Exploring the Potential of Ionothermal Syntheses for High-performance Lithium-ion Battery Anode Materials

Runming Tao
University of Tennessee, Knoxville, RTAO3@VOLS.UTK.EDU

Follow this and additional works at: https://trace.tennessee.edu/utk_graddiss

Part of the Materials Chemistry Commons

Recommended Citation
https://trace.tennessee.edu/utk_graddiss/6952
To the Graduate Council:

I am submitting herewith a dissertation written by Runming Tao entitled "Exploring the Potential of Ionothermal Syntheses for High-performance Lithium-ion Battery Anode Materials." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

Sheng Dai, Major Professor

We have read this dissertation and recommend its acceptance:

Bhavya Sharma, Ampofo K. Darko, Bin Hu

Accepted for the Council:

Dixie L. Thompson

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)
Exploring the Potential of Ionothermal Syntheses for High-performance Lithium-ion Battery Anode Materials

A Dissertation Presented for the Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Runming Tao
December 2021
Copyright © 2021 by Runming Tao

All rights reserved.
ACKNOWLEDGEMENTS

I would like to first thank my major advisor Prof. Sheng Dai for allowing me to part of his enthusiastic research group. Throughout my Ph.D. research career here, there was never a shortage of ideas, group members and/or projects to push me forward. I also would like to thank my committee members Dr. Bhavya Sharma, Dr. Ampofo Darko and Dr. Bin Hu for contributing their time and feedback to my research progress.

Under Prof. Dai’s great support and help, I had lots of opportunities to study and work with so many people at the University of Tennessee Knoxville and Oak Ridge National Laboratory in the last four and half years. My sincere appreciation goes out to Dr. Xiao-Guang Sun, Dr. Jiyuan Liang, Dr. Guang Yang, Dr. Jagjit Nanda, and Dr. Ethan Self for their valuable advice, guidance and support. I am also thankful for many exchange students, visiting scholars and post-doctors: to Tian Jin and Chi-Linh Do-Thanh for the safety guidance; to Juntian Fan and to Tao Wang for the assistances of the assemble and test of batteries during the Covid-19 period, respectively; to Tianyu Zhang, Jixin Liu, Ziyang Lu, Hao Chen and Hailong Lvu for the help on some particular experiments.

I would also like to express my sincere gratitude to my family for their continuous support in my life. My parents always are the strongest advocates of mine. Besides them, I would like to thank my relatives in Nashville, TN and Boston, MA for their encouragement and care since I arrived the U.S.. Last but not the
least, I would thank the Buys’ family for the initiation and instruction of my life in the U.S. based on their piety and kindness.
ABSTRACT

Renewable energy storage systems are regarded as the solution to the environmental and energy crises caused by the burning of fossil fuels in vehicles. Unfortunately, owing to the limits to the electrochemical performance of the current anode materials, lithium-ion batteries [LIBs] are still lacking strength in the charging rate-capability and thereby cannot fulfill future application requirements in electrical vehicles [EVs].

Particularly, graphite with a high theoretical specific capacity of 372 mAh/g is unsuitable for EVs due to the safety concerns of passivating solid-electrolyte interphase [SEI] resulted from the low operation potential of 0.1 V versus Li/Li⁺. The other common anode material is Li₄Ti₅O₁₂, which exhibits high operating potential of 1.55 V vs Li/Li⁺, excellent rate-capability and zero-strain property together with superior rate capability and excellent cycle life. However, the theoretical specific capacity of Li₄Ti₅O₁₂ is only 175 mAh/g, dramatically impeding the practical application in electric vehicles. Therefore, developing new anode materials with excellent fast-rechargeability and high theoretical specific capacity is an urgent research topic.

