Acta Materialia 141 (2017) 39–46

Contents lists available at ScienceDirect

Acta Materialia

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

Full length article

Integrating multi-length scale high resolution 3D imaging and modelling in the characterisation and identification of mechanical failure sites in electrochemical dendrites

Moshiel Biton*, Farid Tariq, Vladimir Yufit, Zhangwei Chen, Nigel Brandon

Department of Earth Science and Engineering, Imperial College London, London, UK

ARTICLE INFO

Article history:
Received 28 February 2017
Received in revised form
2 September 2017
Accepted 4 September 2017
Available online 6 September 2017

Keywords:
Zn-air battery
FIB-SEM tomography
Dendrites
Micromanipulators
Imaging

ABSTRACT

The Zn-air battery system is attractive because of its potentially high power density, environmental compatibility and low-cost materials [1]. This paper is focused on understanding the degradation of Zn air batteries, in particular the evolution of Zn dendrites, one of the main degradation mechanisms. Complementary tomographic techniques allow the direct 3D imaging and characterisation of complex microstructures, including the observation and quantification of dendrite growth. Here we present results from 3D x-ray and FIB-SEM tomography of Zn dendrite formation in a zinc-air battery, down to resolutions of tens of nanometers, enabling analysis of complex micro-structures. This approach is shown to be effective in understanding how electrochemical dendrites grow, and demonstrates that tomography coupled with modelling can provide new insights into dendrite growth in electrochemical systems.

1. Introduction

The Zn-air battery system is attractive because of its high power density, environmental compatibility and low-cost materials [1,2]. The rechargeable zinc electrode is based on the formation of insoluble ZnO in the electrode on discharge, that is reduced to metallic zinc on charging.

In the Zn-air system, when charging, Zn dendrites may grow out from the anode and possibly penetrate the separator, leading to Zn loss and eventually an internal short-circuit when the dendrites reach and contact the cathode. Dendrite growth is not limited to the Zn systems and is one of the failure mechanisms in various Li-ion battery systems as well [3].

In order to improve battery performance it is important to characterise real electrode structures and understand how their 3D structure may affect performance [4]. X-ray and dual focused ion beam and scanning electron microscope (FIB-SEM) technology have been attracting interest in the field of batteries and fuel cells to characterise their electrode structure [4–9].

Yufit et al. recently presented work showing the application of 3D imaging to monitor the growth of multiple dendrites in the Zn-air system [20]. This work focuses on a novel approach for high resolution 3D imaging of a single dendrite, linking this with mechanical in-situ testing and computational modelling to better understand the nature and properties of dendrites formed in the Zn-air battery system.

2. Experimental

A new methodology was developed to capture high resolution 3D images of a single Zn dendrite. This was achieved by cutting a small piece of carbon tape and attaching a single dendrite onto it under a microscope (Fig. 6). The dendrite was then covered with a micro drop of epoxy of a volume of 0.5–20 μl using a micropipette to ensure its mechanical stability during the Zeiss Auriga FIB-SEM slice and view process (Fig. 7). Imaging was carried out using a Ga ion beam of 30 kV with current 20 nA was used to serially section and polish the sample surface while an electron beam captured secondary electron images of the surface. The process was repeated until 300 images were captured to provide a full size dendrite. Image foreshortening and alignment corrections were applied using FEI Avizo Fire 8 and reconstruction of the data.

Prior to modelling, the measured 3D microstructure of the dendrite with the neck connecting to the square base was converted into a volumetric finite-element (FE) mesh using

* Corresponding author.
E-mail address: m.biton13@imperial.ac.uk (M. Biton).

http://dx.doi.org/10.1016/j.actamat.2017.09.008
1359-6454/

Simpleware ScanIP combined with adaptive meshing strategy (Simpleware, Exeter, UK). After meshing, the model was imported into ABAQUS CAE (Dassault Systèmes, France) for static loading simulation. The base of the model was fixed with no displacement or rotation permitted. One of the branches near the top of the dendrite was statically loaded with a point force parallel to the base plane for the simulation of the bending process performed in accompanying micro-mechanical measurements using micromanipulator, Kleindiek Nanotechnik, (Reutlingen, Germany). The in-situ micro bend test was carried out using the MM3A-EM micromanipulator shown in Fig. 10a inside an Auriga 40 FIB-SEM for high resolution imaging simultaneously to the bending test, and is described in detail elsewhere [10,11]. In this study, a mechanical model of a single dendrite is demonstrated; the dendrite is considered as polycrystalline zinc, with a Poisson's ratio of 0.26 and an elastic modulus of 97 GPa [12], with the assumption that the polycrystalline zinc is isotropic, linear and elastic. A maximum principal stress criterion was considered in this study to identify the critical stress, and hence, the critical force required to fracture this particular single dendrite.

3D imaging and tomography of the cell was carried out using GE Phoenix v|tome|x and GE Phenix Nanotom S X-ray micro-CT machines (GE, Boston, USA) X-ray. The electrochemical cell was placed into the X-ray machines for in-operando radiography and 3D tomography experiments.

A new generation of a Zn-air cell was designed to study the early stages of the growth. Dendritic growth was established from a polished Zn tip with a diameter of 200 μm.

