

Supporting Information for

Facet-Controlled $\text{LiMn}_2\text{O}_4/\text{C}$ as Deionization Electrode with Enhanced Stability and High Desalination Performance

Yuxin Jiang¹, Liyuan Chai^{1,2,3}, Dehe Zhang⁴, Fangping Ouyang^{4,5}, Xiangyuan Zhou¹, Sikpaam I. Alhassan¹, Sailin Liu⁶, Yingjie He¹, Lvji Yan¹, Haiying Wang^{1,2,3,*}, and Wenchao Zhang^{1,2,3,*}

¹School of Metallurgy and Environment, Central South University, Changsha 410083, P. R. China

²Chinese National Engineering Research Center for Control and Treatment of Heavy Metal Pollution, Changsha 410083, P. R. China

³Water Pollution Control Technology Key Lab of Hunan Province, Changsha 410083, P. R. China

⁴School of Physics and Electronics, Hunan Key Laboratory for Super-Microstructure and Ultrafast Process, and Hunan Key Laboratory of Nanophotonics and Devices, Central South University, Changsha 410083, P. R. China

⁵State Key Laboratory of Powder Metallurgy, and Powder Metallurgy Research Institute, Central South University, Changsha 410083, P. R. China

⁶School of Chemical Engineering and Advanced Materials, Faculty of Sciences, Engineering and Technology, The University of Adelaide, Adelaide 5005, Australia

*Corresponding authors. E-mail: haiyw25@csu.edu.cn (Haiying Wang), wenchao.zhang@csu.edu.cn (Wenchao Zhang)

S1 Supplementary Figures and Tables

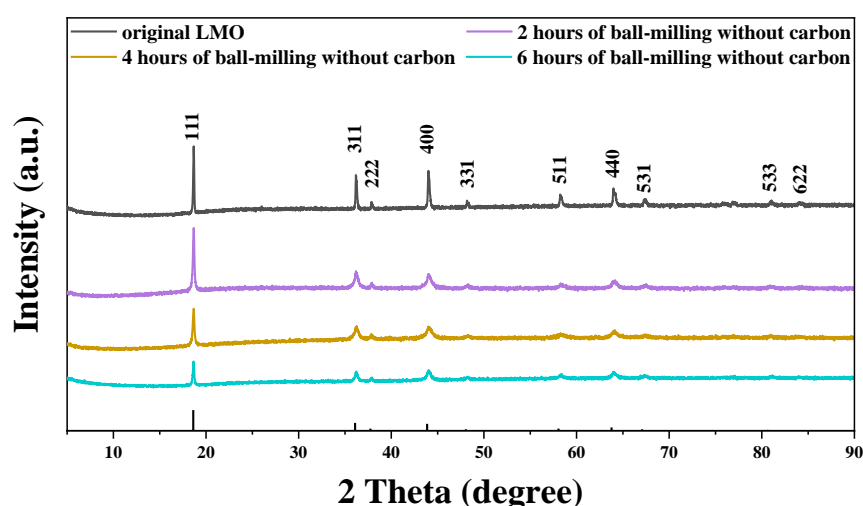


Fig. S1 Comparison of X-ray diffraction (XRD) patterns of LMO after the ball-milling processes of different time lengths without incorporation of carbon

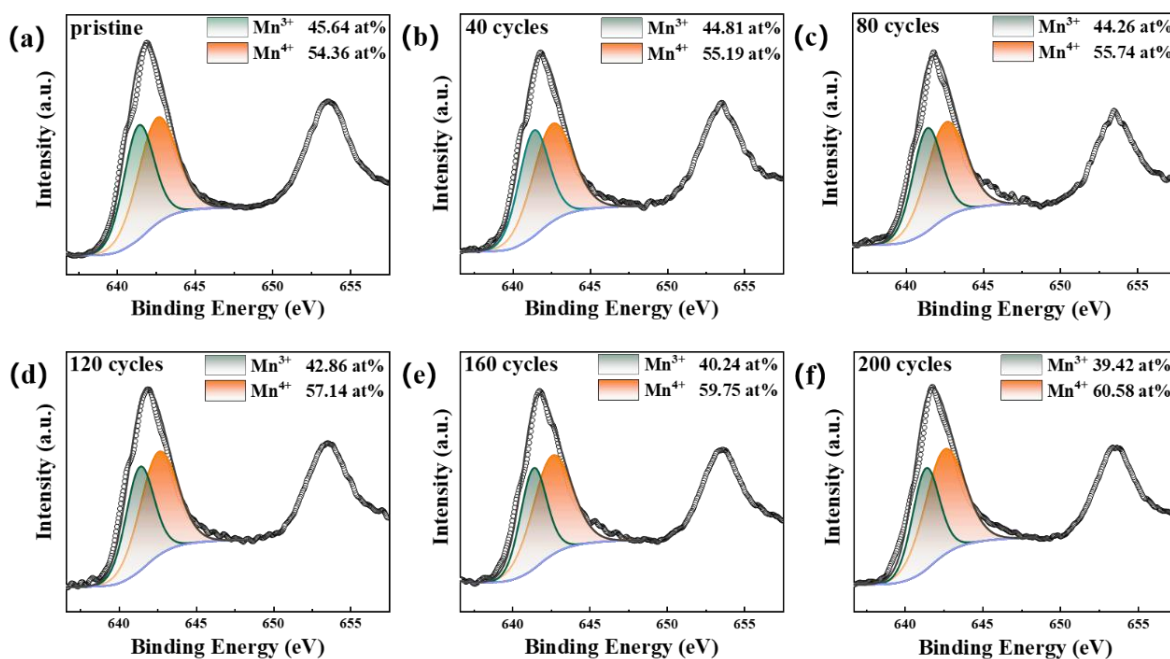


Fig. S2 X-ray photoelectron spectroscopy (XPS) results of Mn2p of original LMO during the cycling tests in 10 mM LiCl solution

