Supporting Information
©XMU and CCS

Surface Structures and Properties of High-Voltage $LiCoO_2$: Reviews and Prospects

Jianjun Fang[a,b] Yuhao Du[a] Zijian Li[a] Wenguang Fan[a,*] Hengyu Ren[a] Haocong Yi[a] Qinghe Zhao[a,*] Feng Pan[a,*]

ACCEPTED

Table S1. The electrochemical performance of surface modulated LCO.

Category	Voltage	Initial coulombic efficiency	Stability	References
Al_2O_3 coating	2.75-4.4	¥	97% at 0.5C after 50 cycles	[1]
	3-4.5	\	73% at 0.5C after 500 cycles	
MgO coating	2.5-4.5	¥	75% at 0.1mA/cm^2 70 cycles	[2]
ZnO coating	2.75-4.5	¥	98.2% at 0.5C after 50 cycles	[3]
TiO_2 coating	3-4.5	¥	86.5% at 1C after 100 cycles	[4]
LATP coating	3-4.5	¥	93.2% at 0.2C after 50 cycles	[5]
LAGP coating	3-4.5	¥	88% at 1C after 400 cycles	[6]
F anions	3-4.6	93.07%	82.5% at 0.5C after 100 cycles	[7]
	3-4.6	\	78% at 0.5C after 500 cycles	[8]
P anions	3-4.6	93.10%	88.6% at 0.5C after 200 cycles	[9]
	3-4.6	95.94%	87% at 1C after 300 cycles	[10]
B anions	3-4.6	¥	95% at 1C after 100 cycles	[11]
	3-4.6	94.93%	94.6% at 1C after 100 cycles	[12]
Se anions	3-4.6	94.60%	72.9% at 1C after 1000 cycles	[13]
S anions	3-4.6	97.72%	77.85% at 1C after 100 cycles	[14]
Co-O Framework	3-4.65	¥	83.2% at 1C after 500 cycles	[15]
	3-4.6	\	96.7% at 0.5C after 100 cycles	[16]
	3-4.6	\	95.2% at 1C after 800 cycles	[17]

ACCEPTED

Table S2. The electrochemical performance of CEI modulated LCO.

Category	Voltage	Initial coulombic efficiency	Stability	References
$Li_4Mn_5O_{12}$ coating	3-4.55	¥	83% at 0.5C after 300 cycles	[18]
Mg-rich surface	3-4.6	¥	78% at 0.5C after 200 cycles	[19]
$LiMg_xNi_{1-x}PO_4$ coating	3-4.7	¥	78% at 0.5C after 200 cycles	[20]
ZrO_2 nano-rivets	3-4.7	¥	78.2% at 1C after 100 cycles	[21]
$Zr_3(PO_4)_4$ coating	3-4.6	¥	91% at 1C after 300 cycles	[22]
LATP coating	3-4.6	¥	88.3% at 0.5C after 100 cycles	[23]
APTES-drived coating	3-4.5	94.8%	79.5% at 0.2C after 100 cycles	[24]
SPTF additive	3-4.65	¥	70.3% at 1C after 300 cycles	[25]
BBSI additive	3-4.6	¥	81.3% at 0.5C after 300 cycles	[26]
F-HTCN additive	3-4.6	¥	72% at 1C after 300 cycles	[27]
DPD-F additive	3-4.6	90%	69.2% at 1C after 200 cycles	[28]
3-TPIC additive	3-4.6	¥	81% at 0.5C after 150 cycles	[29]
LiDFBP+ LiOTFP additive	2.7-4.6	¥	51% at 1C after 1000 cycles	[30]
KSeCN additive	3-4.6	93.6%	70.4% at 1C after 1000 cycles	[31]
AIP additive	3-4.6	¥	97.8% at 1C after 200 cycles	[32]
TMSB additive	3-4.6	97.2%	98.5% at 0.5C after 200 cycles	[33]
IF additive	2.75-4.45	¥	95% at 1/3C after 500 cycles	[34]
DOL additive	3-4.2	95%	80% at 1/3C after 150 cycles at −40 °C	[35]

ACCEPTED

References

[1] Cho J, Kim Y J, Park B. Novel $LiCoO_2$ cathode material with Al_2O_3 coating for a Li ion cell[J]. Chem. Mater., 2000, 12(12): 3788-3791.

