Chemical Physics Letters 563 (2013) 58–62

Contents lists available at SciVerse ScienceDirect

Chemical Physics Letters

journal homepage: www.elsevier.com/locate/cplett

Self-weakening in lithiated graphene electrodes

Hui Yang [a], Xu Huang [a], Wentao Liang [a], Adri C.T. van Duin [b,*], Muralikrishna Raju [b], Sulin Zhang [a,*]

[a] Department of Engineering Science and Mechanics, Pennsylvania State University, University Park, PA 16802, USA
[b] Department of Mechanical and Nuclear Engineering, Pennsylvania State University, University Park, PA 16802, USA

ARTICLE INFO

Article history:
Received 30 October 2012
In final form 25 January 2013
Available online 1 February 2013

ABSTRACT

We present a molecular dynamics study of the fracture mechanisms of lithiated graphene. Our modeling results reveal that lithium diffusion toward the crack tip is both energetically and kinetically favored owing to the crack-tip stress gradient. The stress-driven lithium diffusion results in lithium aggregation around the crack tip, chemically weakening the crack-tip bond and at the same time causing stress relaxation. Our simulations show that the chemical weakening effect is the dominant factor, which manifests a self-weakening mechanism in lithiated graphene. The atomistic understanding of the degradation mechanism provides guidance for the lifetime extension in the design of graphene-based electrodes.

1. Introduction

Graphene and carbon nanotubes (CNTs) not only possess outstanding mechanical properties and electronic characteristics, but also hold significant promise as anode materials in lithium (Li) ion batteries (LIBs) [1–7]. Due to their high electrical conductivity, they have been used as conducting additives to other active materials in electrodes [8,9]. Because of their unique geometries, CNTs and layered graphene possess enhanced energy storage capacities [10–13] as compared to the conventional Li-graphite anodes. Owing to their great flexibility and high fracture strength, they are also expected to exhibit longer cycle life [14,15] than conventional carbonaceous anodes.

Recent experimental studies evidenced that CNTs undergo mechanical degradation upon electrochemical cycling, and showed that CNTs were broken into smaller pieces after up to a few hundred or thousand cycles [16–18]. More recently, Liu et al. reported that lithiation drastically embrittles multi-walled carbon nanotubes (MWCNTs) [18], but not layered graphene [19,20]. It was argued that the different mechanical responses stem from in the geometrical constraints of MWCNT and layered graphene. For MWCNTs, the inter-wall Li intercalation causes ~6% hoop strain [18]. In contrast, graphene in layered geometry can freely bend into the third dimension [19], thereby suppressing the buildup of high in-plane stretching energy that would cause fracture. Despite the obvious difference in the lithiated multi-layered graphene and MWCNTs, the embrittlement of MWCNTs remains to be understood from a mechanics perspective, given the fact that a pristine CNT can sustain an in-plane strain up to 20% or even larger [21].

During lithiation of an MWCNT, Li intercalation into the graphene layers generates tensile stress in the hoop direction. The intercalated Li can be regarded as adatoms of the graphene layers, which also chemically weakens the graphene. Previous molecular orbital theory calculations showed that the presence of a single Li weakens the pristine graphene by ~30% [18]. Owing to these weakening factors, small cracks may nucleate, either homogeneously, or from preexisting atomic vacancies. The nucleation processes are beyond the scope of the present Letter. Instead, we herein carry out molecular dynamics (MD) simulations to elucidate the lithiation-induced failure mechanisms of monolayer graphene, with a focus on the effect of Li on the propagation of a preexisting crack in monolayer graphene. While the focus of the present Letter is lithiated monolayer graphene, the modeling results can be straightforwardly extended to CNTs by taking into account of the curvature effects. We show that the stress gradient at the crack tip drives Li adatoms migrating toward the crack tip. The aggregation of Li at the crack tip lead to two consequences: weakening the crack-tip bond due to the local chemical Li–C reaction and causes stress relaxation of the high Li-concentration region. Through MD simulations, we identify that the chemical weakening effect is the dominant factor on the crack propagation in graphene. We further point out that the stress-diffusion coupling effect and the crack-tip Li-aggregation induced fracture behavior are universal in the degradation of electrodes. Our studies offer a fundamental guidance to the cycle life extension of CNT- and graphene-based anodes in LIBs, and shed light on the failure mechanisms of other important anode materials such as Si.

2. Methodology

In our MD simulations, the interatomic interactions are modeled by the ReaxFF reactive force field. The ReaxFF combines a

---

* Corresponding authors.
E-mail addresses: acv13@engr.psu.edu (A.C.T. van Duin), suz10@psu.edu (S. Zhang).

0009-2614/$ - see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.cplett.2013.01.048

bond-distance/bond order relationship with a geometry-dependent charge calculation, and provides a highly transferable method, applicable to covalent, metallic and ionic materials and their interfaces [22–24]. The ReaxFF generally fits not only thermodynamic properties at equilibrium states, but also kinetic properties including reaction barriers, both from first-principles based simulations. The ReaxFF has been adequately shown to provide an accurate account of the chemo-mechanical behavior of the hydrocarbon systems, while capable of treating thousands of atoms [25–27]. We have tested the accuracy of the ReaxFF after introducing Li into the hydrocarbon system. For instance, the migration barrier from one hollow site (the center of the hexagons) to another on a monolayer graphene calculated by the ReaxFF differs only 3% from the density functional theory (DFT) calculations [28,29]. The functional form of the ReaxFF and parameters are given in Supplementary.

