Composites: Part B 65 (2014) 69–79

Contents lists available at ScienceDirect

Composites: Part B

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

Modeling mechanical stress and exfoliation damage in carbon fiber electrodes subjected to cyclic intercalation/deintercalation of lithium ions

Andrejs Pupurs [a,b], Janis Varna [a,*]

[a] Department of Engineering Sciences and Mathematics, Luleå University of Technology, SE-971 87 Luleå, Sweden
[b] Swerea SICOMP, SE-941 26 Piteå, Sweden

ARTICLE INFO

Article history:
Received 22 June 2013
Received in revised form 30 September 2013
Accepted 5 November 2013
Available online 15 November 2013

Keywords:
A. Carbon fiber
C. Finite element analysis (FEA)

ABSTRACT

Gradients in lithium ion concentration distribution in carbon fiber are accompanied by non-uniform fiber swelling leading to development of mechanical stresses. During lithium deintercalation these stresses may lead to initiation and growth of radial cracks in the fiber. The subsequent cycle of intercalation may result in arc-shaped cracks deviating from the tip of the radial cracks. These phenomena decrease the mechanical properties of fibers if used in structural batteries and reduce the charging properties of the battery by decreased diffusivity of lithium ions and by exfoliating layers on the fiber surface. The crack propagation and possible damage evolution scenarios are analyzed using linear elastic fracture mechanics. The crack geometry dependent ion concentration distributions and the elastic stress distributions were found using finite element software ANSYS.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

One of the materials with a potential for use as electrodes in lithium-ion batteries is carbon fiber. Due to their graphitic structure of stacked graphene planes, the carbon fibers are able to accommodate ion intercalation (reversible inclusion of ions); the electrochemical properties of commercially available carbon fibers have been reported in [1]. In future structural batteries these carbon fibers will also have a load bearing function. During the service life of rechargeable battery, the fibers will be subjected to multiple ion intercalation/deintercalation (charge/discharge) cycles, which are accompanied by non-uniform fiber swelling. Non-uniform swelling in each intercalation/deintercalation cycle results in formation of mechanical stresses, which can lead to micro-damage in fibers, which in turn leads to degradation of mechanical properties [2]. After moderate number of cycles of Li-ion intercalation/deintercalation no degradation of the longitudinal elastic modulus of fibers was reported in [3]. However, the initiation of micro-damage after a large number of applied cycles is probable. Fiber degradation may also affect the ion diffusivity and the number of charge–discharge cycles with high energy efficiency. Therefore, to ensure the durability of this type of batteries, mechanical degradation mechanisms in carbon fibers during service life have to be analyzed to develop guidelines for material selection.

This paper deals with analyzing initiation and propagation of possible damage mechanisms in cyclic intercalation/deintercalation of the carbon fiber.

During the intercalation process, lithium ions enter the fiber via the interface by diffusion process, schematically shown in Fig. 1a. In the beginning the ion concentration has a gradient with high concentration at the fiber surface. The increase of ion concentration in the material leads to anisotropic volumetric changes (swelling) in the transversally isotropic carbon fiber characterized by two swelling coefficients β_z and β_r, in the axial and radial directions respectively. Due to the concentration gradient the outer region of the fiber would have larger free swelling strains than the inner region. Since the displacement continuity has to be satisfied, internal stresses appear in the fiber, see the 1st column in Fig. 1b: radial stresses, σ_r, are positive (the outer region, by attempting to expand more, applies radial tractions to the inner part), whereas hoop stresses, σ_θ, are negative in the outer region and positive in the inner region (attempt of the outer region to expand in θ – direction is constrained by the inner region, which due to lower concentration of ions does not expand as much). The only possible (but not very realistic as follows from analysis presented further) damage mode in this step is formation of arc cracks (marked with dashed line in 1st column in Fig. 1b) governed by the radial strength of the fiber. At the end of the diffusion process the concentration gradient decays and so do all the mechanical stresses. The radial diffusion process in the fiber as well as in spherical particles has been analyzed previously, for example in [2,4,5] using series expansion, obtaining

* Corresponding author. Tel.: +46 920 49 1649.
E-mail address: Janis.Varna@ltu.se (J. Varna).

