Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supplementary Information

Aqueous rechargeable dual-ion battery based on fluoride ion and sodium ion electrochemistry

Zishuai Zhang[1#], Xiaoqiao Hu[1#], Yu Zhou[1], Shaofeng Wang[1], Lingmin Yao[2], Hui Pan[3], Chin-yuan Su[4], Fuming Chen[1], Xianhua Hou[1]**

[1] Guangdong Engineering Technology Research Center of Efficient Green Energy and Environment Protection Materials, Guangdong Provincial Key Laboratory of Quantum Engineering and Quantum Materials, School of Physics and Telecommunication Engineering, South China Normal University, Guangzhou 510006

[2] School of Physics and Electronic Engineering, Guangzhou University, 510006

[3] Institute of Applied Physics and Materials Engineering, University of Macau, E12

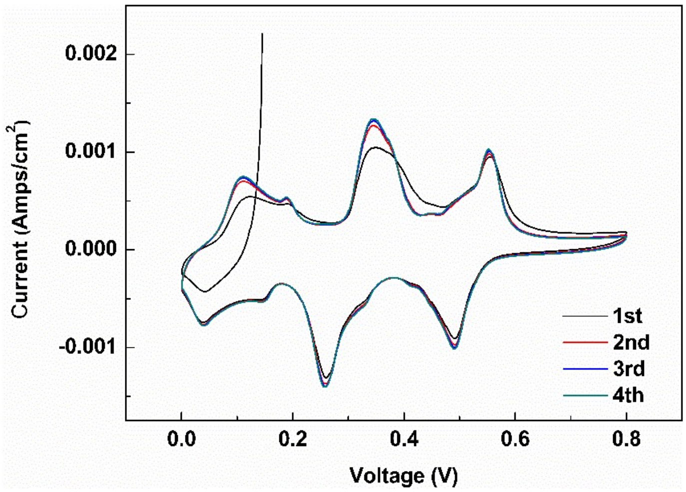
[4] Department of Mechanical Engineering, National Central University, Taiwan, 32001

# These authors contributed equally to this work

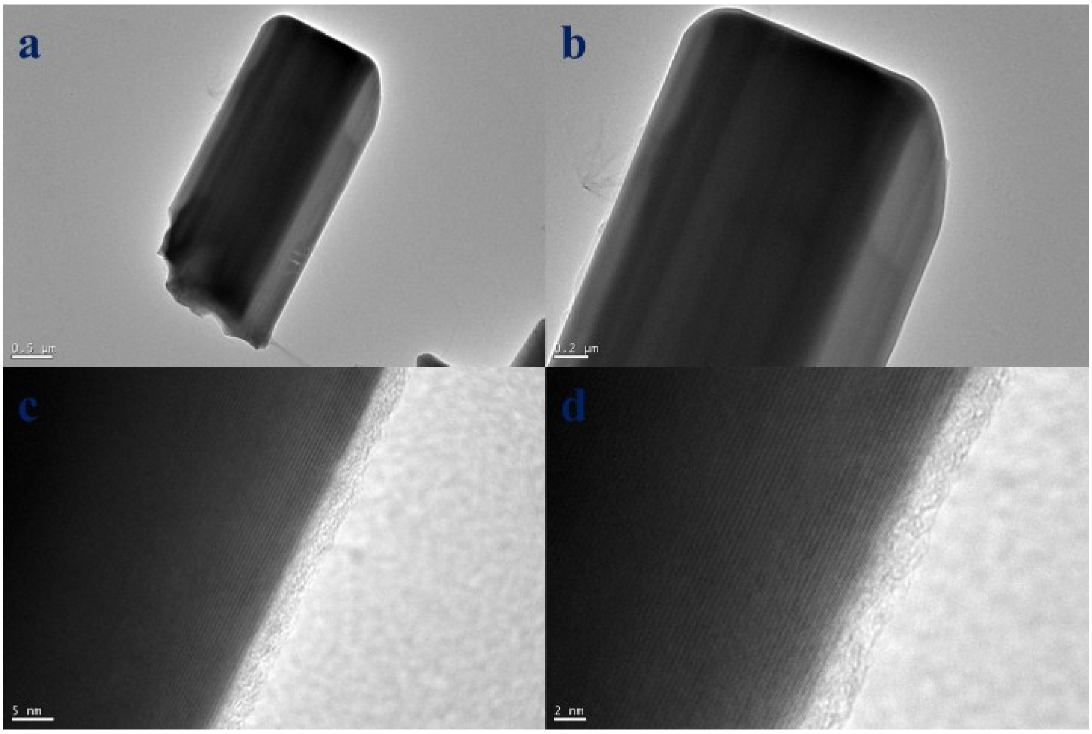
**E-mail:fmchen@m.scnu.edu.cn; houxianhua@m.scnu.edu.cn*

