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Investigation of the mechanical behaviour of lithium-ion batteries by an indentation technique

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ABSTRACT

Indentation is an alternative technique for the measurement of a material's elastoplastic properties. It can be used when the classical tensile test approach is not feasible (thin film, very small components, etc.). This paper presents the results of experiments in which this technique has been exploited to investigate the mechanical properties of the multi-layered structure of lithium-ion batteries with the aim of gaining a better understanding of their mechanical integrity. Indentation tests were performed separately on different layers of a lithium-ion battery using a Berkovich indenter. In order to perform the tests, fused silica substrate (which has well-known mechanical properties) was used to constrain the samples. The elasticity of the anode and the current collectors were obtained from the unloading curve of the measured indentation load–displacement data. Also, the individual stress–strain curves were calculated through reverse engineering of the loading curve. A commercial finite element software (ABAQUS) was used to perform numerical simulations comprising axisymmetric elements representing the Al and Cu foil current collectors. Micro-tensile tests were also carried out on these foils. Agreement was obtained between the outcomes of the micro-tensile and the results of the reverse engineering of the indentation tests. A micro-structure analysis was also performed to give an insight into the structure of the battery components which is necessary for small scale mechanical characterization.

1. Introduction

Energy in the form of electricity can be generated from different renewable sources, such as wind and solar, which have a high potential to meet the growing demand with low emission. The utilization of the generated electricity from these sources requires efficient electrical energy storage and batteries are one of the most appropriate storage system.

A rechargeable Lithium-ion battery consists of two electrodes separated by an electrolyte for ionic conduction. Energy conversion in the lithium-ion (Li-ion) batteries takes place via reversible intercalation/de-intercalation processes of the lithium ions between the electrodes. This kind of battery has become more popular with the growing use of mobile devices and its popularity has been further augmented due to its increasing usage in hybrid electric vehicles. However, three safety issues have an impact on the use of Li-ion batteries: the electrical, thermal and mechanical integrity. The aim of the present paper is to investigate the mechanical properties of the components, thus addressing the third issue.

A Li-ion battery cylindrical cell is composed of layers of electrodes made of coated aluminium and copper foils and a separator, a polymeric component, which is rolled or stacked inside the casing. The coated foils are about 0.1–0.2 mm thick and the uncoated foils (current collectors) have a thickness of 10–13 μm. The number of layers in the battery cells depends on the application.

Generally, when an electrical current is applied to the Li-ion battery in a charging process, lithium ions moves out of the cathode ($LiCoO_2$) and become trapped inside the anode storage medium which is usually graphite. Conversely, during a battery discharge process, the lithium ions travel back to the cathode and produce an electrical current.

The understanding of the mechanical integrity requires a deep insight into the mechanical behaviour of Li-ion battery cells. Different possible scenarios have already been investigated and published in the literature. Sahraei et al. [1] performed tests on pouched and bare lithium-ion cells under five loading conditions such as through-thickness compression, in-plane unconfined compression, in-plane confined compression, hemispherical punch indentation and three-point bending. The individual compression stress–strain curves were calculated from the measured load–displacement data for the active anode

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and cathode materials. In another study Sahraei et al. [2] proposed a simple model of a single cell. This model was developed for the safety assessment of batteries under mechanical abuse conditions. They performed various tests on a 18,650 lithium-ion cell such as indentation by a hemispherical punch, lateral indentation by a cylindrical rod, compression between two flat plates, and three-point bending. However, further studies in the literature focus more on the behaviour of the battery cell as an assembly while the individual mechanical behaviour of the lithium-ion battery components needs more attention.

An indentation test, as an advanced version of a conventional hardness test, is widely used in different structural applications and in various engineering research fields such as automotive and aerospace industries. Since indentation tests can be implemented in a relatively non-destructive manner and provide an array of information about the material under investigation, several studies have been performed to evaluate the behaviour of the materials by this technique. Indentation tests further require a low amount of sample preparation and many research efforts have thus been undertaken to probe the elastic and plastic properties of bulk material with this technique [3–7]. However, when a multi-layer structure is under evaluation, the problem is more complex than for a bulk material because the substrate can influence the indentation load–displacement curve. Its effect depends on several factors: hardness, elastic modulus, and the yield stress of both film and substrate. Different scenarios have already studied such as a film on an elastic or elastoplastic substrate [8–10]. Moreover, several studies measuring the fracture toughness of brittle [11] and of ductile materials [12] have been performed due to its application potential in macro to nanoscales.

