Stable crack growth in nanostructured Li-batteries

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Abstract

The formation of damage, which results from the large volume expansion of the active sites during electrochemical cycling, in rechargeable Li-batteries, is modelled from a fracture mechanics viewpoint to facilitate the selection of the most effective electrode materials and configurations. The present study is a first step towards examining stable cracking in such high-energy storage devices, by considering three different configurations at the nanoscale, which are currently at an experimental stage. As a result, stability diagrams concerning crack growth are constructed and compared for the following cases: (a) the electrodes are thin films, (b) the Li-insertion sites in the anode are nanofibre-like inclusions, (c) the active sites in both electrodes are spherical.
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1. Introduction

Due to the small Li-intercalation of carbon, which is used as a base material for negative electrodes in rechargeable Li-batteries, extensive research is being performed, for over two decades in order to find alternative anode materials. This research has suggested that some of the best candidates are Sn and Si, due to their high capacity (990 and 4000 mAh g^{-1}). These materials, however, have not been used commercially because of their large volume expansion upon Li-insertion (during the charge/discharge cycle), which results in crumbling and severe cracking of the electrode after continuous electrochemical cycling [15]. It is therefore anticipated that modelling fracture in these high-energy storage devices will provide further insight towards the behavior of these material systems, and allow for the selection of other appropriate materials.

A first attempt to model the mechanical response of Li-batteries, from a purely elastic point of view, during an electrochemical cycle was done by Aifantis and Hackney [1]. The stress-induced inside the electrodes was modelled by treating them as thin films that consisted of disc-shaped Li-ion active sites embedded in an inert glass or ceramic matrix (Fig. 1). This study is a first step towards modelling the most important effect that this cycling deformation process has: cracking. As was shown in experimental evidence provided by Aifantis and Hackney [1] (Fig. 2), continuous electrochemical cycling on a single crystal of LiMn$_2$O$_4$ resulted in multiple fractures on its surface, producing nanocrystals (Fig. 2). It is believed that continuous cycling would have the same effect on LiMn$_2$O$_4$ if it were the active site of the cathode; the individual nanoparticles, however, produced by fracture, would no longer be in electrical contact with the remainder of the electrode. As a result the material that fractures loses electrical contact with the electrode and becomes unable to respond to the applied voltage required for charging or controlling the discharge of the battery; hence the electrode becomes unsuitable for further use [1,2].

Moreover, the fracture of individual particles increases the surface area available to chemical attack by the corrosive agents of the battery (HF and residual H$_2$O) that are believed to attack the surfaces of the active material [1]. In fact, it is reasonable to expect that the chemical instability

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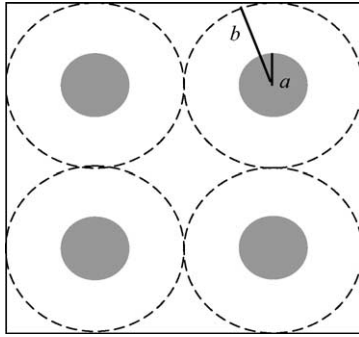 *E-mail address:* k.aifantis@damtp.cam.ac.uk (K.E. Aifantis).

Fig. 1. Idealized geometry of the electrode: Li-insertion particles (shaded) embedded in a glass (blank) matrix. A unit cell is defined by a circle of radius *b* surrounding a circular particle of radius *a*.

Fig. 3. Radial cracking configuration assumed for the unit cell.

of the active particle surfaces may interact with the mechanical stress to enhance the structural instability of the material component under consideration (stress corrosion cracking). Many battery developers have taken the approach of using large particle sizes in order to reduce the surface area available to chemical attack. However, this will accentuate the problem associated with stress concentrations at the surface of the particles. An alternative method that can be used is to develop a composite material in which nanoscale electrochemically active material is encased in large particles of a chemically inert matrix [3]. This method not only reduces the surface area of the active material available to chemical attack, but also minimizes the gradients in concentration responsible for fracture, since the active material component of the composite has a nanometre length scale. Therefore, throughout the present work, both electrodes are taken to consist of Li-active sites (with a nanometre diameter) embedded periodically in an inert, with respect to Li, matrix.