To simulate Li-mediated crack propagation in graphene, we adopt a size-reduced model (1910 carbon atoms in total) consisting of a small circular-shaped domain cut around a crack tip [30,31], as shown in Figure 1. In classical fracture mechanics, the asymptotic stress profile σ_{ij} for a plane-stress condition in the region *sufficiently* close to a crack tip can be written as:

$$\sigma_{ij} = \frac{K_\mathrm{I}^\mathrm{app}}{\sqrt{2\pi r}}\Theta_{ij}(\theta), \tag{1}$$

where r and θ are the polar coordinates with the origin O sitting at the crack tip, Θ is the known angular dependent function, i and j are the two Cartesian coordinate indices. Note that the asymptotic stress at the crack tip is dominated by a single loading parameter, i.e., the applied stress intensity factor (SIF) $K_\mathrm{I}^\mathrm{app}$, independent of the geometry of the specimen. Such a domain at the crack tip is known as the K-dominant zone. In our simulation model, the domain size is chosen such that its outer boundary falls in the K-dominant zone. Such a small system can effectively model a long crack that extends self-similarly under applied K load with considerably reduced computational cost.

To generate the asymptotic stress profile described in Eq. (1) in the atomic system around a crake tip, we impose the crack-tip displacement on the atoms consistent with the asymptotic stress field. To begin with, the pristine graphene system is dynamically relaxed at 10 K free of any constraints using the Berendsen thermostat. Starting from the relaxed system, atoms about 3 Å from the outer boundary (red dots in Figure 1) are held fixed, while the remainder of atoms is set free. All the atoms in the system are then displaced according to the displacement field of the crack-tip asymptotic solution dictated by the applied SIF, with the origin O taking as the center of the circular graphene:

$$\begin{Bmatrix} u_x \\ u_y \end{Bmatrix} = \frac{K_\mathrm{I}^\mathrm{app}}{2\mu}\sqrt{\frac{r}{2\pi}}(\kappa - \cos\theta)\begin{Bmatrix} \cos(\theta/2) \\ \sin(\theta/2) \end{Bmatrix}, \tag{2}$$

where μ is the shear modulus of the lattice, $\kappa = (3 - \nu)/(1 + \nu)$, and $\nu = 0.4$ is the Poisson's ratio directly obtained from MD simulations. Due to the applied $r^{1/2}$-dependent displacement, a crack appears with the crack tip at O. The stress distribution of the strained circular graphene can be obtained by evaluating the Virial stress at all the atomic sites, followed by the interpolation over the entire graphene surface [32]. Our simulations demonstrate that the Virial stress distribution agrees very well with the continuum asymptotic

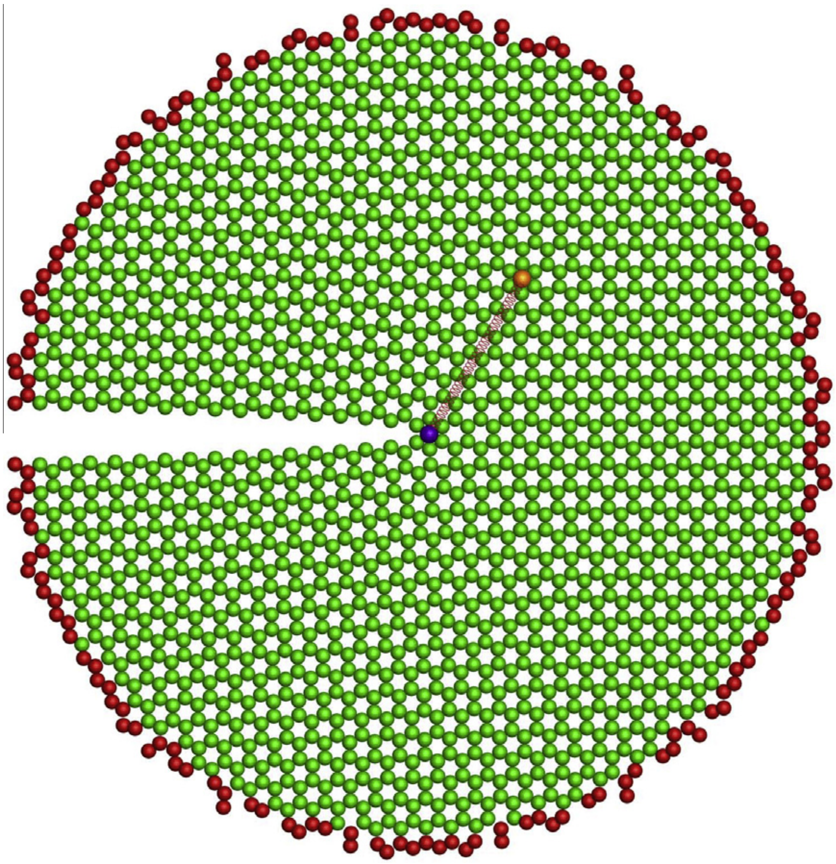

Figure 1. The size-reduced simulation model for analyzing the lithiation induced fracture in graphene. The circular domain can be loaded by prescribing the displacement field in Eq. (2), where the red dots represent the carbon atoms that are fixed, while the green dots are free carbon atoms. In determining the mobility of Li adatom, a dummy atom at the crack tip (purple) is connected to the Li adatom (gold) at the far with a virtual spring of high stiffness. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)