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Tortuosity Anisotropy in Lithium Ion Battery Electrodes Studied by Synchrotron X-ray Tomography

M. Ebner*, D.-W. Chung†, R. E. García†, V. Wood*

*:Dept. of Information Technology and Electrical Engineering, ETH Zurich, 8092 Zurich, Switzerland.
†: School of Materials Engineering, Purdue University, 701 West Stadium Avenue, West Lafayette, IN 47907.

The development of high performance lithium-ion batteries (LIB) for electric vehicle applications demands electrodes with optimized ionic and electronic transport properties to provide cells with high specific energy and power densities.[1] Minimal values for porosity and tortuosity are desirable. The empirical Bruggeman relation $\tau=\varepsilon^{-1/2}$ is widely used to calculate tortuosity from porosity and provides good estimations for homogeneous electrodes, consisting of spherical particles with sufficiently narrow particle size distribution.[2,3] Its applicability to real LIB electrodes has been questioned; however, this has not been experimentally proven due the challenges of imaging three-dimensional electrode microstructure.

We perform synchrotron radiation x-ray tomographic microscopy (SRXTM) at the Swiss Light Source to quantify microstructure of electrodes, fabricated from non-spherical $LiCoO_2$ (LCO) and spherical $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) particles with varying content of nanometer-scale carbon black (CB) and binder (PVDF) after calendaring. The obtained tomography datasets are used as geometric inputs for numerical, three dimensional diffusion simulations to determine tortuosity in direction of compression and parallel to the current collector.[3] We find that electrodes featuring non-spherical active material particles exhibit pronounced tortuosity anisotropy, especially when electrode porosity is reduced by calendaring.

The tortuosity – porosity relation of electrodes featuring spherical particles agrees reasonably well with the Bruggeman relation, and there is no significant anisotropy in the tortuosity between the direction in-plane with the current collector and the direction normal to it. Electrodes fabricated from non-spherical LCO particles, however, show a significant increase in tortuosity in the compaction direction. Because the nanometer-scale carbon black and the polymeric binder cannot be resolved by the used technique, we analyze electrode tortuosity by considering two extreme cases: omitting CB/PVDF contribution and the case of CB/PVDF filling the pore space as a homogeneous network. Although there is a shift in tortuosity between these cases, the degree of anisotropy in tortuosity is virtually unchanged.

In lithium ion batteries, ion transport through porous electrodes is most important in the direction perpendicular to the current collector, so tortuosity in this direction should be carefully minimized. Our results indicate that non-spherical particles tend to align their long axis horizontally during electrode preparation indicating that the use of spherical particles is advantageous.

[1] S. J. Dillon, K. Sun, *Curr. Opin. Solid St. M.* **2012**, 16, 153.
[2] D. A. Bruggeman, *Ann. Phyisk* **1935**, 416, 636.
[3] B. Vijayaraghavan, D. R. Ely, Y.-M. Chiang, R. García-García, R. E. García, *J. Electrochem. Soc.* **2012**, 159, A548.

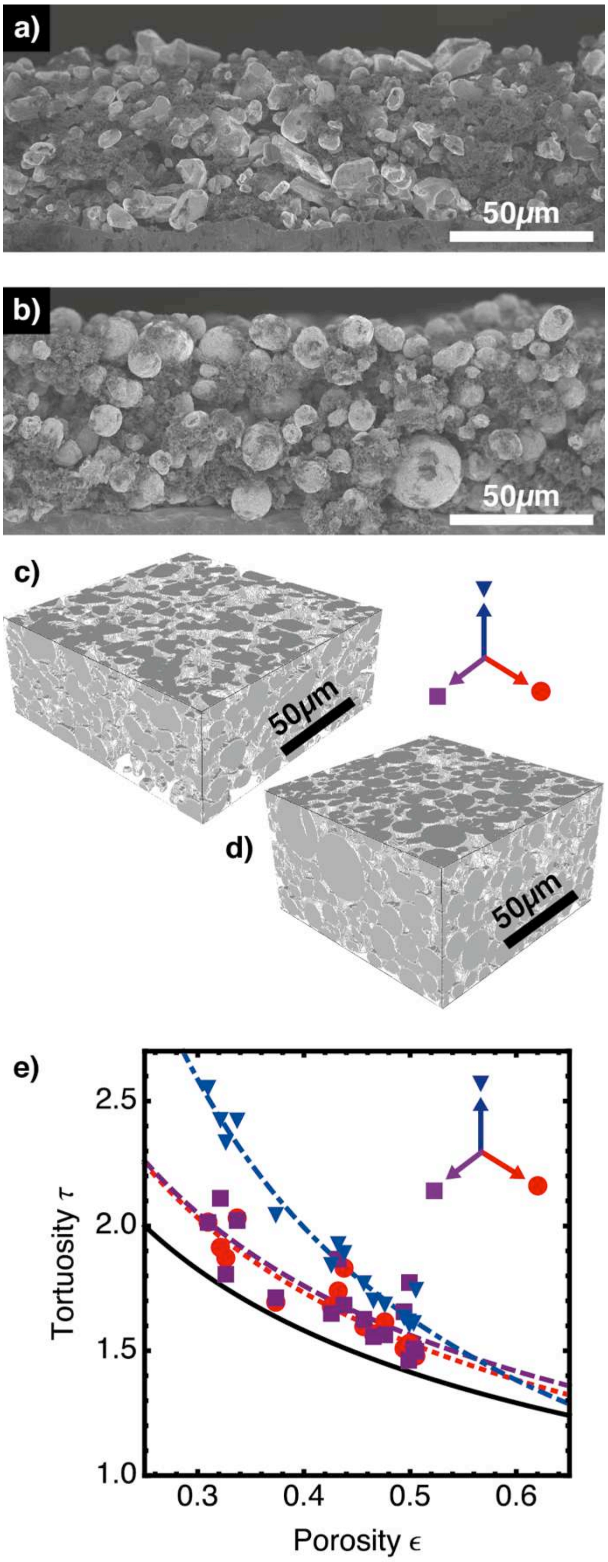

Figure 1: Scanning electron microscopy cross-sections of electrodes fabricated from non-spherical LCO (a) and spherical NMC particles (b). Three-dimensional visualization of electrode microstructure obtained by synchrotron x-ray tomography from LCO (c) and NMC (d) containing electrodes. Directional tortuosity vs. porosity (e) of LCO electrodes, extracted from tomographic microstructure (markers) and least square error fit (broken lines) to $\tau=\beta\varepsilon^{-\alpha}$. The solid black line constitutes the Bruggeman relation, i.e. $\beta=1$, $\alpha=1/2$.