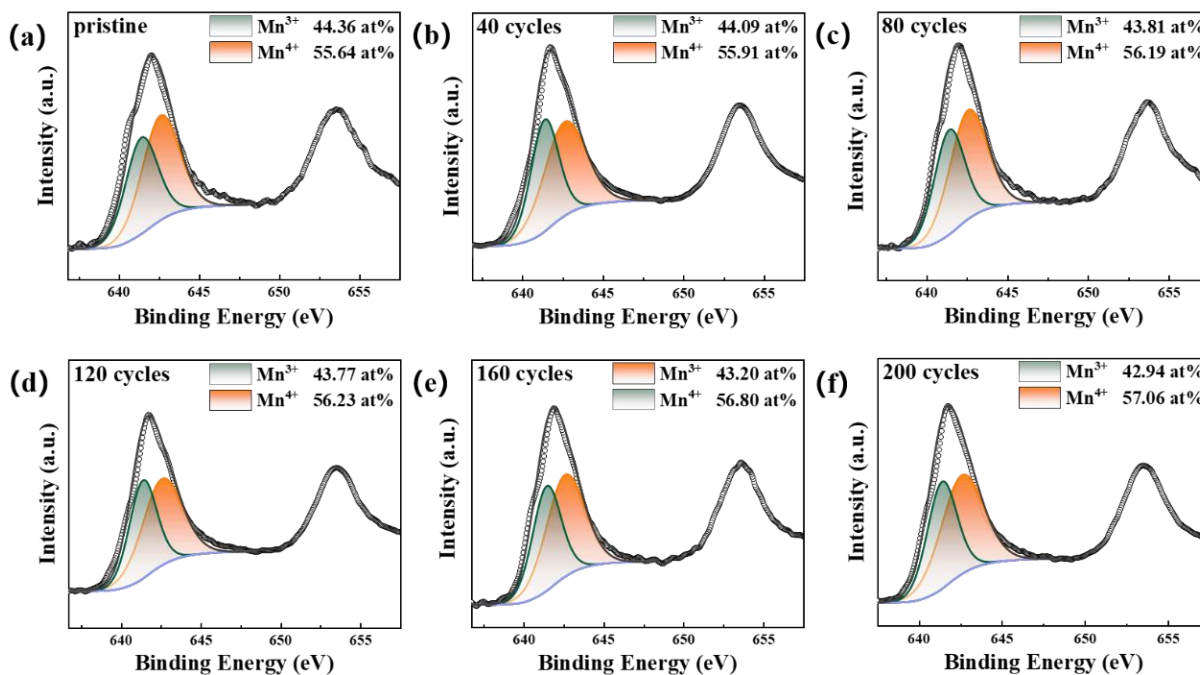


Fig. S3 XPS results of Mn2p of LiMn₂O₄/C during the cycling tests in 10 mM LiCl solution

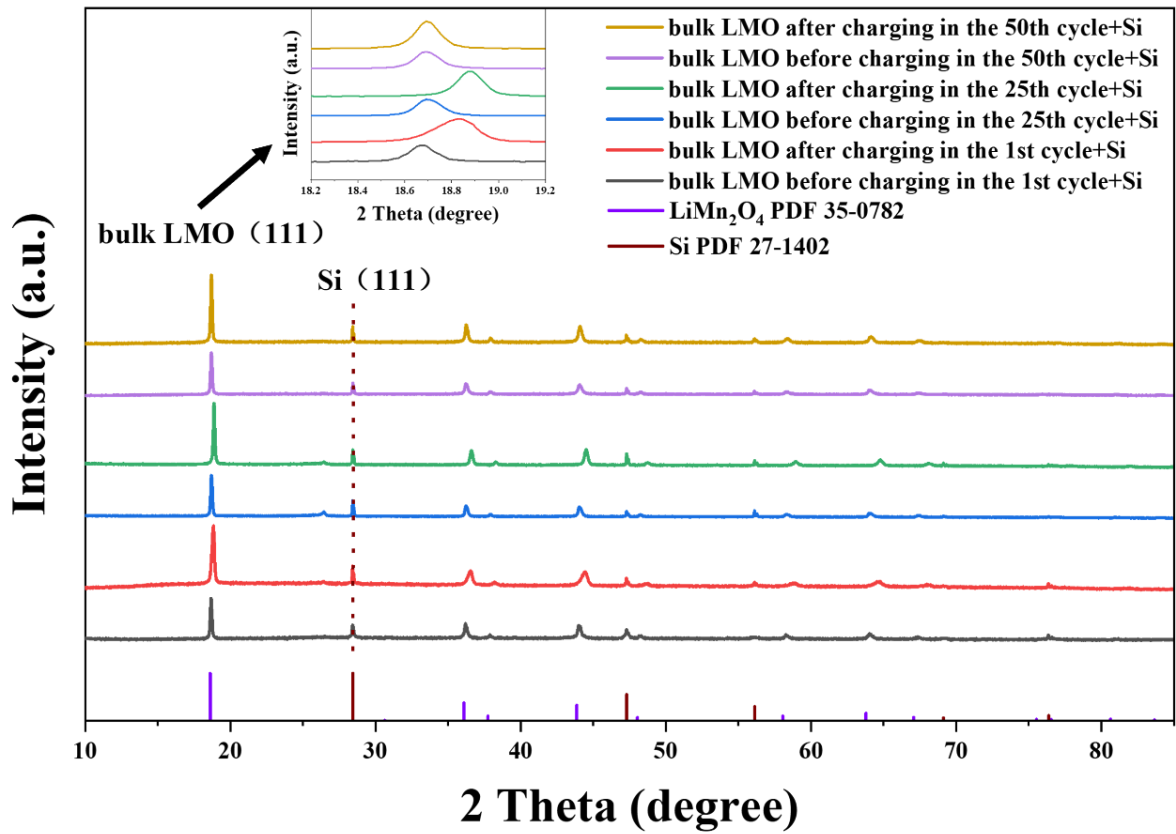


Fig. S4 XRD patterns of the of bulk LMO before and after charging in different cycles (in 1.0 M LiCl solution) mixed with silicon powder