ORCID ID: https://orcid.org/0000-0002-0108-9831

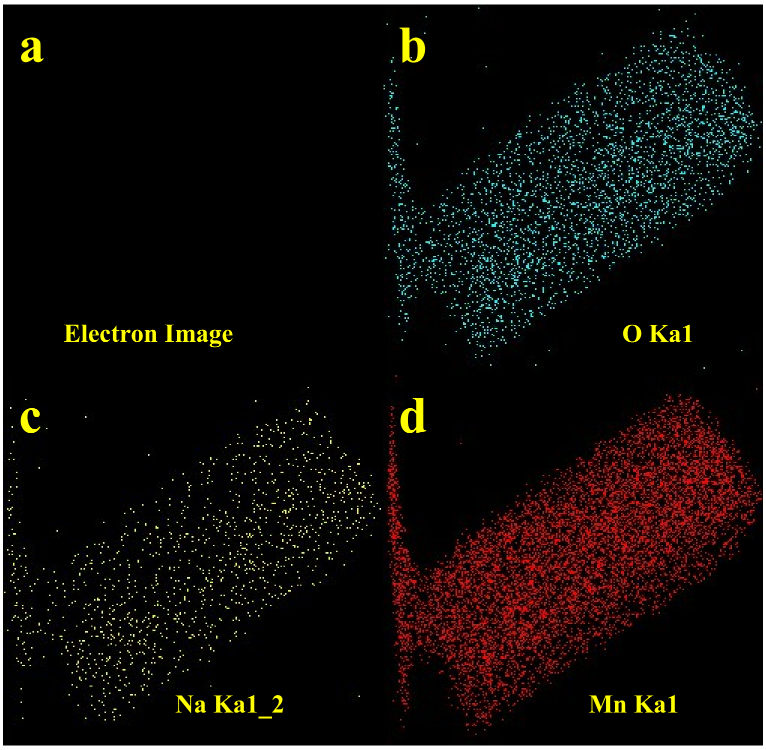
Supplementary Figures:



Supplementary Figures 1. CV curves of the 3 electrodes in aqueous 0.8 M NaF electrolyte, working electrode: NMO, counter electrode: platinum; reference electrode: standard saturated Ag/AgCl electrode.



Supplymentary Figure 2 (a-d) HRTEM imagines of the NMO cathode after discharge process.



Supplementary Figure 3 (a-d) the mapping images of NMO cathode after discharge process.

Supplementary Table 1 Battery and electrode parameters of BiF_3-NMO aqueous fluoride ion battery system

Cell reaction	$xBiF_3 + 3Na_{0.44}MnO_2 \rightarrow xBi + 3Na_{0.44-x}MnO_2 + 3xNaF$ (x_{max}=0.22)
N [a]	3
Specific capacity of BiF_3 (theoret.) Ah/kg [b]	302.3
Specific capacity of $Na_{0.44}MnO_2$ (theoret.) Ah/kg [c]	60.7
Specific capacity of cell (theoret.) Ah/kg [d]	50.5

[a] N is the electron transfer number of 1mole BiF_3 electrode reaction.

[b] The calculation of the specific capacity of the electrode material is based on the active BiF_3.

[c] The calculation of the specific capacity is based on the active NMO.

[d] The calculation of the specific capacity is based on the active BiF_3 and NMO.