[2] Wang Z, Wu C, Liu L, Wu F, Chen L, Huang X. Electrochemical evaluation and structural characterization of commercial $LiCoO_2$ surfaces modified with MgO for lithium-ion batteries[J]. J. Electrochem. Soc., 2002, 149(4): A466.

[3] Shen B, Zuo P, Li Q, He X, Yin G, Ma Y, Cheng X, Du C, Gao Y. Lithium cobalt oxides functionalized by conductive Al-doped ZnO coating as cathode for high-performance lithium ion batteries[J]. Electrochim. Acta, 2017, 224: 96-104.

[4] Zhou A, Lu Y, Wang Q, Xu J, Wang W, Dai X, Li J. Sputtering TiO_2 on $LiCoO_2$ composite electrodes as a simple and effective coating to enhance high-voltage cathode performance[J]. J. Power Sources, 2017, 346: 24-30.

[5] Yang Q, Huang J, Li Y, Wang Y, Qiu J, Zhang J, Yu H, Yu X, Li H, Chen L. Surface-protected $LiCoO_2$ with ultrathin solid oxide electrolyte film for high-voltage lithium ion batteries and lithium polymer batteries[J]. J. Power Sources, 2018, 388: 65-70.

[6] Li Z, Li A, Zhang H, Ning F, Li W, Zangiabadi A, Cheng Q, Borovilas J J, Chen Y, Zhang H, Xiao X, Ouyang C, Huang X, Lee W-K, Ge M, Chu Y S, Chuan X, Yang Y. Multi-scale stabilization of high-voltage $LiCoO_2$ enabled by nanoscale solid electrolyte coating[J]. Energy Stor. Mater., 2020, 29: 71-77.

[7] Mao S, Shen Z, Zhang W, Wu Q, Wang Z, Lu Y. Outside-in nanostructure fabricated on $LiCoO_2$ surface for high-voltage lithium-ion batteries[J]. Adv. Sci., 2022, 9(11): 2104841.

[8] Fan T, Kai W, Harika V K, Liu C, Nimkar A, Leifer N, Maiti S, Grinblat J, Tsubery M N, Liu X, Wang M, Xu L, Lu Y, Min Y, Shpigel N, Aurbach D. Operating highly stable $LiCoO_2$ cathodes up to 4.6 v by using an effective integration of surface engineering and electrolyte solutions selection[J]. Adv. Funct. Mater., 2022, 32(33): 2204972.

[9] Wang X, Wu Q, Li S, Tong Z, Wang D, Zhuang H L, Wang X, Lu Y. Lithium-aluminum-phosphate coating enables stable 4.6 V cycling performance of $LiCoO_2$ at room temperature and beyond[J]. Energy Stor. Mater., 2021, 37: 67-76.

[10] Yang X, Wang C, Yan P, Jiao T, Hao J, Jiang Y, Ren F, Zhang W, Zheng J, Cheng Y, Wang X, Yang W, Zhu J, Pan S, Lin M, Zeng L, Gong Z, Li J, Yang Y. Pushing lithium cobalt oxides to 4.7 v by lattice-matched interfacial engineering[J]. Adv. Energy Mater., 2022, 12(23): 2200197.

[11] Pu W, Meng Y, Wang Y, Ge Y, Li X, Wang P, Zhang Z, Guo Y, Xiao D. Investigation of the $LiBH_4$ modification effect on cycling stability and high-rate capacity of $LiCoO_2$ cathodes[J]. ACS Appl. Energy Mater., 2021, 4(7): 6933-6941.

[12] Chen J, Chen H, Zhang S, Dai A, Li T, Mei Y, Ni L, Gao X, Deng W, Yu L, Zou G, Hou H, Dahbi M, Xu W, Wen J, Alami J, Liu T, Amine K, Ji X. Structure/interface coupling effect for high-voltage $LiCoO_2$ cathodes[J]. Adv. Mater., 2022, 34(42): 2204845.