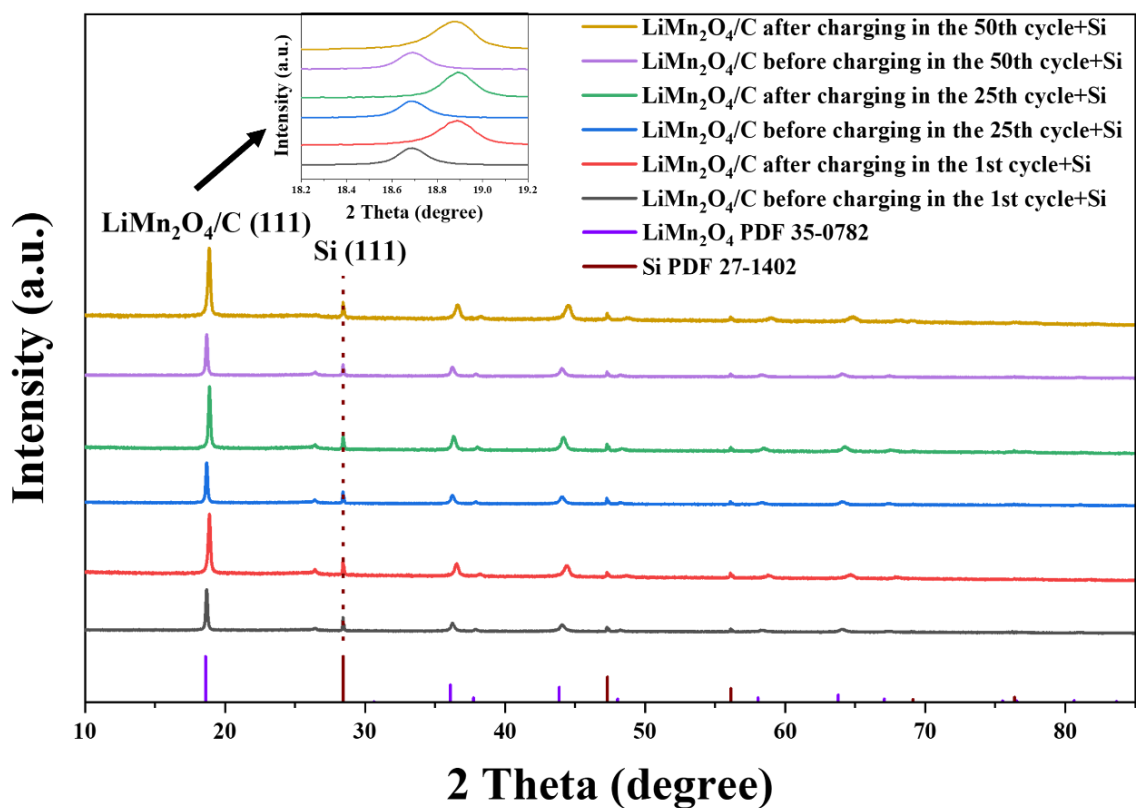


Fig. S5 XRD patterns of $\text{LiMn}_2\text{O}_4/\text{C}$ before and after charging in different cycles (in 1.0 M LiCl solution) mixed with silicon powder

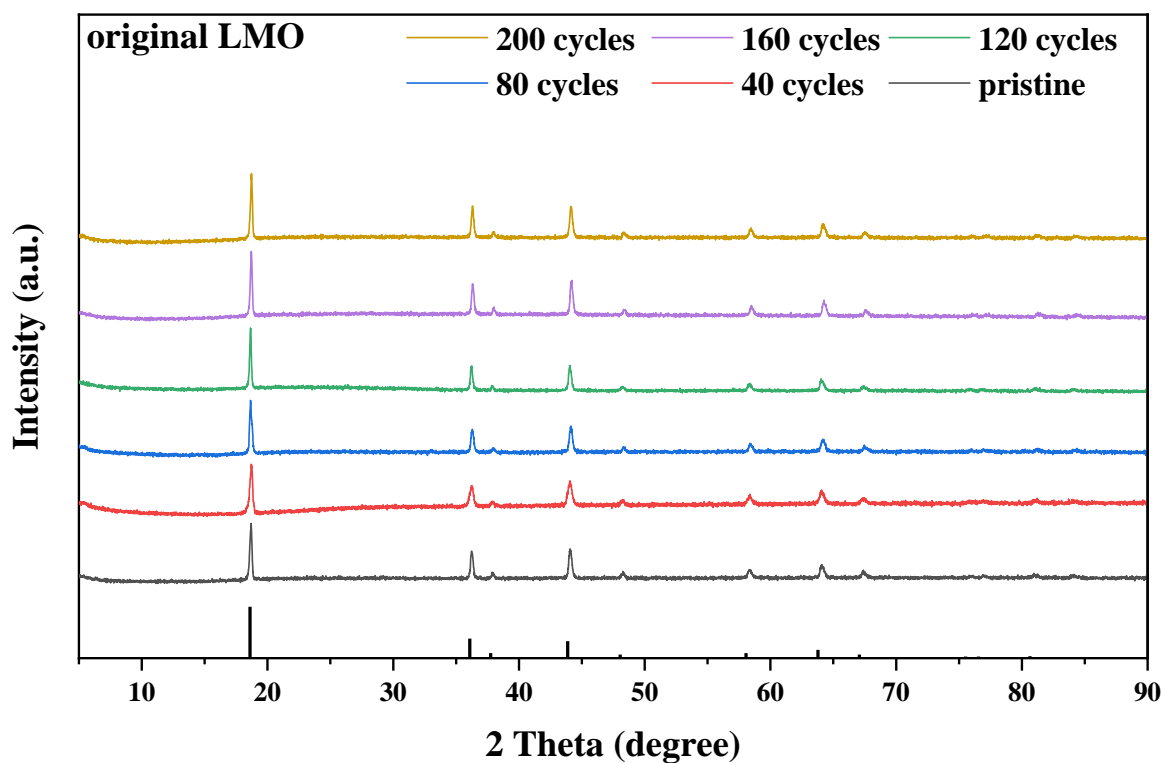


Fig. S6 XRD patterns of LMO during the cycling tests in 10 mM LiCl solution

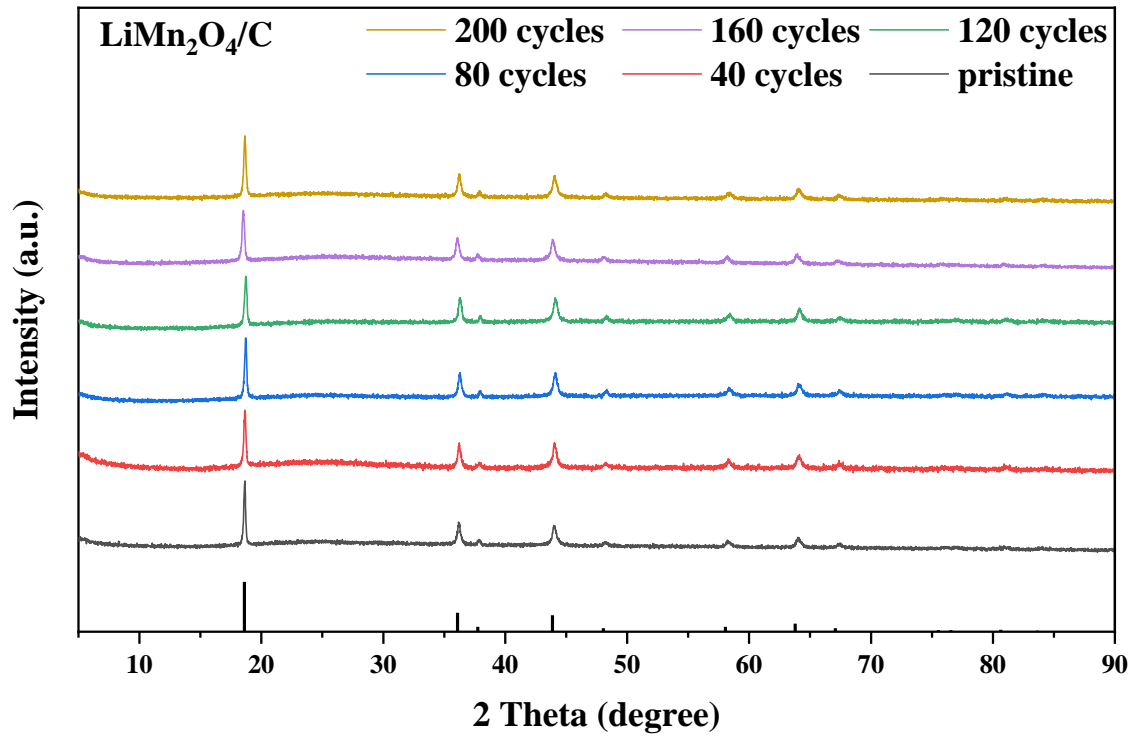


Fig. S7 XRD patterns of $\text{LiMn}_2\text{O}_4/\text{C}$ during the cycling tests in 10 mM LiCl solution

