

Growth and Evolution of Lead Dendrites during Electrochemical Migration under TEM

Minghua Sun, Kaiyang, Niu, Hong-Gang Liao, Haimei Zheng

Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA USA

Electrochemical deposition of dendritic structures is one of the common factors responsible for the degradation of the performance of lead-acid, zinc-air or lithium-metal batteries. Dendritic growth can result in short-circuit between the two electrodes. It is also a critical failure mechanism in microelectronic packaging. There have been many studies on dendritic growth. However, the crystallization and branching mechanisms remain elusive. Recent development of in situ electrochemical cell transmission electron microscopy (TEM) provides the opportunity to better understand the electrochemical deposition of dendrites^{1,3}. Here, we have developed electrochemical TEM liquid cells with improved resolution and reaction control, which allow tracking the dendrites formation and evolution with great details. Observation reveals unprecedented dynamic information of dendrite shape evolution and branching. The influences of electric field and electrolyte concentration on the dendritic growth were also studied in situ.

FIG 1 shows our homemade electrochemical liquid cell set up and the results of Pb dendritic growth by real time TEM. When an electric field is applied, a needle-shaped trunk grows and then rapidly develops into fork-like branches with sharp tips. One tip gets thicker and the other one remains sharp and continue to split. This kind of tip-splitting propagates and the trunk grows towards the electric field direction. These developed branches are asymmetric which may be caused by non-uniformity of electric field or extremely non-equilibrium electrochemical migration process. Details are shown in Fig. 1b-c.

Based on both in situ and ex situ studies, we have developed a growth model of lead dendrites due to electrochemical migration. FIG 2 shows a schematic diagram of the growth mechanisms of lead dendrites, where the tip of a dendrite is mainly composed of polycrystalline nanograins. With the increasing amount of nanocrystalline grains aggregated on the surface, the grain size becomes larger and the dendrite grows rapidly along axial direction. Meanwhile, reconstruction and coalescence of these polygrains occur and they re-orient to establish epitaxial relation with $\langle 100 \rangle$ dendritic backbone. However, there are two possible processes at the earlier stages of growth: (I) the initiation tip may be polycrystalline and they later re-orient to $\langle 100 \rangle$ direction; (II) the initial nucleation can also be $\langle 100 \rangle$ oriented single crystal and both monomer attachment and aggregated growth proceed in parallel. Further in situ studies will be conducted to elucidate the initial stages of growth.

References

- [1] M. J. Williamson, R. M. Tromp, P. M. Vereecken, R. Hull, F. M. Ross, *Nature Materials* **2**, 532 (2003).
- [2] X. Chen, K. W. Noh, J. G. Wen, S. J. Dillon, *J. Acta Materialia* **60**, 192 (2012).
- [3] E. R. White *et al.*, *ACS Nano* **6**, 6308 (2012).