[13] Fu A, Zhang Z, Lin J, Zou Y, Qin C, Xu C, Yan P, Zhou K, Hao J, Yang X, Cheng Y, Wu D-Y, Yang Y, Wang M-S, Zheng J. Highly stable operation of $LiCoO_2$ at cut-off ≥ 4.6 v enabled by synergistic structural and interfacial manipulation[J]. Energy Stor. Mater., 2022, 46: 406-416.

[14] Du F, Fan Z, Ding L, Wang Y, Shi W, Zhang J, Qu H, Yu X, Chen Y, Zheng J. Surface engineering based on element interdiffusion and interfacial reactions to boost the performance of $LiCoO_2$ cathode material[J]. Chem. Eng. J., 2023, 474: 145952.

[15] Li Z, Yi H, Ren H, Fang J, Du Y, Zhao W, Chen H, Zhao Q, Pan F. Multiple surface optimizations for a highly durable $LiCoO_2$ beyond 4.6 v[J]. Adv. Funct. Mater., 2023, 33(46): 2307913.

[16] Li Y, Zan M, Chen P, Huang Y, Xu X, Zhang C, Cai Z, Yu X, Li H. Facile solid-state synthesis to in situ generate a composite coating layer composed of spinel-structural compounds and Li_3PO_4 for stable cycling of $LiCoO_2$ at 4.6 V[J]. ACS Appl. Mater. Interfaces, 2023, 15(44): 51262-51273.

[17] Li M, Bai F, Yao Q, Wang H, Li P. Double function-layers construction strategy promotes the cycling stability of $LiCoO_2$ under high temperature and high voltage[J]. Electrochim. Acta, 2023, 449: 142197.

[18] Liu J, Wang J, Ni Y, Liu J, Zhang Y, Lu Y, Yan Z, Zhang K, Zhao Q, Cheng F, Chen J. Tuning interphase chemistry to stabilize high-voltage $LiCoO_2$ cathode material via spinel coating[J]. Angew. Chem. Int. Ed., 2022, 61(35): e202207000.

[19] Wang L, Ma J, Wang C, Yu X, Liu R, Jiang F, Sun X, Du A, Zhou X, Cui G. A novel bifunctional self-stabilized strategy enabling 4.6 V $LiCoO_2$ with excellent long-term cyclability and high-rate capability[J]. Adv. Sci., 2019, 6(12): 1900355.

[20] Zhuang Z, Wang J, Jia K, Ji G, Ma J, Han Z, Piao Z, Gao R, Ji H, Zhong X, Zhou G, Cheng H-M. Ultrahigh-voltage $LiCoO_2$ at 4.7 v by interface stabilization and band structure modification[J]. Adv. Mater., 2023, 35(22): 2212059.

[21] Zhang W, Cheng F, Chang M, Xu Y, Li Y, Sun S, Wang L, Xu L, Li Q, Fang C, Wang M, Lu Y, Han J, Huang Y. Surface-interspersed nanoparticles induced cathode-electrolyte interphase enabling stable cycling of high-voltage $LiCoO_2$[J]. Nano Energy, 2024, 119: 109031.

[22] Ye B, Cai M, Xie M, Dong H, Dong W, Huang F. Constructing robust cathode/electrolyte interphase for ultrastable 4.6 V $LiCoO_2$ under -25 °C[J]. ACS Appl Mater Interfaces, 2022, 14(17): 19561-19568.

[23] Wang Y, Zhang Q, Xue Z-C, Yang L, Wang J, Meng F, Li Q, Pan H, Zhang J-N, Jiang Z, Yang W, Yu X, Gu L, Li H. An in situ formed surface coating layer enabling $LiCoO_2$ with stable 4.6 V high-voltage cycle performances[J]. Adv. Energy Mater., 2020, 10(28): 2001413.

[24] Wang F-M, Chemere E B, Chien W-C, Chen C-L, Hsu C-C, Yeh N-H, Wu Y-S, Khotimah C, Guji K W, Merinda L. In situ Co–O bond reinforcement of the artificial cathode electrolyte interphase in highly delithiated $LiCoO_2$ for high-energy-density applications[J]. ACS Appl. Mater. Interfaces, 2021, 13(39): 46703-46716.

