

IN APPLICATION

Lithiation-Induced Dilation Mapping in a Lithium-Ion Battery Electrode by 3D X-Ray Microscopy and Digital Volume Correlation

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Introduction

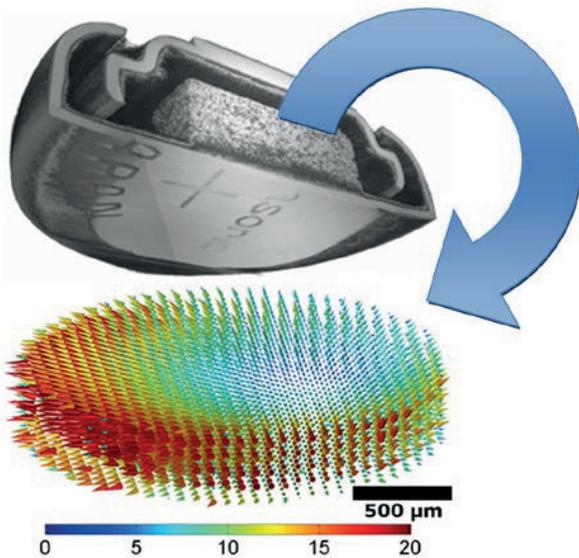


Figure 1 : Cutaway view of the reconstructed image of the battery and vectors showing dilation in the charged state

Microstructural evolution, which can occur during processing and operation, is known to influence the performance and lifetime of energy materials including batteries, fuel cells, super capacitors, hydrogen storage media and photo-catalysts. Whilst the impact of microstructural degradation can be severe, the mechanism of structural evolution at microscopic length scales is often poorly understood due to the difficulty of following such microstructural changes. In the case of batteries, optimization of battery performance can pose conflicting microstructural demands, for example high-rate batteries mandate high volume specific areas for rapid (de-)intercalation of Li⁺ ions, but this requires small grains which reduces the overall battery capacity. In this note quantitative studies of microstructural evolution occurring in a commercial coin cell battery (Panasonic ML414) as a function of battery state of charge are presented, and it is demonstrated how Digital Volume

Correlation (DVC) is enabling new, quantitative insights into these processes.

Changes in the three-dimensional microstructural data is quantified using DVC of time lapse volume images recorded on a laboratory X-ray microscope (Xradia Versa XRM-500), yielding a 4-dimensional (3D + time) analysis through a charge-discharge cycle. This is the first time DVC has been applied to explore in operando the local changes in structure influence battery performance. The volume images acquired had a resolution of 1.25 µm per voxel and one image is shown in Figure 4. DVC parameters utilized 256 x 256 x 256 sub-volume size reducing to 32 x 32 x 32 with 75 % overlap, yielding a grid resolution with 8 pixels steps in three dimensions.



Figure 2 : The Harwell Science and Innovation Campus in Oxfordshire

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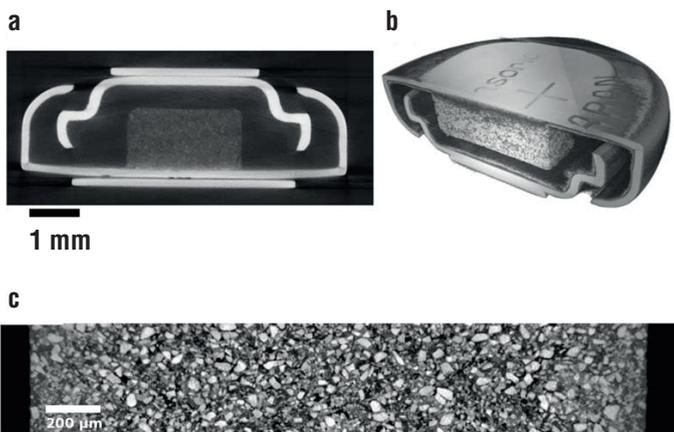


Figure 3: (a) A virtual diametrical slice through battery showing the cell architecture, (b) A cut-away image of the reconstructed cell, showing the manganese oxide cathode attached to the positive (uppermost) battery terminal, and (c) high resolution virtual slice

Results

DVC was used to explore the spatial variation in particle dilation as a function of battery state of charge. In Figure 4 the calculated displacement vectors (overlaid) showed a pre-dominantly uniform 2-3% linear strain directed away from an anchor point of the cathode on the terminal positioned slightly off-centre on the battery casing. After battery discharging, the extent of lithiation of the manganese (III/IV) oxide grains in the electrode is found to be a function of the distance from the battery terminal with grains closest to the electrode/current collector interface having the greatest expansion ($\approx 30\%$) and grains furthest from the current collector and closest to the counter electrode showing negligible dilation. This implies that the discharge is limited by electrical conductivity. For the first time the microstructural evolution processes occurring in a functional complete Li-ion battery have been quantified in-situ in 3 dimensions, providing a unique insight into the relationship between electrode microstructure and cell performance. The dilation of Mn_2O_4 particles as a function of state of charge is found to be dependent upon the distance of individual grains in the electrode from the battery terminal, with grains furthest from the

current collector showing least dilation. In combination with high resolution X-ray microtomography, DVC has allowed a completed analysis and understanding of this complex process. These tools are extremely valuable for studies of this nature and have provided unique insight into the changing relationship between performance and microstructure in battery materials in situ and in operando.

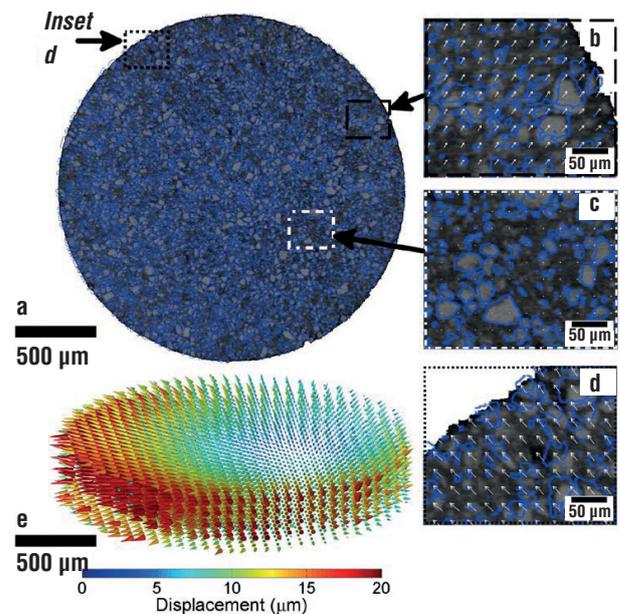


Figure 4: Reconstructed radial slice (grayscale) through the central plane of the cylindrical cathode in the charged state, overlaid in blue with the positions of the Mn_2O_4 grains after battery discharge. Inset figures show the displacement vectors of the grains as determined by DVC.

For further details refer to D.S. Eastwood, V. Yufit, J. Gelb, A. Gu, R.S. Bradley, S.J. Harris, D.J.L. Brett, N.P. Brandon, P.D. Lee, P.J. Withers, and P.R. Shearing, 'Lithiation induced dilation mapping in a Li-ion battery electrode by 3D X-ray Microscopy and Digital Volume Correlation', *Advanced Energy Materials* (2014), article number 1300506, DOI: 10.1002/aenm.201470016