Recently, transition metal oxides [TMOs], possessing high theoretical capacities and operation voltages, are considered to be promising anode materials for EVs. However, their inherent low electrical conductivities and Li⁺ diffusivities still challenge their future usage in EVs. Scientists discovered that nano-scaled TMOs can improve the electrochemical kinetics, while the widely used soft and
hard template preparation methods can cause considerable environmental pollution (the huge CO$_2$ emission from block-polymer burning and the usage of highly toxic etching agents, respectively). Therefore, developing a new strategy to synthesize nano-scaled TMOs is highly desirable.

Herein, ionothermal syntheses, employing ionic liquids as the solvents and/or templates in the preparations to form nanoporous materials, are novelly applied to develop several types of new nanoporous TMO materials. Moreover, unlike the traditional synthesis methods discussed above, the used ionic liquids can be easily recycled to circumvent the potential environmental concerns. More importantly, the prepared TMO materials successfully deliver superb electrochemical performance, which establishes the promising potential of ionothermal syntheses in the preparation of high-performance anode materials and shines new light on the development of fast-rechargeable LIBs in EVs.
TABLE OF CONTENTS

CHAPTER 1 Introduction .................................................................................................................. 1
  1.1 Lithium-ion Batteries: Solution to CO₂ Emission ................................................................. 2
  1.2 Challenges of Current Lithium-ion Batteries ................................................................. 2
  1.3 Traditional Preparations of Transition Metal Oxide Anode Materials ......................... 4
    1.3.1 Solid-state Mechanochemical Synthesis ................................................................. 4
    1.3.2 Hydrothermal and Solvothermal Syntheses ............................................................ 5
    1.3.3 Hard and Soft Templates ......................................................................................... 5
  1.4 Ionothermal Synthesis ....................................................................................................... 6
  1.5 Typical Characterizations of Ionothermally Prepared Anode Materials .................... 8
    1.5.1 Nuclear Magnetic Resonance (NMR) Spectroscopy .............................................. 8
    1.5.2 X-ray and neutron powder Diffractions (XRD and NPD) and Raman Spectroscopy .................................................................................................................. 8
    1.5.3 Scanning and Transmission Electron Microscopies (SEM and TEM) ................. 10
    1.5.4 X-ray Photoelectron Spectroscopy (XPS) ............................................................. 10
    1.6.2 Galvanostatic Intermittent Titration Technique (GITT) ....................................... 11

CHAPTER 2 Ionic Liquid-Directed Nanoporous TiNb₂O₇ Anodes with Superior Performance for Fast-Rechargeable Lithium-ion Batteries ............................................................ 13
  2.1 Publication Statement ........................................................................................................... 14
  2.2 Abstract ............................................................................................................................... 14
  2.3 Introduction ........................................................................................................................ 15
  2.4 Experimental ...................................................................................................................... 19
    2.4.1 Ionic Liquids Syntheses ......................................................................................... 19
    2.4.2 Materials Syntheses ............................................................................................... 21
    2.4.3 Typical Characterizations ...................................................................................... 22
    2.4.4 Electrode Fabrication ............................................................................................. 22
    2.4.5 Electrochemical Property Studies ........................................................................... 23
  2.5 Results ................................................................................................................................ 24
    2.5.1 Structural Characterizations ................................................................................... 24
    2.5.2 Electrochemical Performance Studies ................................................................. 26
  2.6 Discussion ........................................................................................................................... 34
  2.7 Summary ............................................................................................................................. 34
  2.8 Acknowledgements ............................................................................................................ 35

