Computational Analysis of Oxygen Vacancies in Li$_2$MnO$_{3-\delta}$

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Introduction

- Layered lithium-excess transition metal oxides xLi$_x$MnO$_2$ (1-xLiMnO) are of great interest as a new generation of positive electrode materials for Li-ion batteries since they deliver higher reversible capacity exceeding 250 mAh/g. The capacity shown below is large compared to the theoretical capacity of LiCoO$_2$ (274 mAh/g), LiMn$_2$O$_4$ (148 mAh/g), and LiFePO$_4$ (170 mAh/g).
- The Li$_x$MnO$_2$ component is initially inactive due to the 4+ classical charge of the Mn ion. The charge/discharge curves of xLi$_x$MnO$_2$ found experimentally show the clear increase in capacity below 4.4V after the first cycle due to the activation of the Li$_x$MnO$_2$ material via the removal of oxygen, as Li$_{1-x}$MnO$_{2.8}$.
- The role of oxygen vacancy on the performance and degradation of this material is still not clear. In fact, even the amount of oxygen vacancy being generated is debated.
- Experimental work by Yu et al. suggests the Li$_{1-x}$MnO$_{2.8}$ component decreases the diffusion coefficient.
- In this study, computational techniques are used to investigate the effect of the oxygen vacancies on:
  - The voltage and capacity of Li$_{1-x}$MnO$_{2.8}$
  - Structural evolution during delithiation of Li$_{2-x}$MnO$_{2.8}$
  - Kinetics of Li$_{1-x}$MnO$_{2.8}$

Computational Details

- The Vienna Ab initio Simulation Package (VASP) was used for both density functional theory (DFT) and ab initio molecular dynamics (AIMD) calculations. All calculations performed on a 2x1x2 supercell containing 16 formula units (96 atoms in total).
- DFT calculations used the generalized gradient approximation with a Hubbard U correction (GGA+U) of 4.84 eV. The energy cutoff used was 550 eV and a k-points mesh of 3x3x3 was determined to be optimal for the Brillouin zone sampling.
- The AIMD runs were carried out with a Nosé thermostat for 50 ps with a time step of 2 fs at 1500 K. Only the f point was used for the Brillouin zone sampling.

Delithiation Calculations:
- Oxygen vacancies in 8j positions have lowest energy.
- 2x1x1 supercell calculations suggested 0 and Li vacancies cluster.
- Lithium atoms were removed near the oxygen vacancies and an additional lithium atom was removed farther away for comparison.
- Open Circuit Voltage (OCV) associated with removal of lithium ions was calculated using lowest energy configuration:

  \[ E_{fli\text{ vacancy}} = E_{Li_{2-x}MnO_{2.8}} + (x_2 - x_1)E_{Li_{metal}} - E_{Li_{2-x}MnO_{2.9}} \]

  \[ OCV = \frac{E_{fli\text{ vacancy}}}{(x_2 - x_1)F} \]  

Location of Vacancies

- White spheres are oxygen vacancies, yellow polyhedral are lithium vacancies.
- Lithium vacancies are most energetically favorable near oxygen vacancies.

Computation OCV Curve

- Most energetically favorable Li$_{1-x}$MnO$_{2.8}$ structures used to calculate OCV.
- Addition of oxygen vacancies increases theoretical capacity.

Molecular Dynamics

Starting system: 1 Li vacancy

Starting system: 1 Li vacancy, 1 O vacancy

Energy Barrier for Li Displacement

- 7 Li atoms “hopped” when no oxygen vacancies were present
- 1 Li atom “hopped” when one oxygen vacancy was present
- Suggests oxygen vacancies hinder lithium diffusion

Conclusions

- O vacancy in 8j position was determined to be energetically more favorable than in the 4i position due to electrostatic energy.
- O vacancies are necessary to lower voltage for Li removal.
- At 1500K we observed hopping of both Li vacancy and O vacancy. Because the Li vacancy tightly bonds with the O vacancy, less Li diffusion was observed in O vacancy containing structures.
- O vacancies increase barrier for Li diffusion.

Acknowledgments

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References