Consideration of the above electrode configuration along with fabrication methods that are in the experimental stage allows the mechanical modelling for the following three cases: (a) the active sites are disc-shaped platelets and hence the electrodes take the form of thin films; (b) the active sites of the anode are fibre-like inclusions (long cylinders); (c) the active sites in both the anode and cathode are spherical.
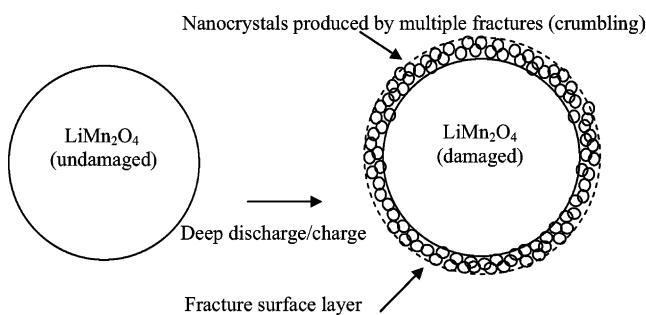
2. Modelling the electrode damage zone

Since experiments [1] have shown that significant damage results from continuous electrochemical cycling it can be assumed that the fracture layer surrounding each active site (Fig. 2) has undergone severe fracture, such that it can support only radial stresses. The damage zone can thus, be modelled by a sufficient number of radial cracks that initiate at the active particle/matrix interface, as shown in Fig. 3. It should be noted that *a* and *b* denote the radii of the active Li-insertion site and surrounding matrix, respectively. The pressure the Li-ions induce into the active site is taken to be uniform, and is set equal to *p*, while the pressure at the outer boundary of the unit cell is taken to be *q*. It should be noted that this configuration is valid upon maximum Li-insertion, therefore, Δ denotes the maximum expansion of the active sites in the absence of the matrix. Finally, the radii of the radial cracks that form as a result of the continuous charge/discharge cycle are assumed to be equal and their length is $\rho - a$. Since the damage region defined by their length $\rho - a$ may be viewed as supporting only radial stresses (σ_r), all the other stress components vanish ($\sigma_\theta = \sigma_{r\theta} = 0$) inside this zone. This approach is, in fact, similar to that adopted by Dempsey et al. [4] in addressing a similar problem in ice mechanics.

3. Thin film electrodes

In hope of increasing process efficiency and optimizing storage capacity (i.e. Li-intercalation in the negative electrode) significant efforts have been made to prepare anodes that are comprised from thin layers. With this fabrication method it is believed that it will be possible to exceed the electrochemical capacity of bulk anode materials by increasing the amount of Li-insertion sites in the thin film. This has been successfully performed for anodes comprising of tin

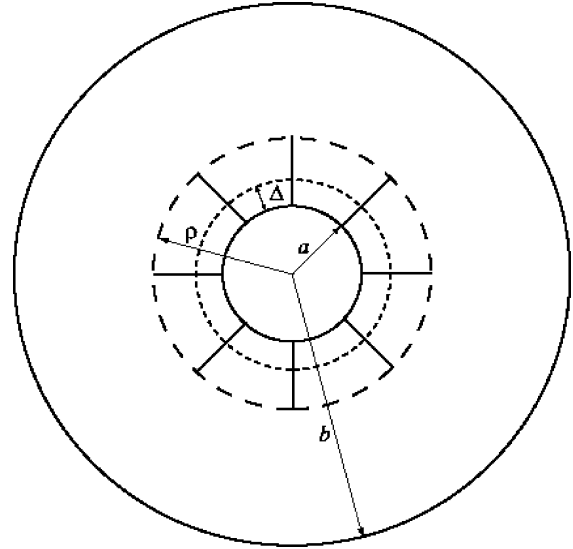Fig. 2. Schematical representation of fracture zone in a single crystal $LiMn_2O_4$ due to nanocrack formation (damaged surface layer).