[25] Yan Y, Weng S, Fu A, Zhang H, Chen J, Zheng Q, Zhang B, Zhou S, Yan H, Wang C-W, Tang Y, Luo H, Mao B-W, Zheng J, Wang X, Qiao Y, Yang Y, Sun S-G. Tailoring electrolyte dehydrogenation with trace additives: Stabilizing the $LiCoO_2$ cathode beyond 4.6 V[J]. ACS Energy Lett., 2022, 7(8): 2677-2684.

[26] Guo K, Zhu C, Wang H, Qi S, Huang J, Wu D, Ma J. Conductive Li+ moieties-rich cathode electrolyte interphase with electrolyte additive for 4.6 V well-cycled Li||$LiCoO_2$ batteries[J]. Adv. Energy Mater., 2023, 13(20): 2204272.

[27] Yang X, Lin M, Zheng G, Wu J, Wang X, Ren F, Zhang W, Liao Y, Zhao W, Zhang Z, Xu N, Yang W, Yang Y. Enabling stable high-voltage $LiCoO_2$ operation by using synergetic interfacial modification strategy[J]. Adv. Funct. Mater., 2020, 30(43): 2004664.

[28] Sun Z, Li F, Ding J, Lin Z, Xu M, Zhu M, Liu J. High-voltage and high-temperature $LiCoO_2$ operation via the electrolyte additive of electron-defect boron compounds[J]. ACS Energy Lett., 2023, 8(6): 2478-2487.

[29] Liu J, Wu M, Li X, Wu D, Wang H, Huang J, Ma J. Amide-functional, Li_3N/LiF-rich heterostructured electrode eectrolyte interphases for 4.6 v Li||$LiCoO_2$ batteries[J]. Adv. Energy Mater., 2023, 13(15): 2300084.

[30] Zhu Y, Wu D, Yang X, Zeng L, Zhang J, Chen D, Wang B, Gu M. Microscopic investigation of crack and strain of $LiCoO_2$ cathode cycled under high voltage[J]. Energy Stor. Mater., 2023, 60: 102828.

[31] Fu A, Lin J, Zhang Z, Xu C, Zou Y, Liu C, Yan P, Wu D-Y, Yang Y, Zheng J. Synergistical stabilization of Li metal anodes and $LiCoO_2$ cathodes in high-voltage Li // $LiCoO_2$ batteries by potassium selenocyanate (KSeCN) additive[J]. ACS Energy Lett., 2022, 7(4): 1364-1373.

[32] Yang J, Liu X, Wang Y, Zhou X, Weng L, Liu Y, Ren Y, Zhao C, Dahbi M, Alami J, Ei-Hady D A, Xu G-L, Amine K, Shao M. Electrolytes polymerization-induced cathode-electrolyte-interphase for high voltage lithium-ion batteries[J]. Adv. Energy Mater., 2021, 11(39): 2101956.

ACCEPTED

[33] Zhang J, Wang P-F, Bai P, Wan H, Liu S, Hou S, Pu X, Xia J, Zhang W, Wang Z, Nan B, Zhang X, Xu J, Wang C. Interfacial design for a 4.6 v high-voltage single-crystalline $LiCoO_2$ cathode[J]. Adv. Mater., 2022, 34(8): 2108353.

[34] Liu J, Yuan B, He N, Dong L, Chen D, Zhong S, Ji Y, Han J, Yang C, Liu Y, He W. Reconstruction of LiF-rich interphases through an anti-freezing electrolyte for ultralow-temperature $LiCoO_2$ batteries[J]. Energy Environ. Sci., 2023, 16(3): 1024-1034.

[35] Jiang H-Z, Yang C, Chen M, Liu X-W, Yin L-M, You Y, Lu J. Electrophilically trapping water for preventing polymerization of cyclic ether towards low-temperature Li metal battery[J]. Angew. Chem. Int. Ed., 2023, 62(14): e202300238.

ACCEPTED