Atomic Mobilities of Li-X-O (X=Co, Ni, Mn) Cathodes and Their Applications

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Abstract: In this paper, the Li-X-O (X=Co, Mn, Ni) cathodes are chosen as the target materials to be investigated. The CALPHAD (CALculation of PHAse Diagram) method, combined with the models of anisotropic diffusion and the diffusion under electrochemical potential gradients, as well as the first-principles calculations, is utilized to develop the atomic mobility descriptions and quantitatively simulate the phase transitions of cathodes during the charging and discharging process, which may provide the important theoretical guidance for the design as well as the property optimization of cathode materials of lithium batteries.

Keywords: Li-X-O (X=Co, Ni, Mn) Cathodes, Atomic mobility, CALPHAD, first-principles calculation

1 Introduction

The cathode materials of lithium batteries determine the electrochemical properties of lithium batteries such as the capacity, voltage and cyclability. The phenomenological study of diffusion kinetics of cathodes is essential for understanding the mechanisms of cathode cyclability affected by the service parameters. So far, it is difficult to utilize a single phenomenological method or first-principles calculation to predict the dynamic relations of "element - composition - structure - electrochemical property" of cathodes due to the limitation of each method.

In this study, the Li-X-O (X=Co, Mn, Ni) cathodes are chosen as the target materials to be investigated. The CALPHAD (CALculation of PHAse Diagram) method [1,2], combined with the models of anisotropic diffusion and the diffusion under electrochemical potential gradients, as well as the first-principles calculations [3], is utilized to develop the atomic mobility descriptions and quantitatively simulate the phase transitions of cathodes during the charging and discharging process.

2 Modeling

The VASP (Vienna Ab-initio simulation package) software package and the NEB (Nudged Elastic Band) method were employed to explore the diffusion barrier of Li ions in cubic spinel $Li_xMn_2O_4$, while the CALPHAD approach was utilized to describe atomic mobilities of different phases in Li-X-O (X=Co, Ni, Mn) cathodes.

3 Result and discussion

The integrated computational approach of materials based on the CALPHAD method and the first-principles calculations has been established. The diffusion model considering the effects of electrochemical potentials and anisotropy and the moving boundary model are built, and the programming is implemented. The codes can obtain atomic mobility descriptions, coupling the thermodynamic database, as well as quantitatively simulate the phase transition process during the charging and discharging process.

The concept of anisotropic atomic mobility [4] based on the CALPHAD method is firstly proposed, and the anisotropic diffusion model is developed. Then, the atomic mobility database of O3 Li-Co-O cathodes is established according to the critically assessed experimental data. After that, the starting times of O3-O3' phase transition changing with the current and crystal orientation during the charging process are simulated. The diffusivity of layered cathodes as a function of crystal orientation, composition and temperature is model-predicted. The simulated results show that the Li-Co-O cathodes have better battery performance as the charging currents are in the range of 7.5~12.5 mA and the crystal orientation θ approaches to zero.

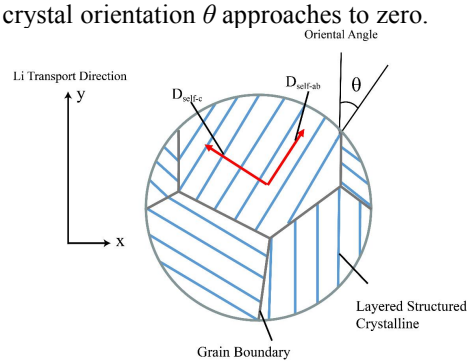

Fig. 1 Schematic diagram of microstructure of O3-layered hexagonal $LixCoO_2$

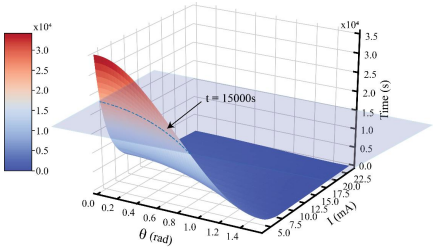

Fig. 2 Schematic diagram of microstructure of O_3-layered hexagonal $LixCoO_2$

The atomic mobility database of O3, O3' and H1-3 phases of Li-Ni-O cathodes are established, and the diffusion kinetics of cathodes is quantitatively simulated. The concentration profiles, phase fractions and moving boundary process during the charging and discharging process are model-predicted. The simulated results show that reducing charging currents within the range of 4.5~15 A/m^2 may avoid the formation of H1-3 phase; when the H1-3 phase formation cannot be prevented considering to realize fast charging process, increasing the charging current slightly can lower the maximum content of H1-3 and O1 phases, and then relieve the capacity face of Li-Ni-O cathodes.

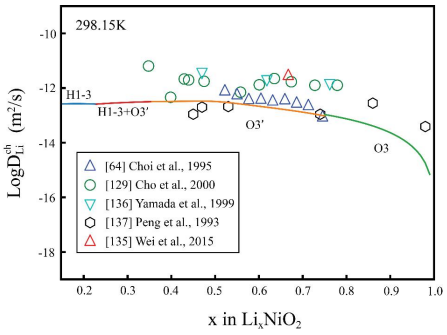

Fig. 3 Calculated chemical diffusion coefficients as a function of compositions at 298.15K based on the Li-Ni-O thermodynamic descriptions and the obtained atomic mobility

Furthermore, the reliable experimental data of diffusivity is firstly filtered, and the atomic mobility database of spinel Li-Mn-O cathodes are established by means of the CALPHAD method and the first-principles calculations, considering the effect of the grain boundaries. Then, the evolutions of $LiMnO_2$ phase fraction, capacity as well as the cell voltage under different current densities and cycles during the discharging process are quantitatively simulated. The electrochemical properties changing with the currents are model-predicted. The simulated results show that larger discharging currents may cause more serious capacity fade, which can be avoided when the current density is in the range of 0~0.367mA/cm^2.

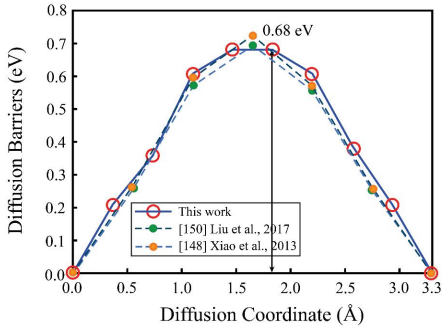

Fig. 4 First-principles calculated diffusion barriers of Li in the spinel LixMn$_2$O$_4$ along the migration pathway of 8a-16c-8a sites in the present work, compared with those in the literature

Conclusion

Accurate atomic mobility descriptions of Li-X-O (X=Co, Mn, Ni) cathodes were established by using the CALPHAD approach together with first-principles calculations. Moreover, the phase transitions of cathodes during the charging and discharging process Li-X-O (X=Co, Mn, Ni) cathodes were quantitatively simulated.

Acknowledgments

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