CHAPTER 3 Ionothermally Synthesized Nano-porous Ti₀.₉₅W₀.₀₅Nb₂O₇ as a Novel High-Rate Anode Material for Lithium-Ion Batteries ................................................................. 36
  3.1 Abstract ............................................................................................................................... 37
  3.2 Introduction ........................................................................................................................ 37
  3.3 Experimental Section ........................................................................................................ 39
    3.3.1 Synthesis of nano-porous Ti₀.₉₅W₀.₀₅Nb₂O₇ (NPTWNO) material ......................... 39
    3.3.2 Synthesis of bulk TiNb₂O₇ (TNO) material .......................................................... 40
    3.3.3 Typical Characterizations ....................................................................................... 40
    3.3.4 Electrochemical property studies ......................................................................... 41
  3.4 Results ............................................................................................................................... 41
3.4.1 Structural Characterizations ................................................................. 42
3.4.2 Electrochemical Performance Studies .................................................. 44
3.5 Discussion ................................................................................................. 46
3.6 Summary .................................................................................................... 47
3.7 Acknowledgements .................................................................................... 48
CHAPTER 4 Comprehensively Revealing Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$: A Novel High-
performance Anode Material for Fast-rechargeable Lithium-ion Batteries ...... 49
  4.1 Publication Statement .............................................................................. 50
  4.2 Abstract .................................................................................................. 50
  4.3 Introduction .............................................................................................. 51
  4.4 Experimental .......................................................................................... 54
    4.4.1 Preparation of ionic liquid: 1-Butyl-3-methylimidazolium
        bis(trifluoromethylsulfonyl)imide .......................................................... 54
    4.4.2 Synthesis of M$_3$Nb$_{14}$O$_{44}$ materials ........................................... 55
    4.4.3 Typical characterizations ................................................................. 55
    4.4.4 Neutron powder diffraction experiments ....................................... 57
    4.4.5 Aberration-corrected scanning transmission electron microscope
        analysis .................................................................................................. 57
    4.4.6 Electrode fabrication and electrochemical performance studies ...... 58
    4.4.7 Operando XRD experiments ............................................................ 59
    4.4.8 Density functional theory (DFT) computational quantum mechanical
        modelling studies .............................................................................. 60
  4.5 Results ...................................................................................................... 61
    4.5.1 Structural Characterizations ............................................................ 61
    4.5.2 Electrochemical Performance Studies ............................................. 68
  4.6 Discussion ............................................................................................... 84
  4.7 Summary .................................................................................................. 85
  4.8 Acknowledgements .................................................................................. 86
CHAPTER 5 Conclusion ................................................................................... 87
  5.1 Synopsis .................................................................................................. 87
  5.2 Outlook .................................................................................................... 88
REFERENCES ................................................................................................. 90
APPENDIX ...................................................................................................... 101
VITA ................................................................................................................ 171
LIST OF TABLES

Table 2-1. Characterization results of the prepared NPTNO and BTNO materials. ....................................................................................................................................... 120
Table 2-2. Comparison of the measured Li⁺ diffusion coefficient of several ReO₃-type materials. ......................................................................................................................................... 121
Table 2-3. Capacity comparison among various anode materials. Theoretical capacities: TNO = 387.6 mAh/g, Li₄Ti₅O₁₂ = 175 mAh/g, TiO₂ bronze = 335 mAh/g, and TiO₂ anatase = 167.5 mAh/g. ........................................................................................................ 122
Table 4-1. Lattice parameters of MWNO, MNO and WNO obtained from powder XRD Rietveld refinements. Crystallite size is abbreviated as C.S............. 168
Table 4-2. The site occupancies of the cations in WNO and MWNO obtained from the NPD Rietveld refinements. ........................................................................ 168
Table 4-3. The calculated cation-oxygen bond length in WNO and MWNO from the NPD Rietveld refinements.................................................................................. 169
Table 4-4. Average discharge capacities of MWNO, MNO and WNO at multiple current rates in the rate performance test ......................................................... 170
Table 4-5. \(D_{\text{Li}⁺}(\text{m}²/\text{s})\) obtained from GITT. ............................................................................................................................... 170
Table 4-6. Lattice parameters of the cycled MWNO electrode at charge state (3.0 V) obtained from XRD Rietveld refinement. ...................................................... 170
LIST OF FIGURES

