

Atomic Resolution of Lithium Ions in LiCoO₂

Yang Shao-Horn^{1,2,*}, Laurence Croguennec², Claude Delmas²,
E. Chris Nelson³ and Michael A. O'Keefe³

¹ Department of Mechanical Engineering, Massachusetts Institute of Technology
77 Massachusetts Ave., Cambridge, Massachusetts 02139, USA

² Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and
Ecole Nationale Supérieure de Chimie et Physique de Bordeaux
Université Bordeaux I

87 av. Dr A. Schweitzer, 33608 Pessac cedex, France

³ Materials Sciences Division, Lawrence Berkeley National Laboratory,
1 Cyclotron Road, Berkeley, California 94720, USA.

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by its trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.

Ernest Orlando Lawrence Berkeley National Laboratory – LBNL-52100

Atomic Resolution of Lithium Ions in LiCoO₂

Yang Shao-Horn^{1,2,*}, Laurence Croguennec², Claude Delmas²,
E. Chris Nelson³ and Michael A. O'Keefe³

¹ Department of Mechanical Engineering, Massachusetts Institute of Technology
77 Massachusetts Ave., Cambridge, Massachusetts 02139, USA

² Institut de Chimie de la Matière Condensée de Bordeaux-CNRS and
Ecole Nationale Supérieure de Chimie et Physique de Bordeaux
Université Bordeaux I

87 av. Dr A. Schweitzer, 33608 Pessac cedex, France

³ Materials Sciences Division, Lawrence Berkeley National Laboratory,
1 Cyclotron Road, Berkeley, California 94720, USA.

Introduction

LiCoO₂ is the most common lithium storage material used as positive electrode in lithium rechargeable batteries. Ordering of lithium and vacancies has a profound effect on the physical properties of Li_xCoO₂ and the electrochemical performances of lithium batteries [1-4]. However, probing lithium ions has been difficult using traditional X-ray and neutron powder diffraction techniques due to lithium's relatively low scattering power compared with those of oxygen and transition metals. We have succeeded in simultaneously resolving columns of cobalt, oxygen, and lithium atoms in layered LiCoO₂ battery material using experimental focal series of LiCoO₂ images obtained at sub-Ångstrom resolution in a mid-voltage transmission electron microscope [5]. Lithium atoms are the smallest and lightest metal atoms, and scatter electrons only very weakly. We believe our observations of lithium to be the first by electron microscopy, and that they show promise for direct visualization of the ordering of lithium and vacancy in transition metal oxides.

Results and Discussions

X-ray powder diffraction refinements showed that the LiCoO₂ sample in this study could be indexed to a hexagonal cell with *S.G.* $R\bar{3}m$ and lattice parameters of $a = b = 2.8138$ Å and $c = 14.052$ Å. In order to estimate the resolution required to resolve lithium ions, we computed a series of images from the LiCoO₂ structure along the [110] direction using the weak-phase object approximation over the resolution range 2 Å to 0.6 Å. As shown in Fig. 1, the lithium ions should be visible at 1.0 Å resolution, and become clearer at 0.8 Å, where all three atom types should be clearly distinguished.

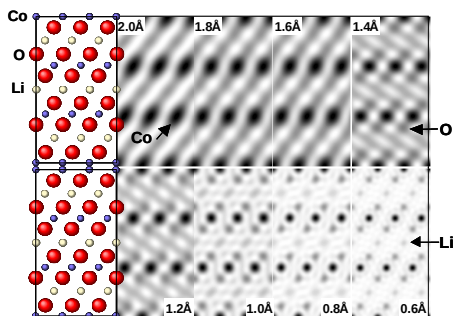


Fig. 1 Lighter atoms need improved resolution. Images of LiCoO₂ in the [110] zone axis simulated under thin-crystal ("weak-phase-object") conditions for increasing resolution (marked) show atoms of cobalt visible at 2 Å resolution, oxygen at 1.4 Å, and lithium at 1 Å.

An exit surface wave (ESW) phase image reconstructed from experimental images of a thin edge of a LiCoO₂ crystal along the [110] zone axis shows all three types of atoms in LiCoO₂ (Fig. 2a). Comparison with a simulated ESW phase image based on a crystal model of 17 unit cells thick (48 Å) at 0.9 Å resolution (Fig. 2b), reveals that all the atom peaks have the characteristics predicted by the simulations and clearly show the positions of all the atom columns over an area of several unit cells. The O-Co-O units can clearly be distinguished in the experimental image, with each fuzzy cobalt peak flanked by a pair of bright oxygen atoms, and the weak spots lying between them can be identified as the electron scattering intensities of the lithium ions (arrowed in both Figs 2a-2b). It is clear that the oxygen atoms lie closer to the cobalt than to the lithium in Fig. 2a, just as in the simulated ESWs (Fig. 2b), providing additional confirmation for our identification of these atom columns [6].

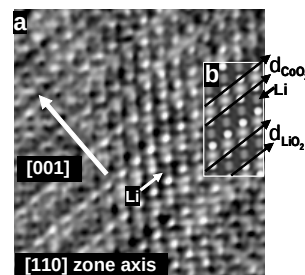


Fig. 2 Experimental image of Li atom columns confirmed by simulation. a, LiCoO₂ ESW-phase image, reconstructed from 20 experimental images, shows lithium ions in rows (arrowed) between O-Co-O groups. b, Insert is ESW-phase simulation for 48 Å thickness and 0.9 Å resolution.

References

- Ohzuku, T. & Ueda, A. *J. Electrochem. Soc.* **141**, 2972-2977 (1994).
- Reimers, J. N. & Dahn, J. R. *J. Electrochem. Soc.* **139**, 2091-2097 (1992).
- Shao-Horn, Y., Levasseur, S., Weill, F. & Delmas, C. *J. Electrochem. Soc.* **150**, A366-A373 (2003).
- Vandervan, A. & Ceder, G. *Electrochemical and Solid State Letters* **3**, 301-304 (2000).
- Shao-Horn, Y., Croguennec, L., Delmas, C., Nelson, E.C. & O'Keefe, M.A. *Nature Materials*, in press July (2003).
- Work partially supported by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.