Supplementary table 2 comparison of BiF_3-NMO and various aqueous rechargeable batteries

Cell type	Electrolyte	Capacity retention (%)	Initial capacity ($mAhg^{-1}$)	Ref.
Aqueous rechargeable lithium ion batteries				
MnO_2//Li	1.0 M Li_2SO_4	85% (2400) at 50 mAg^{-1}	170 Wh kg^{-1}	[1]
$LiMn_2O_4$//Li	0.5 M Li_2SO_4	~100% (30) at 100 mAg^{-1}	115 $mAhg^{-1}$	[2]
$LiCoO_2$//Li	0.5 M Li_2SO_4	N.A.	~465 Wh kg^{-1}	[3]
$LiFePO_4$@C//LiV_3O_8	9 M $LiNO_3$	~91.8% (100) at 10 C	90	[4]
Aqueous rechargeable sodium and potassium ion batteries				
$Na_2FeP_2O_7$//$NaTi_2(PO_4)_3$	1.0 M Na_2SO_4	2.0 $mAcm^{-1}$	~45	[5]
$Na_3MnTi(PO_4)_3$//$Na_3MnTi(PO_4)_3$	1.0 M Na_2SO_4	98% (100) at 1 C	56.5	[6]
$Na_3V_2(PO_4)_3$//$NaTi_2(PO_4)_3$	1.0 M Na_2SO_4	50%(50) at 10 Ag^{-1}	58	[7]
Aqueous rechargeable multivalent metal ion batteries				
Todorokite MnO_2//Zn	1.0 M $ZnSO_4$	Stable up to 50 cycles	98	[8]
α-MnO_2//Zn	1.0 M $ZnSO_4$	~100%(100) at 6C	~100	[9]
$ZnMn_2O_4$@C//Zn	3.0 M $Zn(CF_3SO_3)_2$	94%(500) at 500 mAg^{-1}	85	[10]
Aqueous rechargeable hybrid batteries				
NaFe-PB//Zn	1.0 M Na_2SO_4	80% (1000) at 300 mAg^{-1}	74.0	[11]
$Na_3V_2(PO_4)_3$-C//Zn	0.5M CH_3COONa+0.5 M $Zn(CH_3COO)_2$	77% (200) aNt 0.5 C	91	[12]
NMO-BiF_3	0.8 M NaF	62.8% (10) at 100 mAg^{-1}	123.4	this work

Reference:

[1] S.L. Chou, Y.X. Wang, J.T. Xu, J.Z. Wang, H.K. Liu, S.X. Dou, Electrochem. Commun. 31 (2013) 35e38
[2] X.J. Wang, Y.Y. Hou, Y.S. Zhu, Y.P. Wu, R. Holze, Sci. Rep. 3 (2013) 1401.
[3] X. Wang, Q. Qu, Y. Hou, F. Wang, Y. Wu, Chem. Commun. 49 (2013) 6179e6181.
[4] M.S. Zhao, G.L. Huang, W.G. Zhang, H.Y. Zhang, X.P. Song, Energy & Fuels 27 (2013) 1162e1167.
[5] K. Nakamoto, Y. Kano, A. Kitajou, S. Okada, J. Power Sources 327 (2016) 327e332.
[6] H. Gao, J.B. Goodenough, Angew. Chemie-International Ed. 55 (2016) 12768e12772.
[7] Q. Zhang, C. Liao, T. Zhai, H. Li, Electrochim. Acta 196 (2016) 470e478.
[8] J. Lee, J.B. Ju, W.I. Cho, B.W. Cho, S.H. Oh, Electrochim. Acta 112 (2013) 138e143.
[9] C. Xu, B. Li, H. Du, F. Kang, Angew. Chem. Int. Ed. 51 (2012) 933e935
[10] N. Zhang, F. Cheng, Y. Liu, Q. Zhao, K. Lei, C. Chen, X. Liu, J. Chen, J. Am. Chem. Soc. 138 (2016) 12894e12901.
[11] L.P. Wang, P.F. Wang, T.S. Wang, Y.X. Yin, Y.G. Guo, C.R. Wang, J. Power Sources 355 (2017) 18e22.
[12] G.L. Li, Z. Yang, Y. Jiang, W.X. Zhang, Y.H. Huang, J. Power Sources 308 (2016) 52e57.