Joule, Volume *7*

Supplemental information

The promise of high-entropy materials for high-performance rechargeable Li-ion and Na-ion batteries

Wei Zheng, Gemeng Liang, Qiong Liu, Jingxi Li, Jodie A. Yuwono, Shilin Zhang, Vanessa K. Peterson, and Zaiping Guo

Supplemental information

Table S1. Crystal parameters for high entropy battery materials.

	Materials	Space group	*a* (Å)	*b*(Å)	*C* (Å)	V (Å^3)	*α* (°)	*β* (°)	*γ* (°)	Ref.
Cathodes	$LiNi_{0.8}Mn_{0.13}Ti_{0.02}Mg_{0.02}Nb_{0.01}Mo_{0.02}O_2$	*R*-3*m*	2.8962	2.8962	14.28896	103.8	90	90	120	[1]
	$Li_{1.0}[Li_{0.15}Mn_{0.50}Ni_{0.15}Co_{0.10}Fe_{0.025}Cu_{0.025}Al_{0.025}Mg_{0.025}]O_2$	*C*2/*m*	4.94451(9)	8.57307(3)	5.0235(1)	/	90	109.3161(6)	120	[2]
	$Li_{1.3}Mn^{2+}_{0.1}Co^{2+}_{0.1}Mn^{3+}_{0.1}Cr^{3+}_{0.1}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$	*Fd*-3*m*	4.2544	4.2544	4.2544	77.0 04	90	90	90	[3]
	$NaCu_{0.12}Ni_{0.12}Mg_{0.12}Co_{0.15}Fe_{0.15}Mn_{0.1}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$	*R*-3*m*	3.02349(6)	3.02349(6)	16.0893(6)	124.9(2)	90	90	120	[4]
	$Na_{0.6}(Ti_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Ru_{0.2})O_2$	*P*63/*mmc*	2.91455(1)	2.91455(1)	11.13772(9)	81.936 (1)	90	90	120	[5]
	$Na_{3.4}Fe_{0.4}Mn_{0.4}V_{0.4}Cr_{0.4}Ti_{0.4}(PO_4)_3$	*R*-3*c*	8.7158	8.7158	21.7979	1434.05	90	90	120	[6]
	$Na_x(FeMnNiCuCo)[Fe(CN)_6]$	*Fm*-3*m*	10.271(1)	10.271(1)	10.271(1)	1083.4(4)	90	90	90	[7]
Anodes	$Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$	*Fd*-3*m*	4.2330(6)	4.2330(6)	4.2330(6)	75.848	90	90	90	[8]
	$CrNiMnFeCu)_3O_4$	*Fd*-3*m*	8.346(2)	8.346(2)	8.346(2)	581.346	90	90	90	[9]
	$Gd(Co0.2Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})O_3$	*Pbnm* (62)	5.220	5.466	7.589	216.53	90	90	90	[10]
Electrolyte	$Li_7La_3Zr_{0.4}Hf_{0.4}Sn_{0.4}Sc_{0.4}Ta_{0.4}O_{12}$	*Ia*-3*d*	12.94713	12.94713	12.94713	2170.238	90	90	90	[11]
	$Li_3LaPrNdTeWO_{12}$	$Ia\bar{3}d$	12.58487(4)	12.58487(4)	12.58487(4)	1993.18(2)	90	90	90	[12]
	$NaTi_{1/2}Zr_{1/2}Sn_{1/2}Hf_{1/2}P_3O_{12}$	*R*-3*c*	8.6607(2)	8.6607(2)	22.4023(5)	1455.24(7)	90	90	120	[12]
	$LiTi_{1/2}Zr_{1/2}Sn_{1/2}Hf_{1/2}P_3O_{12}$	*R*-3*c*	8.6994(3)	8.6994(3)	21.6289(4)	1417.58(8)	90	90	120	[12]

Table S2. Summary for advantages and disadvantages of high entropy battery materials.

