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Rapid, Non-Invasive Method for Quantifying Particle Orientation Distributions in Graphite Anodes

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For materials with 1D or 2D lithiation pathways and non-spherical particle shapes, knowledge of the crystallographic grain orientation in the particle and the active particle orientation in the porous electrode is important for quantifying battery performance. Here we study graphite anodes and show how X-ray diffraction based texture measurements can be used to quantify both the particle orientation, which develops during the coating and calendaring process, and the grain orientation within a specific type of graphite. This lab-based, non-invasive approach to study electrode structure and active particles can assist in engineering improved lithium ion batteries.

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In order to optimize a lithium ion battery, it is important to understand the lithium transport pathways within the active material as well as the lithium transport through the pore space of the electrode, which is governed by the shape and orientation distribution of particles in the electrode. Here, we present X-ray diffraction (XRD)-based texture measurements as a quantitative, non-invasive method to characterize the crystallographic grain orientation of particles and the orientation of these particles within lithium ion battery porous electrodes.

The importance of this structural information is highlighted in the case of graphite, which is the most widely used active material for negative lithium ion battery electrodes. The two-dimensional structure of graphite is responsible for the anisotropy of its electronic, ionic, and thermal conductivity as well as its mechanical properties. For active materials such as graphite that exhibit a preferred orientation at the single particle level, this technique can be used to extract the particle orientation distribution, the grain orientation distribution within the particles, and information about particle deformation and fracture during manufacturing.

Experimental

Measurement setup.—The concept of XRD texture measurements is to obtain the orientation distribution of crystal planes in a sample. To perform a texture measurement, the intensity of X-rays diffracted from a sample at a fixed scattering angle is recorded for all possible orientations. The 2θ angle is chosen to satisfy the Bragg condition of a crystal direction of interest. Here we measure the orientation of (002) planes in a graphite electrode, so 2θ = 26.53° is chosen. Orientation is described by the elevation angle α and an azimuth angle β of the scattering vector k, which is normal to the crystal planes that contribute to the recorded intensity.

Texture measurements can be obtained by either (1) keeping the source and detector fixed to probe the desired 2θ angle and tilting the sample using an Eulerian cradle, or (2) keeping the sample fixed and moving both the source and detector along coupled trajectories. We use the latter approach, which is shown in Figure 1a. The electrode is positioned with the current collector parallel to the xy-plane. This requires an XRD system with an in-plane axis, which allows the detector to rotate out of the xz-plane.

Discrete steps for α and β are chosen. To vary α, the diffraction plane sweeps from being orthogonal to the xy-plane at α = 0° to parallel to the xy-plane at α = 90°. Figure 1 shows the in-plane measurement position at α = 90°, where the diffraction plane is parallel to the sample plane. At each α step, the sample stage is rotated to move the electrode around its surface normal (which is collinear with the z-axis of the goniometer) to allow scanning of β from 0° to 360°. A pole figure is produced by attributing the recorded X-ray intensity to points on a hemisphere defined by a unit vector with α and β and projecting the result stereographically onto the plane (Figure 1b). As described in the SI (part 2), the pole figure is corrected for defocusing, absorption, and background effects. The result is normalized and the intensity is represented in multiples of random distribution (m.r.d.).

An m.r.d. value of 1 corresponds to a random orientation while values higher than 1 indicate a preferred orientation.
Rotationally symmetric samples lead to pole figures with no β dependence. This is the case for the graphite electrodes studied here. In this case, it is convenient to compute the average over β and display the result as a function of the single parameter α (Figure 1b). The m.r.d. value of 11 at α = 0° indicates that the [002] direction is 11-fold more likely to be in the z-direction than for a uniform distribution. This indicates that the (002) planes in graphite are preferentially aligned parallel to the current collector, which is expected from previous investigations using SEM and X-ray tomographic microscopy and can be explained by the alignment of graphite particles with their major axes parallel to the current collector during fabrication.6,10

Deconvoluting particle orientation and grain orientation within particles.—In porous electrodes containing polycrystalline particles, the measured orientation distribution f(α) is a convolution of the particle orientation distribution p(α) and the grain orientation distribution within a single particle g(αp). Here, αp is the elevation angle relative to the particle plane (Figure 2a). This is important for battery grade graphite, where the basal planes exhibit a preferred orientation around the particle pole.24,25 Indeed, both a grain orientation distribution within particles as well as a particle orientation distribution within the electrode can be seen from cross-sectional SEM images (Figures 2b, 2c). Such images, however, are not suited to quantify both of them unambiguously.