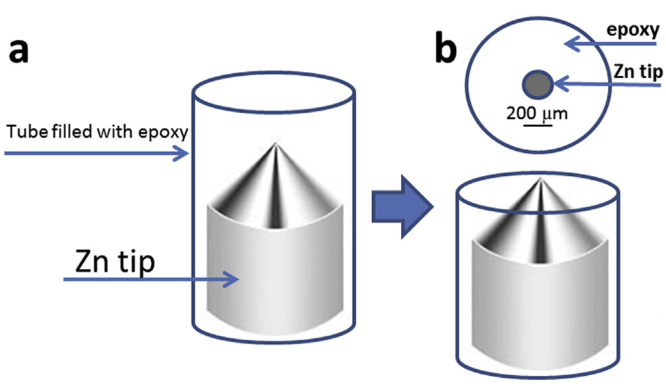

Fig. 1. Schematic illustration of the new cell procedure (a) the original cell is filled with epoxy. (b) Cut and polished - on the top, a plan view of an epoxy surrounded Zn tip, with a diameter of 200 μm, is shown.

The cells were modified and only a small area, 0.0314 mm^2, of the Zn tip took part in the reaction. This enables *in-situ* X-ray imaging experiments and to focus only in a small area, in higher resolution and field of view (FOV) than previous experiments. The modification steps that were taken are shown in Fig. 1. First the cell was filled with epoxy to cover the Zn tip (Fig. 1a), the excess epoxy material above the tip was removed using an Accutom 50 (Struers, Copenhagen, Denmark), and then polished to produce a flat surface with an area of 0.0314 mm^2 and to expose only a small area of the Zn tip.

Since the tip or the active area is much smaller than that of the one in previous experiments (i.e. only a circle with a 100 μm radius compared to the whole tip), 2 mA current was found to be sufficient in order to observe massive dendrite growth, as can be seen in Fig. 4i.

3. Results and discussion

A study of dendrite formation in the Zn-air battery system, which is one of the main degradation mechanisms [13]; was reported previously by Yufit *et al* [20]. SEM images (Fig. 2) of the Zn tip were taken in order to better understand dendrite microstructure in high resolution.

The evolution of the dendrites from the nucleation stage through the entire growth to the full sized dendrite can be seen in Fig. 2a. At the edge of the tip, full sized dendrites are seen. In that location the current density is higher resulting in the highest observed growth rate. X-ray tomography imaging was then carried out to capture the geometry of the dendrites in 3 dimensions and to provide surface to volume ratio and quantitative insight into the shape, size, roughness and network of the dendrites.

Long dendrites grow out from the surface of the bulk Zn tip, with competitive growth in denser regions of dendrites (Fig. 3). Dendrites' arms grow outwards from the main trunk to form branches, which can also display herringbone type needles growing out of them. The final structure after 15 min of charging at 10 mA appears as a dense array of dendrites of various heights, roughly reaching ca.200 μm from the bulk surface.

2 mA current was applied for 15 min in order to observe the different steps of the dendritic growth which are presented in the radiographs in Fig. 4. It is seen from the radiographs shown in Fig. 4 and from the video (supplementary material) that the dendrites are continually growing and do not coalesce.

Supplementary video related to this article can be found at https://doi.org/10.1016/j.actamat.2017.09.008.

As indicated, rather than coalescing growing dendrites form a dense "forest" like microstructure with the presence of free

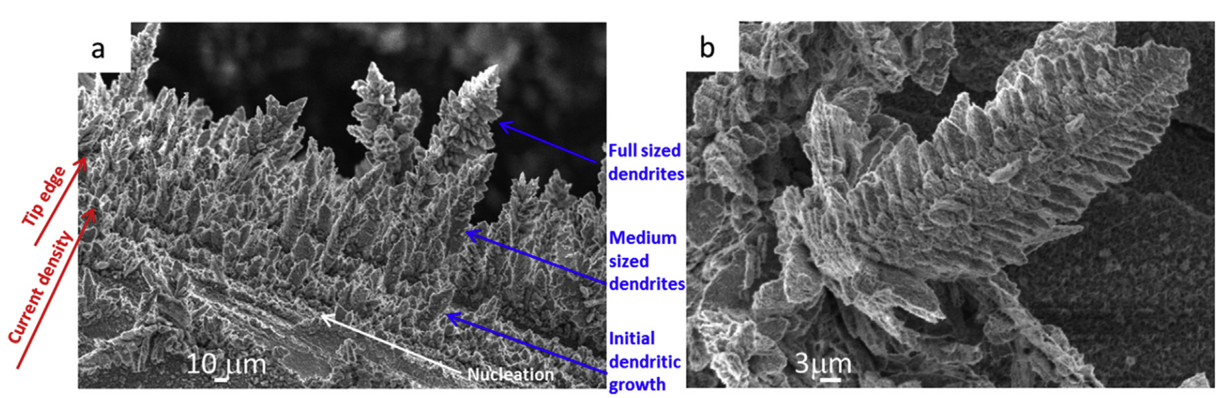

Fig. 2. SE SEM images (a) evolution of Zn dendrite on the Zn anode (b) close-up of single dendrite [14].