly indicates the original location of C-F bonding, and thus is a good electrochemical approach to probe fluorine atoms on graphene providing information for the indirect detection of functional groups.

Acknowledgements

This research is supported by the U.S. Army Corps of Engineers (USACE), Portland District, as part of the injectable acoustic microtransmitter development project. Brad Eppard is the technical lead for USACE and we greatly appreciate his involvement and oversight. The study was conducted at the Pacific Northwest National Laboratory (PNNL) in Richland, Washington, which is operated by Battelle for the U.S. Department of Energy (DOE) under Contract DE-AC05-76RL01830. The authors thank Vorbeck Materials Corporation and Prof. Ilhan A. Aksay of Princeton University, Princeton for providing the graphene. The authors also thank Suree Brown, J. L. Adcock and Sheng Dai of The University of Tennessee, Knoxville for their help in fluorination of graphene. The authors thank Xiaolin Li and Libor Kovarik of PNNL for the XRD and TEM characterization, respectively. The TEM work was performed at the Environmental Molecular Sciences Laboratory (EMSL) located at PNNL, a national scientific user facility sponsored by the DOE, Office of Biological and Environmental Research.

Notes and references