From a single texture measurement, the individual distributions that contribute to the pole figure cannot be separated without prior knowledge of either one of the distributions. This would require either (1) tomographic measurements, particle identification, fitting, and identification of major axes, or (2) measurement of the grain distribution on a statistically significant number of particles through single particle XRD.

Here, we show that it is possible to deconvolve both orientation distributions by compressing electrodes from their initial thickness after coating to various thicknesses. By obtaining pole figure measurements on a series of electrodes of different but known thicknesses and assuming that the grain orientation stays constant for each, we are able to uniquely identify both distributions.

Here, the March model26 which was developed to describe fiber textures in rock formations is used to describe the two contributions.

![Figure 1](https://example.com/figure1.png)

**Figure 1.** a) Experimental setup for in-plane pole figure texture measurements. b) Example result on a graphite electrode of the intensity projection onto the plane is depicted in perspective below the setup, with the green to yellow color scale representing increasing multiples of random distribution values. The profile of the overall measured distribution by the pole figure (solid line) is compared with that of uniform distribution (dashed line).

<table>
<thead>
<tr>
<th>Sample</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness d [μm]</td>
<td>135</td>
<td>129</td>
<td>121</td>
<td>115</td>
<td>109</td>
<td>101</td>
</tr>
<tr>
<td>Porosity %</td>
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<td>0.497</td>
<td>0.470</td>
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</tbody>
</table>

For the grain orientation within the particle, the March-Dollase function is chosen, which was developed for volume conserving compression and is implemented in most Rietveld refinement programs as a texture parameter to account for deviating peak heights:27

\[
g(α_p) = \left( r_p^2 \cos^2 α_p + \frac{1}{r_p^2} \sin^2 α_p \right)^{-3/2},
\]

where \(r_p\) is the particle orientation parameter, which can have values between 0 (in the case of single crystals) and 1 (for the case of a uniform grain distribution).

For the particle orientation distribution, we derive a novel, modified March function that approximates uniaxial compression of porous electrodes

\[
p(α) = r_p \left( r_p^2 \cos^2 α + \sin^2 α \right)^{-3/2},
\]

where \(r_p\) is the orientation parameter of the particle distribution. This allows for a change in the sample volume, which occurs in the battery electrodes during calendaring. We demonstrate that this is a valid expression by studying porous electrodes made with particles of boron nitride single crystals (SI, part 3).

The full spectrum of possible distributions from uniform (\(r_p = 1\), \(r_p = 1\)) to perfectly aligned or single crystalline (\(r_p = 0\), \(r_p = 0\)) can be described through a single orientation parameter \(r_p/\sqrt{d}\). Furthermore, the orientation parameter \(r_p\) of the particle orientation distribution can be linked to the thickness \(d\) of the electrode \(r_p = d/d_0\), where \(d_0\) is a virtual thickness at which the particles in the electrode would have a uniform orientation distribution. Since the grain orientation parameter \(r_g\) is constant and the particle orientation parameter \(r_p\) is linked to the measured thickness, there are only 2 fitting parameters (\(r_g\) and \(d_0\)) for a series of multiple electrodes.

The orientation parameter can be expressed as the degree of preferred orientation (i.e., the fraction (in percent) of aligned crystallites or particles) calculated from the respective distribution profile. A definition for the degree of preferred orientation for March-Dollase function was proposed by Zolotoyabko,28 and we adapt it here for the modified March function describing the particle orientation in a porous electrode (SI, part 3).