In this work we present an indentation approach to individually characterize both coated and uncoated copper current collectors as well as uncoated aluminium current collectors in the Li-ion battery. Specifically, we have studied the mechanical properties of copper and aluminium films on the fused silica substrate. The aluminium/fused silica layered structure is almost elastically homogeneous whereas the copper/fused silica configuration is not. The effect of this elastic modulus mismatch on the indentation properties is taken into account by using Gao's theory. Reverse engineering is adopted through an extensive finite element analysis to define the plasticity of the current collectors. A data comparison in order to validate the novel indentation approach was enabled by conducting micro-tensile experiments on these uncoated films. Furthermore the elastic properties of the anode have been investigated in the cases in which the material of the deposited coating is graphite.

2. Theoretical background

2.1. Indentation on the bulk material

Indentation is a non-destructive method used to investigate the mechanical behaviour of a bulk material. Oliver and Pharr [13] have shown that the elastic modulus of the material can be obtained by analysing the unloading part of a load–displacement curve. The reduced modulus, E^*, has been determined from the measurement of the contact area, A_c, and the compliance term of the specimen which corresponds to the inverse of the unloading slope calculated at the maximum indentation depth, i.e. $C=(dh/dP)_{h=h\max}$, as follows:

$$E^*=\frac{\sqrt{\pi}}{2\beta\alpha\sqrt{A_c}(C-C_f)} \tag{1}$$

The projected contact area (A_c) between the indenter and the material is a function of the contact depth h_c and this parameter, which has to be carefully calculated, is discussed in detail. C_f is the frame compliance of the instrument. β is a correction factor that depends on the indenter shape, where $\beta=1$ for axisymmetric indenters and $\beta=1.034$ for a Berkovich indenter [14].

Considering the fundamental concept of contact mechanics, when two objects (i,ii) are in contact, the indenter and the sample in the indentation test, the relation between the reduced modulus (E^*) of contact and the elastic modulus of two the objects (E_i, E_{ii}) can be expressed as follows:

$$E^*=\left[\frac{1-\nu_i^2}{E_i}+\frac{1-\nu_{ii}^2}{E_{ii}}\right]^{-1} \tag{2}$$

where ν_i and ν_{ii} are the Poisson's ratios of the two objects which are in contact [15].

Generally, in the indentation experiment, deflection of the load frame affects the evaluated reaction force and can be registered by the depth sensor. Therefore, an error proportional to the load is introduced to the displacement reading and the measurement of the instrument compliance is necessary to minimise this error. This correction results in a shift of the indentation load–displacement curve to the left. The compliance of a nanoindenter can be measured by a series of tests at increasing loads on a standard specimen.

Moreover, in order to evaluate the contact area (A_c) and consequently the contact stiffness (S), the geometry of the Berkovich indenter is assumed to be ideal. However, in practice such a perfect indenter can't be manufactured and instead of a perfectly sharp tip, the indenter has a radius. Therefore, for a given contact area, h_c, the actual area is higher than the one based on the perfect sharp tip. The correction factor, α, is usually obtained through a series of tests on a specimen with a known hardness and a Young's modulus. Area correction can be the most important factor and has a significant effect on the accuracy of the results. However, it becomes progressively less important as the indentation depth increases.

In addition, the deformation mode around the indentation is an important factor in the indentation test which affects the calculation of the contact area between the indenter and the sample. In the presence of sinking-in, the Oliver–Pharr method [13] is well-known and widely used where the contact depth (h_c) is calculated from the maximum depth (h_m), the compliance of the indentation instrument (C) and the maximum applied load (P_m):

$$h_c=h_m-\epsilon C P_m \tag{3}$$

where ϵ is a factor which depends of the shape of the indenter. For a flat punch indenter, ϵ equals 1 whereas for spherical and a conical indenter ϵ is equal to 0.75 and 0.72 respectively [13]. In practice, this factor varies between 0.72 and 0.78 due to geometrical imperfections of indenter. In this study, the constant value of 0.75 is used [13].

In the case of a piling-up deformation mode around the indentation the Oliver–Pharr method is not applicable since it underestimates the contact area; therefore Bec et al. [16] have introduced another approach to calculate the contact depth in this mode as follows:

$$h_c=\alpha(h_m-CP_m) \tag{4}$$

where α equals 1.2.

2.2. Indentation on the film

The evaluating of the mechanical properties of the films in a multi-layer structure presents particular challenges. When using instrumented indentation tests the main difficulty in the