Figure 1-1. Working principle of LIBs.\textsuperscript{133} .......................................................... 101
Figure 1-2. Crystal structures of (a). TiNb\textsubscript{2}O\textsubscript{7} \textsuperscript{134} and (b). W\textsubscript{2}Nb\textsubscript{14}O\textsubscript{44} ............................... 101
Figure 1-3. (a). Illustration of solid-state mechanochemical synthesis for bulk TiNb\textsubscript{2}O\textsubscript{7} material. (b). TEM image of the corresponding prepared bulk TiNb\textsubscript{2}O\textsubscript{7} material. ........................................................................................................ 101
Figure 1-4. Schematic of the hydrothermal and solvothermal syntheses.\textsuperscript{5} ........ 102
Figure 1-5. Schematic demonstration of the hydrogen bonding and \pi-\pi stacking mechanism for the porous structure framework.\textsuperscript{15} ........................................ 102
Figure 1-6. Demonstration of hydrolysis (upper) and polycondensation (lower).\textsuperscript{135} .......................................................... 103
Figure 1-7. Scheme of NMR working principle................................................................. 103
Figure 1-8. Scheme of XRD working principle ............................................................... 103
Figure 1-9. Scheme of NPD working principle ............................................................... 104
Figure 1-10. Scheme of Raman spectroscopy working principle ........................................ 104
Figure 1-11. Scheme of XPS working principle .............................................................. 105
Figure 1-13. Scheme demonstration of the typical GITT process .................................... 105
Figure 1-13. Scheme demonstration of the typical GITT process .................................... 105
Figure 2-1. Synthesis scheme of [Bmim][NTf\textsubscript{2}] ......................................................... 106
Figure 2-5. Synthesis scheme of NPTNO material ............................................................ 106
Figure 2-6. Synthesis schematic diagram of the bulk TNO ................................................ 107
Figure 2-2. HNMR spectrum of [Bmim][NTf\textsubscript{2}] in DMSO ........................................ 108
Figure 2-3. HNMR spectrum of [Bmim][NTf\textsubscript{2}] in DMSO ........................................ 109
Figure 2-4. CNMR spectrum of [Bmim][NTf\textsubscript{2}] in DMSO ........................................ 110
Figure 2-7. (a and b). XRD patterns of the prepared TNO materials. (c). XRD Rietveld refinement of TNO700. (d). Crystal structure of TNO700 ...................... 111
Figure 2-8. Raman spectra of TNO700 and TNO850 materials within range from 100 to 1100 cm\textsuperscript{-1} .............................................................................................................. 112
Figure 2-9. (a and b). Nitrogen adsorption-desorption isotherm curves and their corresponding BJH plots of NPTNO materials, respectively ......................................................... 112
Figure 2-10. SEM images and elemental mappings of NPTNO and BTNO materials. (a and b). TNO700. (c and d). TNO850 .......................................................... 113
Figure 2-11. TEM and HRTEM images of the obtained NPTNO materials at different magnifications. (a and b). TNO700. (c and d). TNO850 .................. 114
Figure 2-12. SAED patterns of (a). TNO700 and (b). TNO850 ........................................ 114
Figure 2-13. CV plots of TNO700 half-cell at a scan rate of 0.05 mV/s. (a). TNO700. (b). TNO850. (c). BTNO ......................................................... 115
Figure 2-14. Discharge-charge profiles of the assembled half-cells at a current rate of 0.1 C (38.7 mA/g). (a). TNO700. (b). TNO850. (c). BTNO .................. 115
Figure 2-15. Rate performance test of the assembled half-cells within C rate range from 0.5 C to 50 C .......................................................................................... 115
Figure 2-16. Cyclic performance study of the assembled half-cells at a high C rate of 5 C over 1000 cycles .......................................................... 116
Figure 2-17. Electrochemical performance study of the assembled full-cells in voltage range from 1.5 to 3.5 V. (a and c). Cyclic performance study at 1 and 2 C over 1000 cycles. (b and d). The corresponding charge-discharge curves at 1 and 2 C. ................................................. 116

Figure 2-18. Structural studies of the cycled TNO700. (a). XRD patterns of pristine TNO powder and the cycled TNO electrode at charge state. (b). XPS broad spectra of the uncycled and the cycled TNO electrodes at charge state. (c and d). The HRXPS of C, O, and F elements for the uncycled and the cycled TNO electrodes, respectively. ................................................. 117

