materials design

APPLICATION NOTE

First-Principles Screening of Cathode Materials

First-principles calculations reveal practical design rules for high-rate battery electrodes. The calculated activation barriers for lithium diffusion indicate that cathodes based on intercalation compounds incorporating Ni^{2+} should show significant improvements over widely used materials such as $LiCoO_2$. Based on guidance from simulation, the new cathode material $Li(Ni_{0.5}Mn_{0.5})O_2$ was synthesized and tested, confirming the predictive capability of atomistic simulation for the discovery and optimization of next-generation battery materials.

Keywords: Intercalation compounds, cathode, lithium ion battery, diffusion, first-principles, computations

Background

There is widespread interest in improving the performance and capacity of Li-ion batteries. Cathodes in these devices normally are composed of an intercalation compound, which has a layered structure of transition metal and lithium layers with alternating oxygen layers. Cathodes for high-power applications require high storage capacity and rapid Li transport rates. Lithium motion within the intercalation compound lattice involves transition between minimum energy octahedral sites by passing through a high-energy transition structure. The

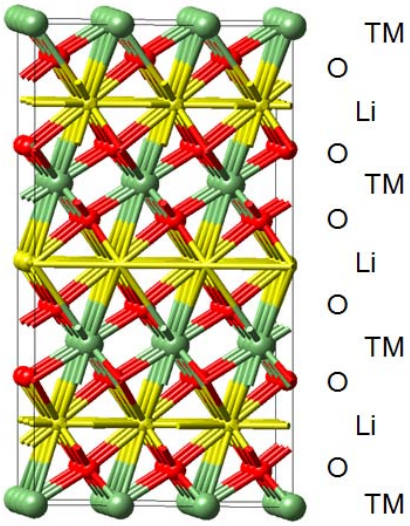

Figure 1. Atomistic structure of lithium / transition metal (TM) intercalation compound ($LiCoO_2$) illustrating the layered structure.

Li transport rate decreases exponentially with the activation energy for Li diffusion. The discovery of strategies to minimize the barrier for Li diffusion can lead to large improvements in Li transport and the rate of charge/discharge for enhanced cathode materials. First-principles calculations were carried out to determine the activation barrier for Li diffusion for various transition metal intercalation compounds informing experiment and allowing the realization of new high-power cathode materials.[1]

Computed Results

The atomistic structure for the lithium/transition metal (TM) intercalation compounds is illustrated in Figure 1. As shown there, intercalation compounds in general have the layered structure, TM:O:Li:O:TM. The minimum energy site for Li in the cathode lattice corresponds to the Li ion in an octahedral configuration. Motion between equilibrium sites involves passing through a tetrahedral configuration which has been shown to roughly correspond to the transition state for Li diffusion in the lattice.[2] Two main factors control the barrier for Li diffusion: 1) the size of the tetrahedral site (strain effect), and 2) electrostatic interactions between Li and the TM in the lattice at the tetrahedral site. Calculations were carried out to evaluate the relative energy of the tetrahedral site, changing the identity of the TM.

The computed activation barriers are presented in Table 1.

Table 1. Calculated Li^+ Diffusion Barriers for Various Transition Metal Intercalation Compounds

Transition Metal	Activation Energy (meV)
Co^{4+}	490
Ni^{4+}	490
Mn^{4+}	340
Ni^{3+}	310
Co^{3+}	310
Cu^{2+}	270
Ni^{2+}	210

These results indicate that intercalation compounds based on low-valent TM such as Ni^{2+} have a significantly lower Li diffusion activation energy and should show improved lithium transport behavior. For Ni^{2+} the predicted Li transport rate would be higher by a factor of ~50 compared to a material like $LiCoO_2$.

With guidance from simulation, the material $Li(Ni_{0.5}Mn_{0.5})O_2$ was synthesized maintaining an ordered structure using ion-exchange methods. In agreement with first-principles predictions, $Li(Ni_{0.5}Mn_{0.5})O_2$ was found to outperform other widely used cathode materials, retaining its energy density at high discharge rates.

Significance

The elucidation of fundamental factors governing the performance of battery materials is a critical step enabling the computational discovery of new materials having enhanced properties. The energetics for the diffusion of atoms in solids can be computed using first-principles methods with high reliability. This opens the door to obtain values for diffusion energetics for systems of varying composition to identify those with the desired energy characteristics. These results can then inform experiment, accelerating the discovery and optimization process for new battery cathode materials, as demonstrated here for the case of lithium nickel manganese oxide.

Methods

The present calculations were performed using the Vienna Ab Initio Simulation Package (VASP).

References

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2. A. Van der Ven and G. Ceder, J. Power Sources **97-98**, 529 (2001).

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