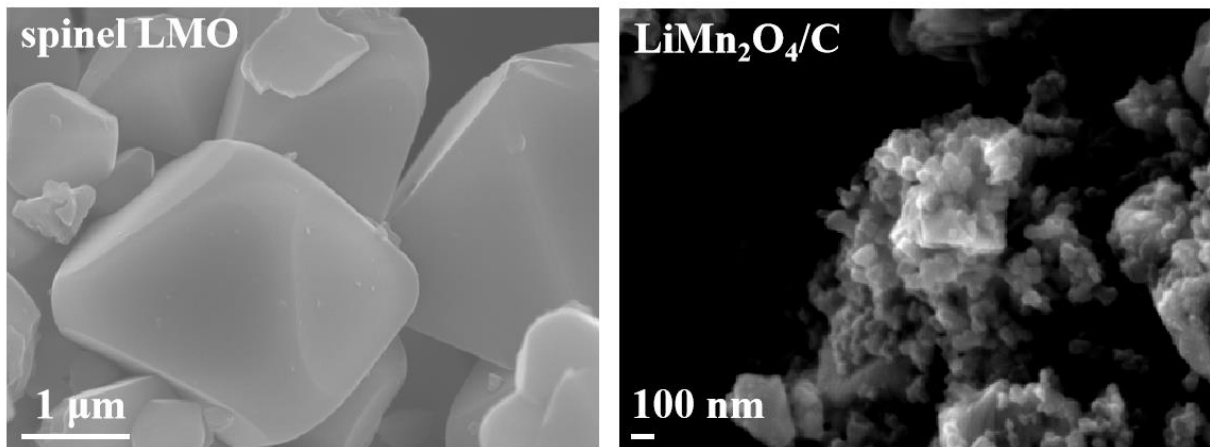


Fig. S8 Scanning electron microscope (SEM) images of LMO and $\text{LiMn}_2\text{O}_4/\text{C}$

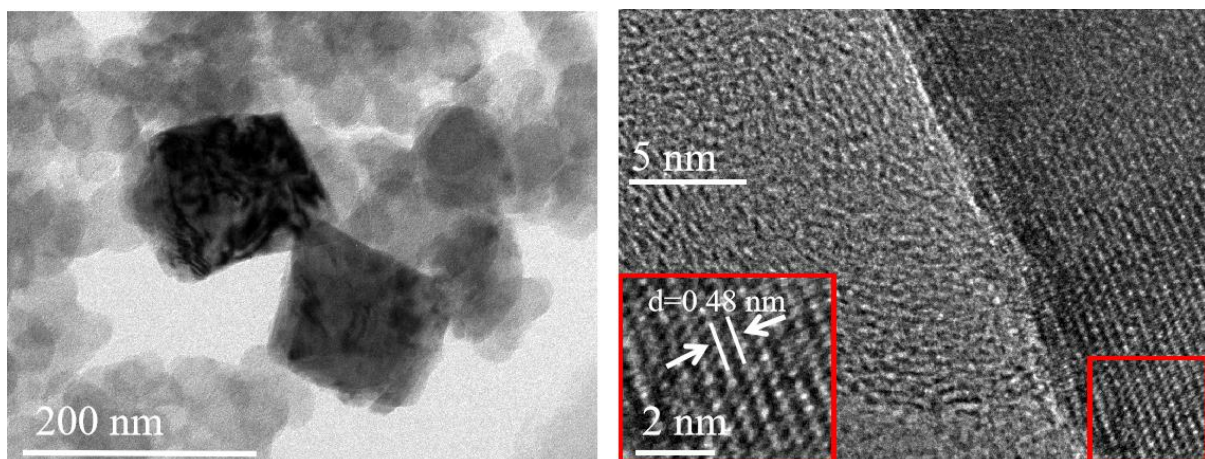


Fig. S9 Transmission electron microscope (TEM) images of $\text{LiMn}_2\text{O}_4/\text{C}$