	Structure	Material	Advantages	Disadvantages	Ref.
Cathodes	Layered	$LiNi_{0.8}Mn_{0.13}Ti_{0.02}Mg_{0.02}Nb_{0.01}Mo_{0.02}O_2$	◆ Mitigate phase evolution during electrochemical process ◆ Suppress oxygen loss and cation mixing	◆ Increased fabrication cost due to the involvement of expensive elements	[1]
		$Li_{1.0}[Li_{0.15}Mn_{0.50}Ni_{0.15}Co_{0.10}Fe_{0.025}Cu_{0.025}Al_{0.025}Mg_{0.025}]O_2$	◆ Suppress the low-potential redox couples Mn^{3+}/Mn^{4+} ◆ Reduce the harmful layer-to-spinel phase evolution	◆ Challenging to achieve particle homogeneity at the elemental level ◆ Low initial coulombic efficiency of 85%	[2]
		$NaCu_{0.12}Ni_{0.12}Mg_{0.12}Co_{0.15}Fe_{0.15}Mn_{0.1}Ti_{0.1}Sn_{0.1}Sb_{0.04}O_2$	◆ Delay the phase evolution from O3 to P3 structure	◆ Low specific capacity of 110 mAh g^{-1} ◆ Challenging to achieve particle homogeneity at the elemental level	[4]
		$Na_{0.6}(Ti_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Ru_{0.2})O_2$	◆ Mitigate Na^+/vacancy ordering ◆ Suppress phase evolution from P2 to OP4 phase ◆ Create a percolating diffusion network to enhance rate performance	◆ High cost due to the involvement of expensive Ru element	[5]
		$Na_{0.62}Mn_{0.67}Ni_{0.23}Cu_{0.05}Mg_{0.09-2y}Ti_yO_2$	◆ Stabilize the crystal structure to restrain volume variation and phase transition	◆ Low air stability and easy to absorb water	[13]
	Rock-salt	$Li_{1.3}Mn^{2+}_{0.1}Co^{2+}_{0.1}Mn^{3+}_{0.1}Cr^{3+}_{0.1}Ti_{0.1}Nb_{0.2}O_{1.7}F_{0.3}$	◆ Prevent the formation of a single dominant short-range order to preserve accessible 0-TM percolation of Li transport	◆ Poor cycling performance (~60% after 20 cycles) ◆ Introduce toxic element Cr	[3]
	NASICON	$Na_{3.4}Fe_{0.4}Mn_{0.4}V_{0.4}Cr_{0.4}Ti_{0.4}(PO_4)_3$	◆ Present a stable trigonal phase	◆ Introduce toxic element Cr ◆ Challenging to achieve particle homogeneity at the elemental level	[6]
	Prussian blue	$Na_x(FeMnNiCuCo)[Fe(CN)_6]$	◆ Mitigate phase evolution	◆ Lower specific capacity of 100 mAh g^{-1}	[7]

Anodes	Rock-salt	$Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$	◆ Improve structural stability	◆ High work voltage	[8]
	Spinel	$(CrNiMnFeCu)_3O_4$	◆ Enhance structural stability during cycles	◆ Introduce toxic element Cr ◆ High discharge voltage	[9]
	Perovskite	$Gd(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})O_3$	◆ Increase oxygen vacancies and mesoporous structure to enhance rate and cycling stability	◆ Introduce toxic element Cr ◆ High cost	[10]
Electrolyte	Garnet	$Li_7La_3Zr_{0.4}Hf_{0.4}Sn_{0.4}Sc_{0.4}Ta_{0.4}O_{12}$	◆ Decrease formation temperature ◆ Better reduction stability	◆ High cost ◆ Significant challenges in repetitive technique	[11]
	NASICON/LISICON/garnet	Series of materials	◆ Create a percolation network that enables enhanced ionic conductivity	◆ Increased fabrication cost due to the involvement of expensive elements ◆ Significant challenges in repetitive technique	[12]
	Liquid eletrolyte	Multiple salt in single dimethoxyethane solvent	◆ Decrease the solvation strength ◆ Promote lithium ions diffusion ◆ Facilitate stable interphase passivation layers	◆ Increased fabrication cost due to the involvement of expensive elements	[14]

Table S3. Comparation between high entropy battery materials and corresponding commercial battery materials.

	Material	Synthetic method	Specific capacity (mAh g^{-1})	Retention[a]	Thermal stability	Cost	Ref.
Cathodes	$LiNi_{0.8}Mn_{0.13}Ti_{0.02}Mg_{0.02}Nb_{0.01}Mo_{0.02}O_2$	Co-precipitation and sintering	~205	1000	Better	Middle	[1]
	$Li_{1.0}[Li_{0.15}Mn_{0.50}Ni_{0.15}Co_{0.10}Fe_{0.025}Cu_{0.025}Al_{0.025}Mg_{0.025}]O_2$	Sol-gel and sintering	~260	100	/	Middle	[2]
	$LiCoO_2$	Solid-state sintering	135-150	500-1000	Low	High	[15]
	$LiMn_2O_4$	Solid-state sintering	100-120	500-2000	Better	Low	[15]
	$LiFePO_4$	Solid-state sintering	130-140	2000-6000	Great	Low	[15]
	$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$	Co-precipitation and sintering	155-220	800-2000	Low	Middle	[15]
Anodes	$Mg_{0.2}Co_{0.2}Ni_{0.2}Cu_{0.2}Zn_{0.2}O$	Solid-state and sintering	~650	500	/	Middle	[8]
	$(CrNiMnFeCu)_3O_4$	Hydrothermal and sintering	~600	400	/	High	[9]
	$Gd(Co_{0.2}Cr_{0.2}Fe_{0.2}Mn_{0.2}Ni_{0.2})O_3$	Sol-gel and sintering	~650	500	/	High	[10]
	Graphite	Multiple technique	300-370	>1000	Great	Low	[16]

[a] The retention indicates the cycling numbers provided in the reference.