Figure 2a presents an approach to deconvolute the particle orientation and intra-particle grain orientations for electrodes made from commercially available graphite particles. A slurry is spread by a doctor-blade onto Cu-foil (SI, part 1) such that the electrode has a virtual thickness at which the particles in the electrode would have a uniform orientation distribution. Since the grain orientation parameter \(r_g\) is constant and the particle orientation parameter \(r_p\) is linked to the measured thickness, there are only 2 fitting parameters (\(r_g\) and \(d_0\)) for a series of multiple electrodes.

### Table I. Thickness, porosity, orientation parameter, and degree of preferred orientation for the six electrodes studied in order to deconvolute the intra-particle grain orientation from the particle orientation in the electrode.

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described with \( r_g = 0.285 \) (the corresponding degree of preferred orientation is 61.17%) and \( d_0 = 1086 \mu m \). This solution converges and the error is estimated in SI (part 2). Inserting the measured thicknesses leads to the particle orientation parameters, which are summarized in Table I together with the degree of preferred orientation.

### Results and Discussion

**Grain orientation within graphite particles and their orientation in electrodes.**—In Figures 2d and 2e the peaks in the m.r.d. at \( \alpha = 0^\circ \) of all distributions indicate that graphite particles are aligned parallel to the current collector and that the grain distributions within the particles show a preferred orientation around the particle poles (see inset in Figure 2a). The lower m.r.d. value for the grain orientations in the particle indicate that the intra-particle grains are less well oriented than the particles themselves. With decreasing porosity, the degree of alignment of the particles increases because of the compression forces during the calendaring process.

**Identifying particle deformation.**—To date, it has been difficult to observe the onset and extent of particle deformation or cracking that can occur during electrode calendaring\(^6\); however, texture analysis presents an opportunity. The modified March model predicts that with decreasing electrode thickness (i.e. decreasing porosity), the particles will increasingly align parallel to the current collector, resulting in a larger m.r.d. value at \( \alpha = 0^\circ \). Figure 3 shows that for electrodes compressed to below 40% porosity, the m.r.d. maximum decreases. We explain this by noting that, at low porosities, the graphite particles are not free to reorient during compression. Rather particle-particle interactions can influence the positioning of particles. Indeed, an SEM cross-sectional image inset of the 28% porosity electrode shows a particle bent around two others. The modified March model proposed above assumes a constant grain orientation distribution and an affine transformation (i.e., one in which planes are preserved) and cannot account for this behavior. Therefore, a deviation from linearity of the maximum m.r.d. values of \( f(\alpha) \) as a function of electrode compression can be a robust method to determine at what point in the calendaring process the deformation is dominated by inter-particle interactions. An extreme deviation from the linear model is an indicator that individual particles are deformed or fractured.

**Summary**

We show that texture measurements can be used to rapidly and non-invasively quantify the particle orientation distribution in porous electrodes, the grain distribution within single particles, and the porosity at which particle interactions begin influencing particle packing. This lets us monitor the onset at which particle deformation is likely to occur. We have extended the March model of texture to porous electrodes so that the individual distributions can be reliably described with a single parameter. While the range of applicability of the model will depend on particle shape, material properties, and processing conditions, in general, texture measurements can contribute to understanding morphological anisotropies of various particle systems.

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**Figure 2.** a) The measured orientation distribution (green symbols) and the deconvoluted individual contributions coming from the particles in the electrode (blue line) and the grains in the particle (red line). b,c) SEM images show these individual contributions. d) Orientation distributions for electrodes with porosities ranging from 0.43 to 0.586. The solid green lines are the result of fitting a convolution of the individual orientation distributions. The corresponding particle orientation distributions (blue) and grain orientation distribution with a single particle (red) are shown in e).

**Figure 3.** The maximum of the overall measured pole figure is plotted versus the electrode porosity. The solid green line indicates the predicted maximum. The shaded area marks a 10% error for the grain orientation distribution. At low porosities, the m.r.d. maximum deviates (red circles) from prediction, indicating inter-particle interactions as shown in the SEM.
Acknowledgments
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References