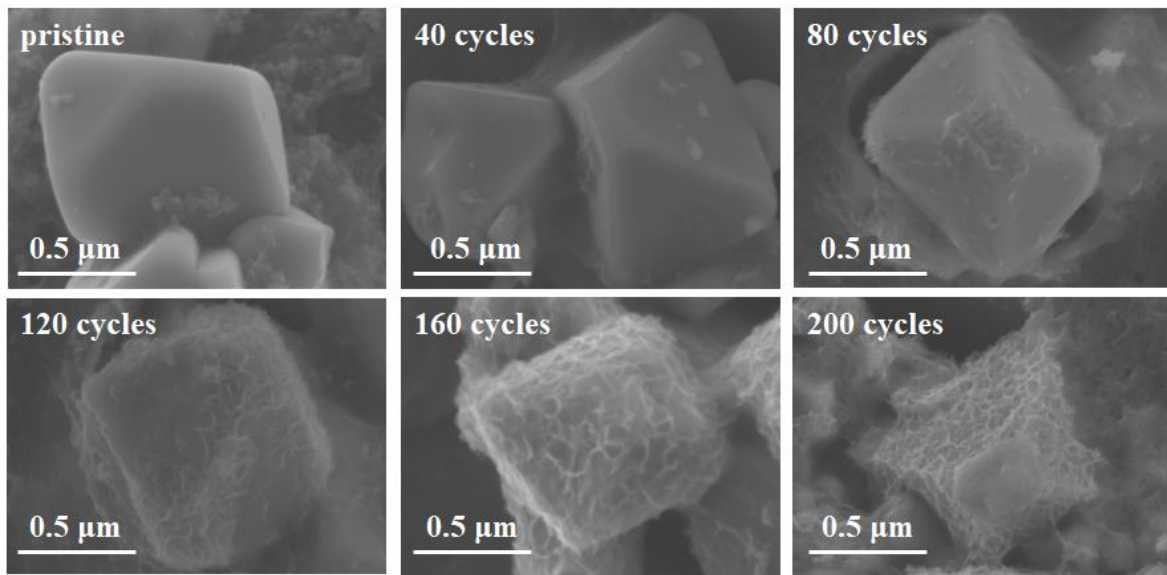


Fig. S10 SEM images of LMO during the cycling tests in 10 mM LiCl solution

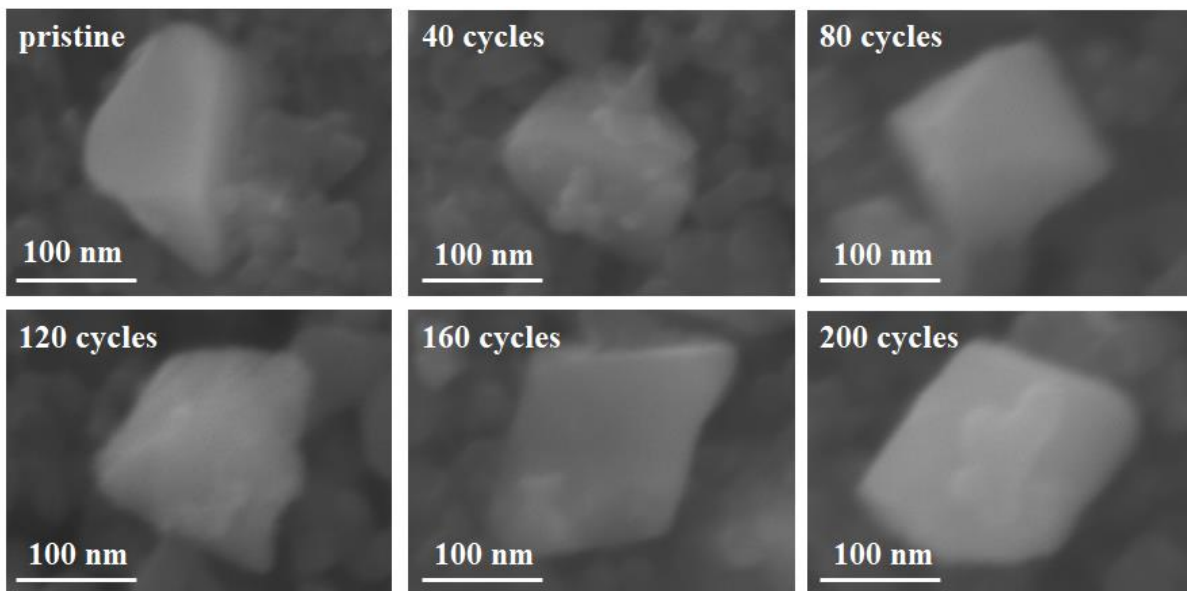
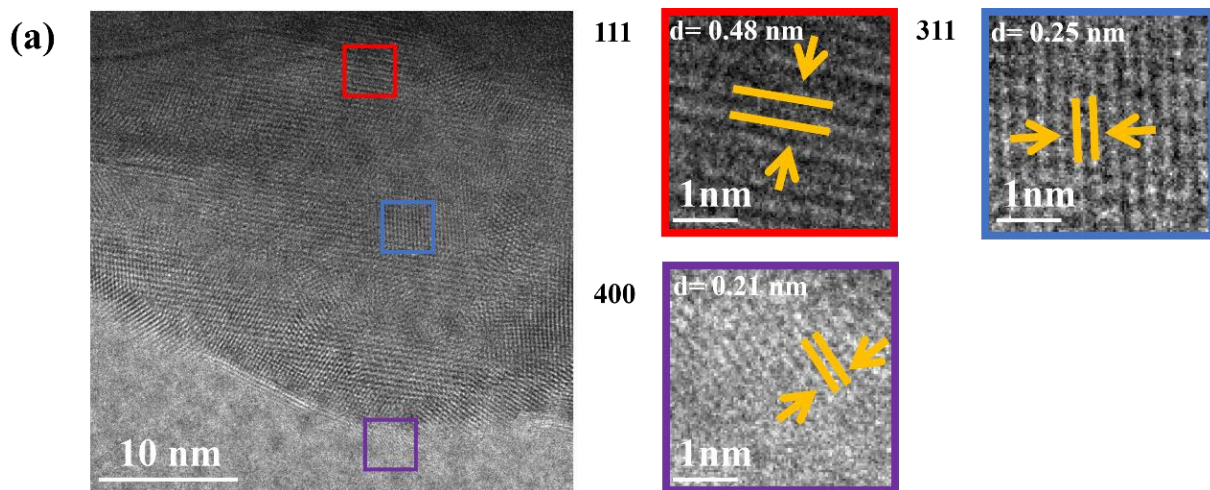


