Atomic Resolution of Lithium Ions in $LiCoO_2$

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Introduction

$LiCoO_2$ 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_xCoO_2 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 $LiCoO_2$ battery material using experimental focal series of $LiCoO_2$ 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 $LiCoO_2$ sample in this study could be indexed to a hexagonal cell with *S.G.* $R\bar{3}m$ and lattice parameters of $\boldsymbol{a} = \boldsymbol{b} = 2.8138$ Å and $\boldsymbol{c} = 14.052$ Å. In order to estimate the resolution required to resolve lithium ions, we computed a series of images from the $LiCoO_2$ 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.

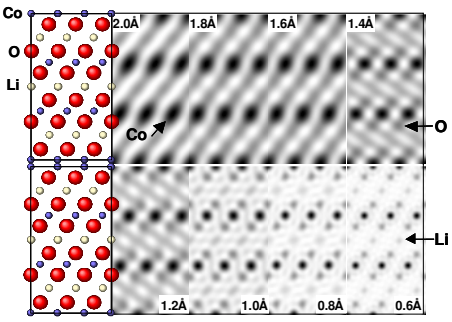

Fig. 1 Lighter atoms need improved resolution. Images of $LiCoO_2$ in the [110] zone axis simulated under thin-crystal ("weak-phase-object") conditions for increasing resolution (marked) show atoms of cobalt visible at 2 Å resolution, oxygen at 1.4 Å, and lithium at 1 Å.

An exit surface wave (ESW) phase image reconstructed from experimental images of a thin edge of a $LiCoO_2$ crystal along the [110] zone axis shows all three types of atoms in $LiCoO_2$ (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].

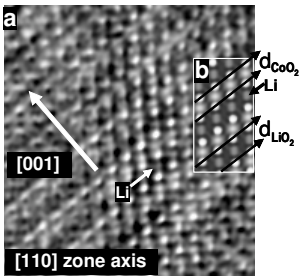

Fig. 2 Experimental image of Li atom columns confirmed by simulation. a, $LiCoO_2$ ESW-phase image, reconstructed from 20 experimental images, shows lithium ions in rows (arrowed) between O-Co-O groups. b, Insert is ESW-phase simulation for 48 Å thickness and 0.9 Å resolution.

References

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