Observation of Lithium Atoms in $LiCoO_2$ Lithium Battery Material by Sub-Ångstrom Electron Microscopy

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Abstract

Sub-Ångstrom TEM of materials is now possible. Techniques of focal-series reconstruction and electron holography are able to retrieve the electron wave at the specimen exit-surface to a resolution limited only by the microscope information limit. SÅ-TEM will become ubiquitous once correction of spherical aberration is widespread. Progress in nanotechology requires that we possess "eyes" to "see" what we build, and HRTEM at sub-Ångstrom resolution has the capability to fill this essential role.

Metal atoms can be routinely imaged in TEM specimens at resolutions from 2Å to 1.5Å, but better resolution (nearer to 1Å) is required to "see" lighter atoms such as oxygen, nitrogen and carbon. Using the LBNL One-Ångstrom Microscope (OÅM), we have followed the successful imaging of carbon atoms in diamond [1] and nitrogen atoms in GaN [2], by investigating the imaging of even lighter atoms in the presence of heavy ones. The OÅM [1] is a combination of a Philips CM300 (modified to extend its information limit and correct for 3-fold astigmatism) with software for reconstruction of the specimen exit-surface electron wave (ESW) from focal-series of images [3,4]. It is capable of 0.78Å resolution [5].

$LiCoO_2$ is one of the most commonly used positive electrode materials in rechargeable lithium batteries. The mechanism of energy storage is based on lithium insertion and extraction from the CoO_2 host structure. Atomic arrangements of lithium ions have a profound effect on the electrochemical performance. The objective of this study was to attempt to atomically resolve the lithium ions.

A series of 20 images was obtained on the OÅM over a defocus range from -3300Å to -2844Å and reconstructed to form an OÅM image (phase of the electron wave at the specimen exit surface) showing all three types of atoms. Image simulations at 0.9Å resolution and 48Å thickness confirm the identification of the atom columns in the experimental image, and show that oxygen atoms appear sharp and bright, Co atoms are bright and fuzzy, and Li atom peaks are weak [6]. Simulations from an artificially de-lithiated model structure, with all of the Li atoms removed, confirm that the weak phase peaks at the Li positions are due to the presence of Li [7].

[1] M.A. O'Keefe et al., *Ultramicroscopy* **89** (2001) 4: 215-241.
[2] C. Kisielowski et al., *Ultramicroscopy* **89** (2001) 4: 243-263.
[3] W.M.J. Coene, A. Thust, M. Op de Beeck & D. Van Dyck, *Ultramicroscopy* **64** (1996) 109-135.
[4] A. Thust, W.M.J. Coene, M. Op de Beeck & D. Van Dyck, *Ultramicroscopy* **64** (1996) 211-230.
[5] M.A. O'Keefe, E.C. Nelson, Y.C. Wang & A. Thust, *Philosoph. Magazine B* **81** (2001) 11: 1861-1878.
[6] Yang Shao-Horn and M.A. O'Keefe et al, *Nature Materials* **2** (2003), 464-467.
[7] Work supported by the Director, Office of Science, through the Office of Basic Energy Sciences, Material Sciences Division, of the U.S. Department of Energy, under contract No. DE-AC03-76SF00098 and National Science Foundation International Research Fellow Award INT-0000429.