Fig. S11 SEM images of LiMn₂O₄/C during the cycling tests in 10 mM LiCl solution



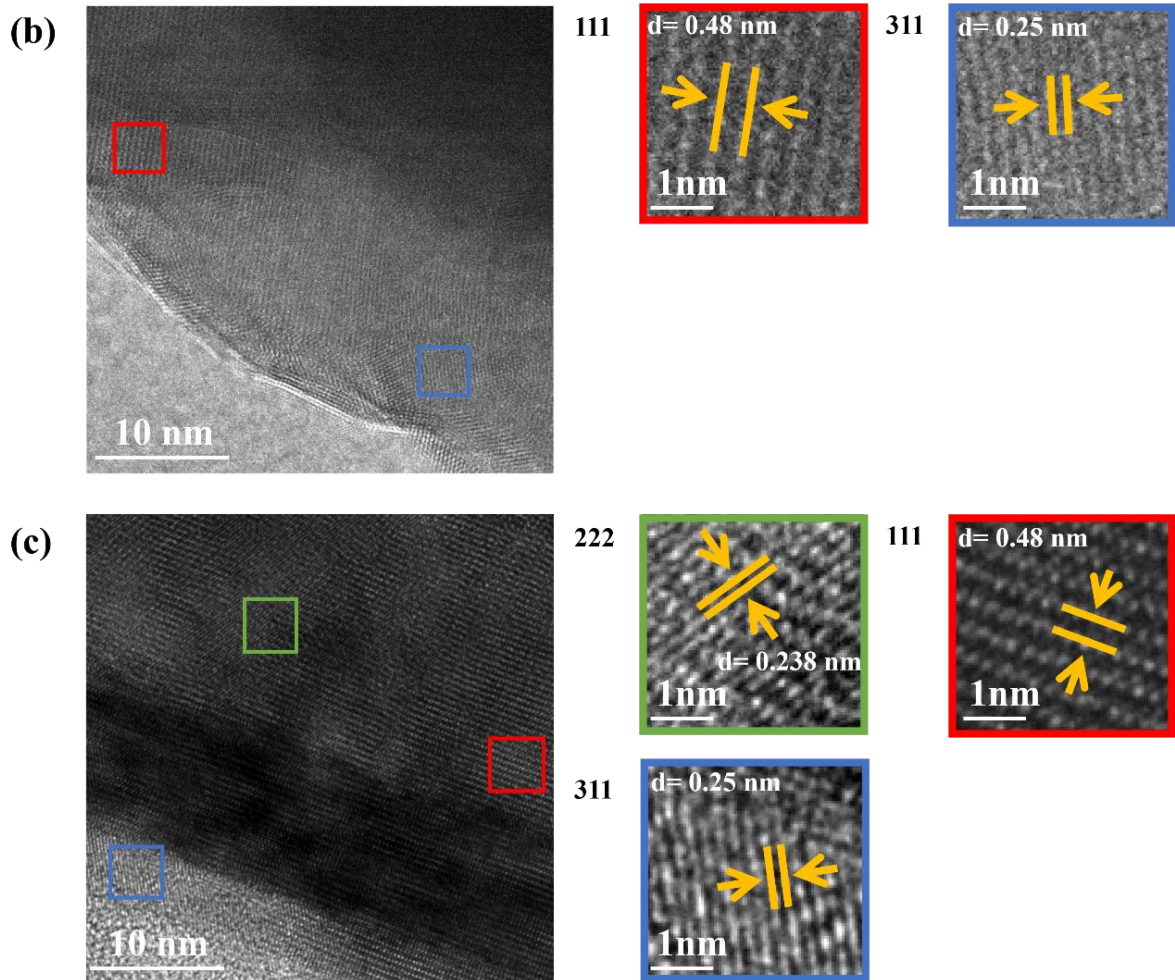


Fig. S12 TEM images of LMO crystal surfaces

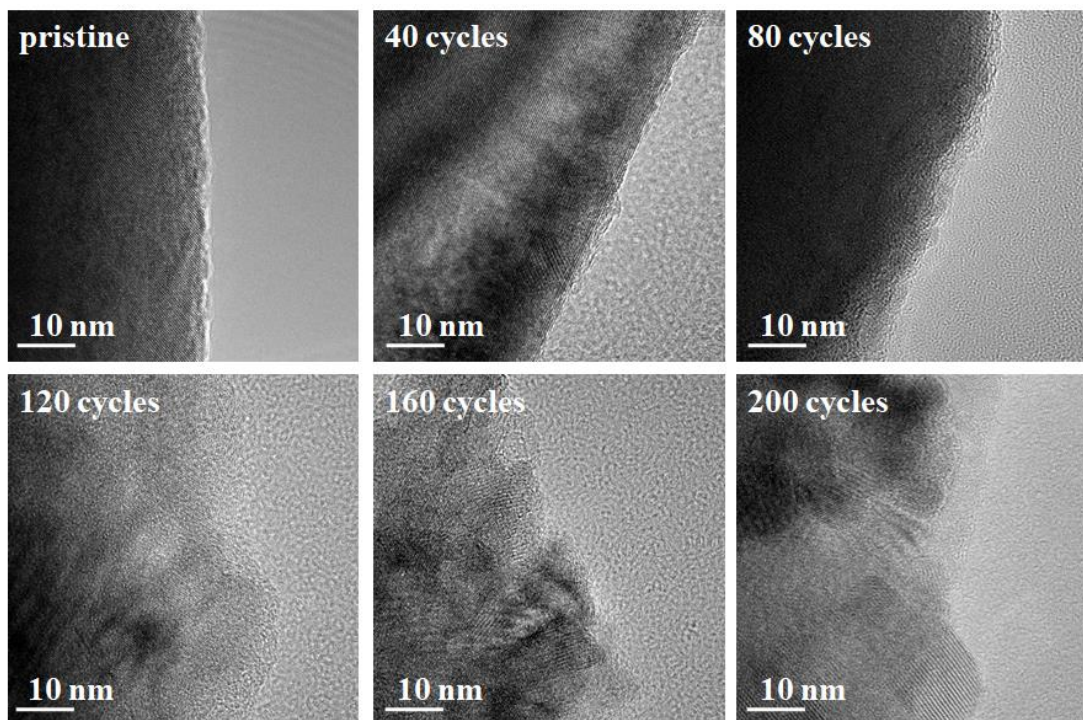


Fig. S13 TEM images of crystal surfaces of LMO after different cycles in 10 mM LiCl solution

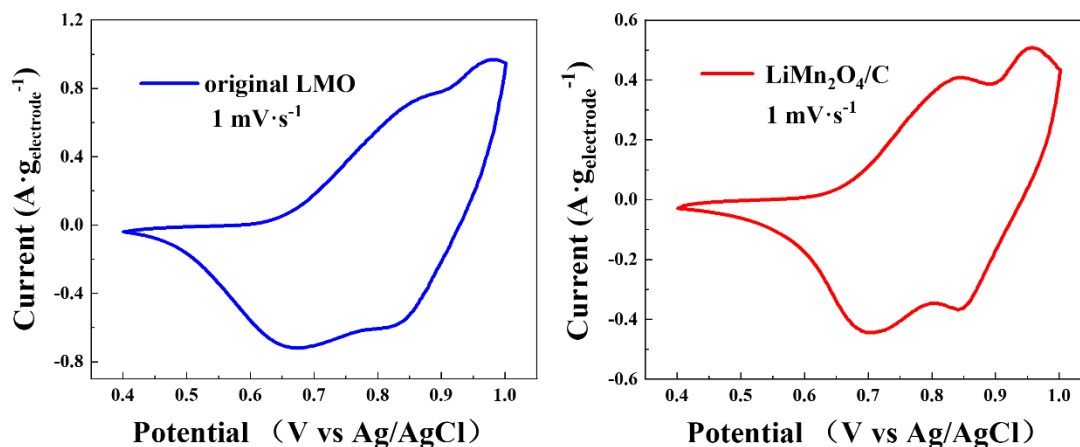


Fig. S14 Cyclic voltammetry results of original LMO and $\text{LiMn}_2\text{O}_4/\text{C}$ with a scan rate of $1.0 \text{ mV}\cdot\text{s}^{-1}$

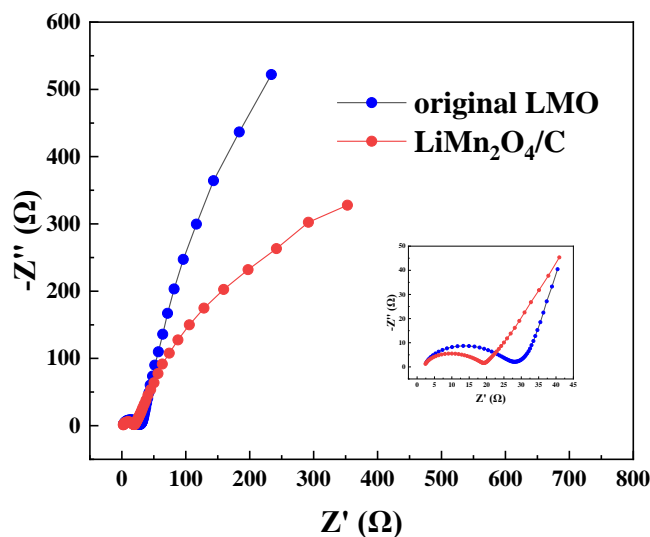


Fig. S15 Comparison of the Nyquist plots

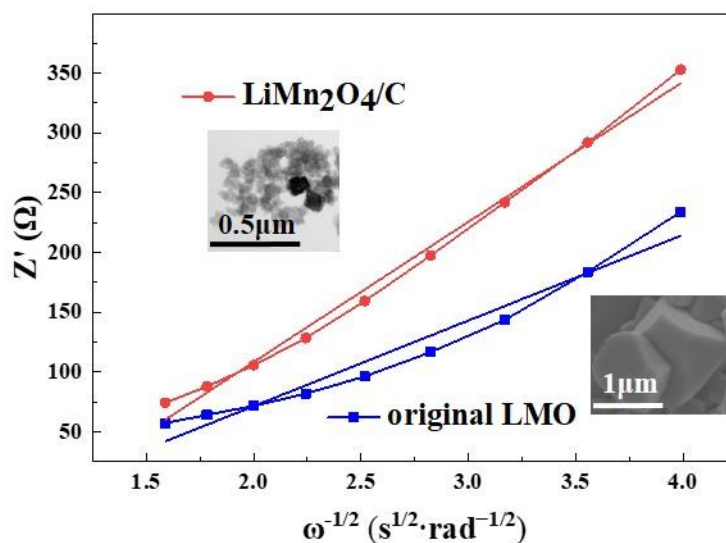


Fig. S16 Fittings of Z' and the reciprocal square root of the angular frequency in the low-frequency region of electrochemical impedance spectroscopy of the materials