References

1. Zhang, R., Wang, C., Zou, P., Lin, R., Ma, L., Yin, L., Li, T., Xu, W., Jia, H., Li, Q., et al. (2022). Compositionally complex doping for zero-strain zero-cobalt layered cathodes. Nature, *610*, 67-73.
2. Song, J., Ning, F., Zuo, Y., Li, A., Wang, H., Zhang, K., Yang, T., Yang, Y., Gao, C., Xiao, W., et al. (2023). Entropy stabilization strategy for enhancing the local structural adaptability of Li-rich cathode materials. Adv. Mater., *35*, e2208726.
3. Lun, Z., Ouyang, B., Kwon, D.H., Ha, Y., Foley, E.E., Huang, T.Y., Cai, Z., Kim, H., Balasubramanian, M., Sun, Y., et al. (2021). Cation-disordered rocksalt-type high-entropy cathodes for Li-ion batteries. Nat. Mater., *20*, 214-221.
4. Zhao, C., Ding, F., Lu, Y., Chen, L. and Hu, Y.S. (2020). High-entropy layered oxide cathodes for sodium-ion batteries. Angew. Chem. Int. Ed., *59*, 264-269.
5. Yang, L., Chen, C., Xiong, S., Zheng, C., Liu, P., Ma, Y., Xu, W., Tang, Y., Ong, S.P. and Chen, H. (2021). Multiprincipal component P2-$Na_{0.6}(Ti_{0.2}Mn_{0.2}Co_{0.2}Ni_{0.2}Ru_{0.2})O_2$ as a high-rate cathode for sodium-ion batteries. JACS Au, *1*, 98-107.
6. Li, H., Xu, M., Long, H., Zheng, J., Zhang, L., Li, S., Guan, C., Lai, Y. and Zhang, Z. (2022). Stabilization of multicationic redox chemistry in polyanionic cathode by increasing entropy. Adv. Sci., *9*, e2202082.
7. Ma, Y., Ma, Y., Dreyer, S.L., Wang, Q., Wang, K., Goonetilleke, D., Omar, A., Mikhailova, D., Hahn, H., Breitung, B., et al. (2021). High-entropy metal-organic frameworks for highly reversible sodium storage. Adv. Mater., *33*, e2101342.
8. Sarkar, A., Velasco, L., Wang, D., Wang, Q., Talasila, G., de Biasi, L., Kubel, C., Brezesinski, T., Bhattacharya, S.S., Hahn, H., et al. (2018). High entropy oxides for reversible energy storage. Nat. Commun., *9*, 3400.
9. Patra, J., Nguyen, T.X., Tsai, C.C., Clemens, O., Li, J., Pal, P., Chan, W.K., Lee, C.H., Chen, H.Y.T., Ting, J.M., et al. (2022). Effects of elemental modulation on phase purity and eletrochemical properties of Co-free high-entropy spinel oxide anodes for Lithium-ion batteries. Adv. Funct. Mater., *32*, 2110992.
10. Jia, Y.G., Chen, S.J., Shao, X., Chen, J., Fang, D.-L., Li, S.S., Mao, A.Q. and Li, C.H. (2023). Synergetic effect of lattice distortion and oxygen vacancies on high-rate lithium-ion storage in high-entropy perovskite oxide. J. Adv. Ceram., *12*, 1214-1227.
11. Wang, Q., Zhao, C., Wang, J., Yao, Z., Wang, S., Kumar, S.G.H., Ganapathy, S., Eustace, S., Bai, X., Li, B., et al. (2023). High entropy liquid electrolytes for lithium batteries. Nat. Commun., *14*, 440.
12. Yan. Zeng, B.O., Yang, Jue. Liu, Young-Woon Byeon, Zijian Cai, Lincoln J. Miara, Yan Wang, Gerbrand Ceder. (2022). High-entropy mechanism to boost ionic conductivity. Science, *378*, 1320–1324.
13. Fu, F., Liu, X., Fu, X., Chen, H., Huang, L., Fan, J., Le, J., Wang, Q., Yang, W., Ren, Y., et al. (2022). Entropy and crystal-facet modulation of P2-type layered cathodes for long-lasting sodium-based batteries. Nat. Commun., *13*, 2826.
14. Jung, S.K., Gwon, H., Kim, H., Yoon, G., Shin, D., Hong, J., Jung, C. and Kim, J.S. (2022). Unlocking the hidden chemical space in cubic-phase garnet solid electrolyte for efficient quasi-all-solid-state lithium batteries. Nat. Commun., *13*, 7638.
15. Future Intelligence Unit. Lithium cathodes industry report: lithium manganese iron

phosphate and high nickel oxdies are still the main direction. https://www.vzkoo.com/document/20220827961d426d3633c591dc42ecb6.html.

16. SOHU. Lithium anodes industry report. https:// www.sohu.com/a/607470099_121127986.