1359-8368/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.compositesb.2013.11.007

Nomenclature

C	relative ion concentration in the fiber with respect to available sites	i	current density
c_0	maximal concentration of ions (when all available sites would be occupied)	F	Faraday's constant
$c=c_0C$	ion concentration in the fiber	V	potential relative to a lithium reference electrode
C_R	saturation concentration of ions in fiber	V_{II}	represents the deviation from ideal solution behavior due to the interaction of insertion species
t	time	U^0	standard cell potential
r_f	fiber radius	β	symmetry factor
t^*	normalized time	R_g	universal gas constant
D	diffusion coefficient	T	temperature
$\tau=\frac{tD}{r_f^2}$	normalized time	f	$=F/R_gT$
Δ	Laplace operator	B	Biot constant
∇	gradient operator	k_c	cathodic rate constant
γ_1	intercalate activity coefficient	k_a	anodic rate constant
N	ion flux		

concentration distribution as a function of the radial coordinate. The stress distribution problem due to described mechanism was solved analytically in a closed form.

During the deintercalation, see the 2nd column in Fig. 1b, the outer region loses the ions first and would shrink, which is constrained by the inner region, which is still in a swelled state. Equilibrium is reached with outer regions being under tensile hoop stresses σ_θ (compressive σ_θ in the inner regions) and compressive radial stresses σ_r. Assuming a fully reversible charge, at the end of the deintercalation the lithium ion concentration reaches zero and the fiber is stress free.

The presented schematic description is correct under assumption that the surrounding mediums have zero elastic properties and do not apply any constraint to the swelling and shrinking of the fiber. This may be true in case of a fiber surrounded by a liquid electrolyte but may become rather different, if the electrolyte is solid and this unit is embedded in other solid materials.

Using the calculated stress distributions, strength based failure criteria have been applied in [2,4] to analyze possible sites, time instants and mechanisms of failure. These criteria are applicable to identify the possible damage initiation but the damage development has to be approached by fracture mechanics methods: small crack has to be introduced and its growth analyzed, by evaluating the available and the required energies for creation of new crack surface.

In repeated intercalation and deintercalation cycles we may expect radial crack initiation and growth during deintercalation as shown in the 2nd column of Fig. 1b. It can start in quasi-static manner from the surface, being arrested, when approaching the central part of the fiber. The radial growth can continue also in a fatigue manner during deintercalation in repeating cycles.

In the first approximation we may assume that radial cracks do not influence the ion diffusion because diffusion is in the radial direction only. Higher order approximation may consider the radial crack as a pathway for the electrolyte infiltration meaning that the ions could also intercalate the fiber from the crack surface. Such possibility is negligible, if the electrolyte is solid or if the viscosity of the electrolyte is high because the radial crack opening is extremely small.

In the initial stage of each intercalation, when the radial tensile stress is high, arc cracks can initiate by deflecting from the tip of the radial crack and propagating in the circumferential direction as shown in the 3rd column in Fig. 1b. Arc cracks affect the diffusion, shielding the ion movement by their open surfaces. In such case the diffusion process does not have the axial symmetry and solution cannot be found analytically by series expansion. Obviously, the stress distributions also become dependent on the hoop coordinate and can only be found numerically.

The diffusion process can be very complex, generally speaking, as the system to analyze contains an electrolyte, where the ion concentration can change and have a gradient and the fiber/

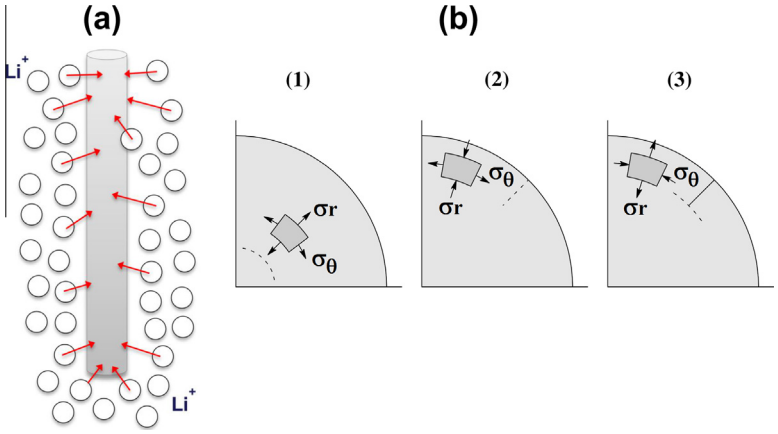

Fig. 1. Lithium ion diffusion in a carbon fiber: (a) schematic geometry and (b) possible modes of mechanical damage.

Download English Version:

https://daneshyari.com/en/article/817628

Download Persian Version:

https://daneshyari.com/article/817628

Daneshyari.com