Supplementary Information

Effect of Mg/Al doping at Co site on the structural and electrochemical performance of $LiCoO_2$ cathode materials

Yubai Li, Zheng Wei, Sumei Wu*, Yao Liang, Xiang Liu, Yang Wen, Weiwei Jiang, Tengfei Lu, Yan Cui, Zhihua Zhang*

School of Materials Science and Engineering, Dalian Jiaotong University, Dalian, 116028, P.R. China

To enhance the accuracy of our calculations, we employed the local density approximation (LDA) functional for initial computations and comparisons. The convergence criterion is set at 5.0×10^{-7} eV/ atom and the plane wave cutoff energy is 500 eV. In the optimization process, the iteration is stopped when the maximum force is less than 0.03 eV/ Å, and the $5\times5\times2$ grid Monkhorst-Pack format is adopted to perform k-point sampling integration for the Brillouin Zone (BZ). A Hubbard U correction of 4.9 eV is applied to the Co sites to account for strong electron correlations. We systematically compared the lattice constants and unit cell volumes of $LiCoO_2$ calculated using different exchange-correlation functionals, as shown in Tab. S1. The results indicate that LDA exhibits larger deviations compared to experimental values than the PBE. Based on this comparative analysis, we selected the PBE functional for all subsequent calculations in this study due to its superior accuracy in predicting the structural parameters of $LiCoO_2$.

To accurately describe the electronic structure and other properties of the system, the U - value testing is conducted. The procedure was conducted as follows: First, we referred to relevant literature to determine the testing range of the *U* - value. Taking Co as an example, the testing range of the *U* - value was set from 4.7 eV to 5.1 eV. Subsequently, a computational model consistent with the research system was constructed and the CASTEP module with appropriate computational parameters was set. The *U*-value in steps of Δ*U* (0.2 eV) was gradually changed for calculations. The calculated band gap values of the system under different *U* values are shown in Figure S1.

Table S1 The lattice constants and volumes of $LiCoO_2$ calculated by different functions

System	Lattice parameter (Å)		Volume (Å^3)	Volume change rate（%）
	a	*c*		
Exp-$LiCoO_2$	2.83	14.12	97.936	——
PBE-$LiCoO_2$	2.876	14.255	102.120	4.2%
LDA-$LiCoO_2$	2.805	13.671	93.166	-4.9%

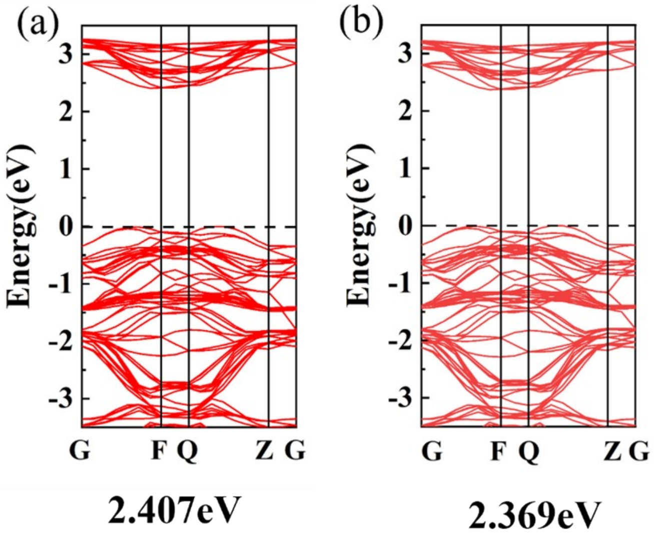

Fig. S1 Band structures of $LiCoO_2$ with different *U* values. (a)*U*=4.7 eV (b)*U*=4.9 eV

Our calculations reveal a clear dependence of the band gap on the Hubbard *U* parameter for the Co 3d orbitals. The calculated band gaps demonstrate a variation with U values: 2.369 eV at U = 4.7 eV and 2.407 eV at U = 4.9 eV. However, the calculation failed to converge when U was increased to 5.1 eV. As reported by Ensling et al.(*Ensling D, Thissen A, Laubach S, et al. Electronic structure of* $LiCoO_2$ *thin films: A combined photoemission spectroscopy and density functional theory study[J]. Physical Review B—Condensed Matter and Materials Physics, 2010, 82(19): 195431.*), the experimental band gap of $LiCoO_2$ is approximately 2.5 eV. Among our tested values, $U = 4.9$ eV yields a band gap (2.407 eV) that shows the best agreement with this experimental reference. Therefore, considering both computational stability and agreement with experimental data, we selected $U = 4.9$ eV as the optimal parameter for all subsequent calculations in this study.