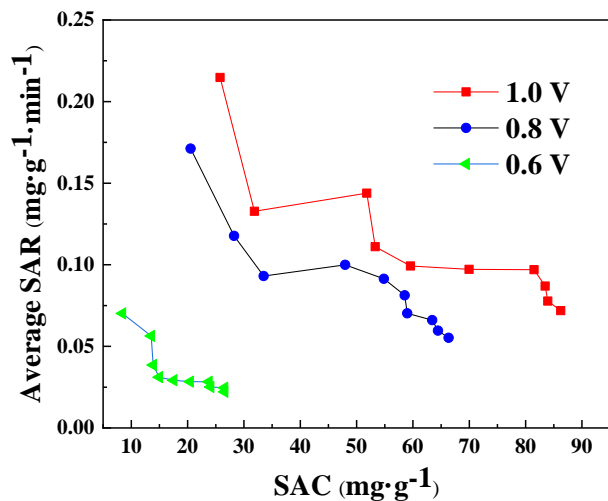


Fig. S17 Deionization Ragone plots

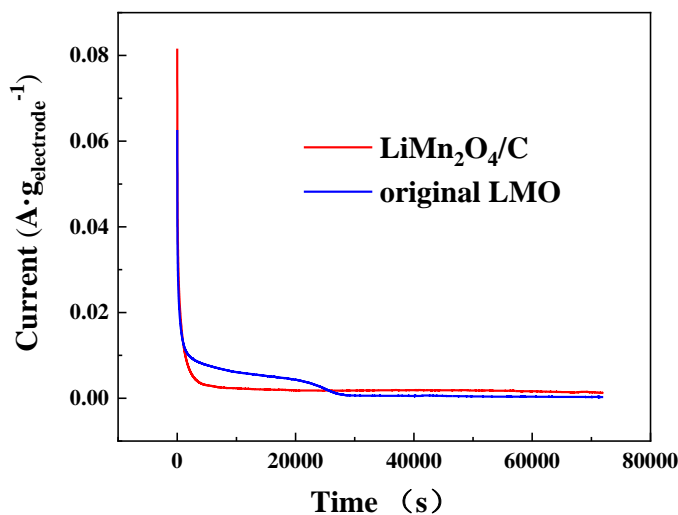


Fig. S18 Constant voltage charging profiles of deionization systems with LiMn₂O₄/C or LMO at 1.0 V with an initial salt concentration of 10 mM

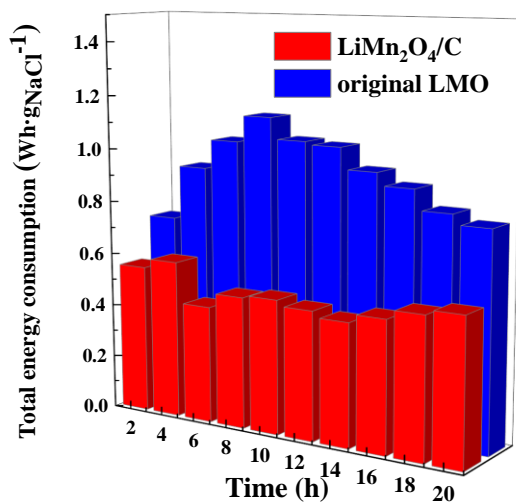


Fig. S19 Energy consumption comparison of the two hybrid deionization systems with different cathodes

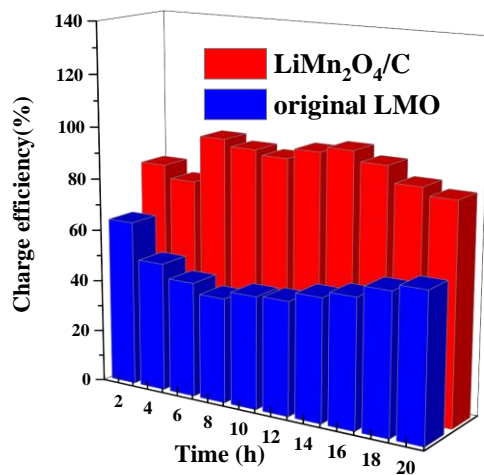


Fig. S20 Charge efficiencies of deionization cells with different cathodes during desalination

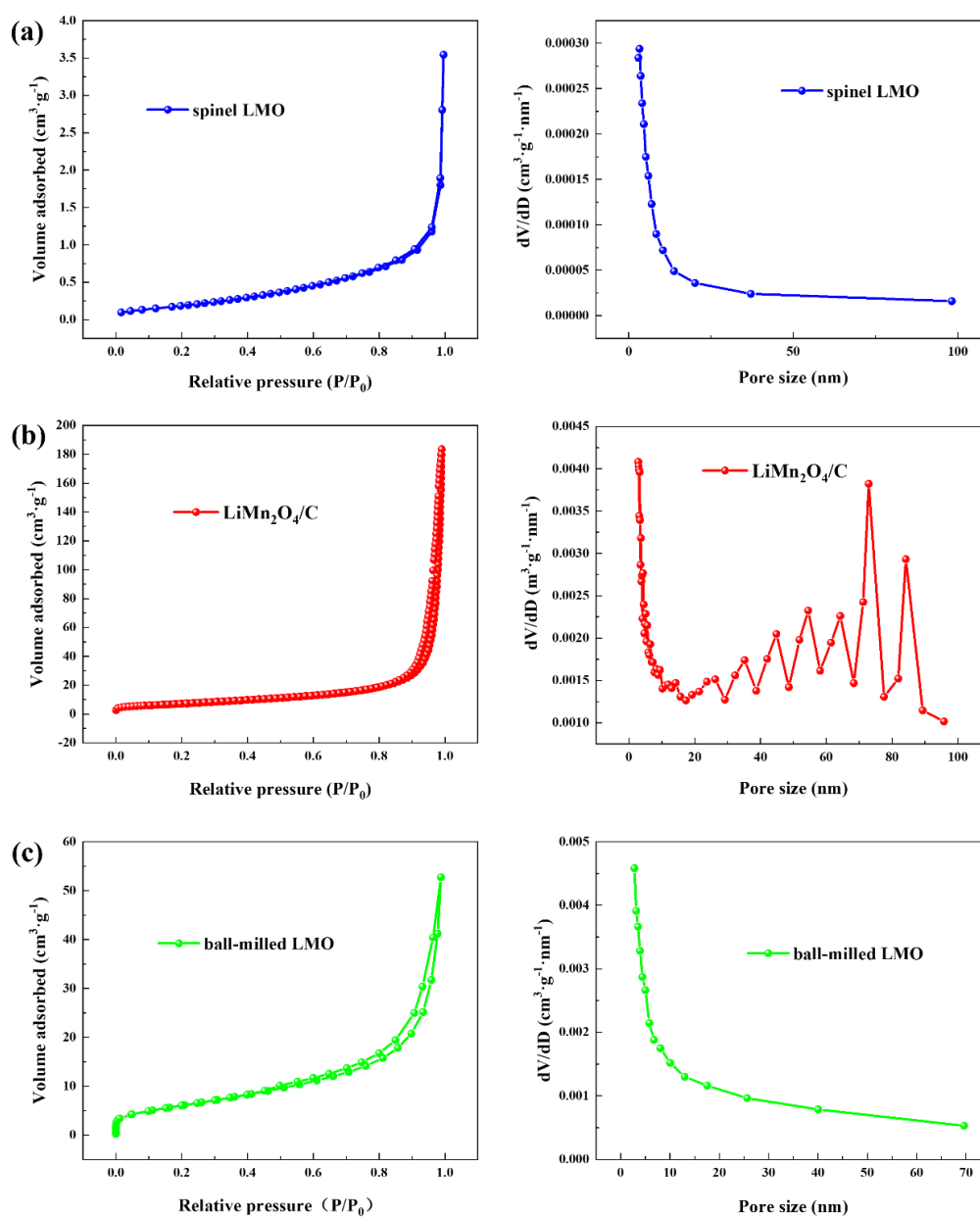


Fig. S21 N_2 adsorption-desorption isotherms and pore sized distributions of (a) original LMO, (b) $\text{LiMn}_2\text{O}_4/\text{C}$, and (c) LiMn_2O_4 after 6 hours of ball-milling

Table S1 Comparison of the intensity ratio values of (111) and other XRD peaks after different time lengths of ball-milling with carbon

Ball-milling time	$I_{(111)}/I_{(311)}$	$I_{(111)}/I_{(400)}$	$I_{(111)}/I_{(440)}$
0 hours	1.94	1.80	3.76
2 hours	2.27	2.34	5.26
4 hours	3.21	3.41	6.61
6 hours	3.38	3.77	7.75

Table S2 Comparison of desalination performances of different battery electrode materials for deionization

Cathode Anode	Applied voltage	Salt concentration	Desalination capacity	References
Na ₂ FeP ₂ O ₇ /C AC	1.2 V	100 mM	32.6 mg·g ⁻¹	[S1]
Na ₄ Mn ₉ O ₁₈ AC	1.2 V	50 mM	31.2 mg·g ⁻¹	[S2]
Porous Ti ₃ C ₂ T _x Porous Ti ₃ C ₂ T _x	1.2 V	171.12 mM	45 mg·g ⁻¹	[S3]
FePO ₄ /rGO rGO	1.8 V	40 mM	85.94 mg·g ⁻¹	[S4]
MoS ₂ AC	1.2 V	400 mM	8.81 mg·g ⁻¹	[S5]
Na ₄ Ti ₉ O ₂₀ /N-doped carbon Ag/rGO	1.4 V	25.67 mM	62.3 mg·g ⁻¹	[S6]
Na ₄ Mn ₁₄ O ₂₇ Na ₄ Mn ₁₄ O ₂₇	1.0 V	500 mM	76.6 mg·g ⁻¹	[S7]
ZIF-67 ZIF-67	1.2 V	40 mM	21.3 mg·g ⁻¹	[S8]
Ag/rGO Na _{1.1} V ₃ O _{7.9} /rGO	1.4 V	34.22 mM	82.2 mg·g ⁻¹	[S9]
LiMn₂O₄/C AC	1.0 V	20 mM	117.3 mg·g⁻¹	this work

Supplementary References

- [S1] S. Kim, J. Lee, C. Kim, J. Yoon, Na₂FeP₂O₇ as a novel material for hybrid capacitive deionization. *Electrochim. Acta* **203**, 265-271 (2016). <https://doi.org/10.1016/j.electacta.2016.04.056>
- [S2] J. Lee, S. Kim, C. Kim, J. Yoon, Hybrid capacitive deionization to enhance the desalination performance of capacitive techniques. *Energy Environ. Sci.* **7**(11), 3683-3689 (2014). <https://doi.org/10.1039/C4EE02378A>
- [S3] W.Z. Bao, X. Tang, X. Guo, S. Choi, C.Y. Wang et al., Porous cryo-dried MXene for efficient capacitive deionization. *Joule* **2**(4), 778-787 (2018). <https://doi.org/10.1016/j.joule.2018.02.018>
- [S4] J. Ma, L. Wang, F. Yu, X.H. Dai, Mesoporous amorphous FePO₄ nanosphere@graphene as a faradic electrode in capacitive deionization for high-capacity and fast removal of NaCl from water. *Chem. Eng. J.* **370**, 938-943 (2019). <https://doi.org/10.1016/j.cej.2019.03.243>
- [S5] F. Xing, T. Li, J.Y. Li, H.R. Zhu, N. Wang et al., Chemically exfoliated MoS₂ for capacitive deionization of saline water. *Nano Energy* **31**, 590-595 (2017). <https://doi.org/10.1016/j.nanoen.2016.12.012>
- [S6] Y.Y. Zhang, K. Yang, H.B. Yu, W.J. Shan, Z.N. Lou et al., Boosting deionization capability by effectively improving sodium-ion storage capacity based on robust interfacial electronic interaction within 3D Na₄Ti₉O₂₀/N-doped porous carbon heterostructures. *J. Mater. Chem. A* **9**(43), 24374-24386 (2021). <https://doi.org/10.1039/d1ta06369c>
- [S7] Y.B. Zhao, A. Gong, Y. Liu, K.X. Li, Facile synthesis and enhanced desalination performance of a novel layered Na₄Mn₁₄O₂₇ made from earth-abundant element in

- capacitive deionization. *Sep. Purif. Technol.* **258**, 118057 (2021).
<https://doi.org/10.1016/j.seppur.2020.118057>
- [S8] Y.Q. Zhang, L. Ji, Y. Zheng, H.W. Liu, X.T. Xu, Nanopatterned metal-organic framework electrodes with improved capacitive deionization properties for highly efficient water desalination. *Sep. Purif. Technol.* **234**, 116124 (2020).
<https://doi.org/10.1016/j.seppur.2019.116124>
- [S9] Z.S. Yue, Y.L. Ma, J.W. Zhang, H. Li, Pseudo-capacitive behavior induced dual-ion hybrid deionization system based on Ag@rGO parallel to Na_{1.1}V₃O_{7.9}@rGO. *J. Mater. Chem. A* **7**(28), 16892-16901 (2019). <https://doi.org/10.1039/c9ta03570b>