Figure 2-19. SEM images and SEM-EDS elemental mappings of NPTNO electrodes. (a) SEM image of uncycled TNO700 electrode. (b) Broad view elemental mappings of uncycled TNO700 electrode. (c) SEM image of 1000 cycled TNO700 electrode. (d) Broad view elemental mappings of 1000 cycled TNO700 electrode TNO700. ................................................. 117

Figure 2-20. HRXPS of Ti and Nb elements for the uncycled and 1000 cycled TNO700 electrodes. (a and b). HRXPS of Ti and Nb for the uncycled TNO700 electrode, respectively. (c and d). HRXPS of Ti and Nb for the 1000 cycled TNO700 electrode, respectively. ................................................. 118

Figure 2-21. GITT Li\textsuperscript{+} diffusivity studies of TNO anodes in half-cells. (a). GITT curves of the TNO electrodes. (b). GITT Li\textsuperscript{+} diffusivity plots of TNO anodes. ................................................. 118

Figure 2-22. Pictures of synthesized ILs. (a) Synthesized [BMIm]Br. (b) [BMIm][NTf\textsubscript{2}]-water washing process. (c) Synthesized [BMIm][NTf\textsubscript{2}]. (d) Recycled [BMIm][NTf\textsubscript{2}]. ................................................. 119

Figure 2-23. Nitrogen adsorption-desorption isotherm Barrett-Joyner-Halenda (BJH) plots of bulk TNO anode. ................................................. 119

Figure 2-24. Raman spectra of the synthesized TNO materials. ......................... 119

Figure 2-25. SEM and SEM EDS elemental mapping images of BTNO. .......... 120

Table 2-1. Characterization results of the prepared NPTNO and BTNO materials. ................................................. 120

Table 2-2. Comparison of the measured Li\textsuperscript{+} diffusion coefficient of several ReO\textsubscript{3}-type materials. ................................................. 121

Figure 3-1. Schematic illustration of NPTWNO preparation via ionothermal synthesis. ................................................. 123

Figure 3-2. (a). XRD patterns and Rietveld refinements of (b). NPTWNO and (c). TNO materials, respectively. ................................................. 123

Figure 3-3. (a). nitrogen adsorption/desorption isotherm of NPTWNO and (b). its corresponding BJH plot. ................................................. 124

Figure 3-4. (a-c). SEM, TEM and HRTEM images of NPTWNO. ......................... 124

Figure 3-5. CV profiles of the NPTWNO-based LIB cell in the potential window of 1.0–3.0 V at a scan rate of 0.05 mV/s. ................................................. 125
Figure 3.6. The initial galvanostatic discharge-charge plots at 0.1 C. (a). NPTWNO. (b). TNO.

Figure 3.7. (a). Rate capability and Coulombic efficiency comparisons between NPTWNO and TNO half-cells at various rates: discharge current rate fixed at 1 C (except the 0.5 C discharge-charge profile). (b). Cyclic performance comparisons between NPTWNO and TNO half-cells at a current rate of 5 C after aging at 0.1 C for 3 cycles.

Figure 3.8. SEM EDX study of NPTWNO material. (a). SEM image and the selected area. (b). EDX spectrum. (c-f). Elemental mappings of Ti, Nb, W and O, respectively.

Figure 3.9. Electron microscopy images of the bulk TNO material. (a). SEM image. (b). TEM image. (c). HRTEM image.

Figure 3.10. Selected area electron diffraction patterns. (a). NPTWNO. (b). TNO.

Figure 3.11. CV profiles of TNO at a scan rate of 0.05 mV/s.

Figure 4.1. Scheme demonstration of the ionothermal synthesis of MWNO material.

Figure 4.2. XRD pattern of MWNO material.

Figure 4.3. Raman spectrum of MWNO material.

Figure 4.4. Broad XPS spectrum of MWNO material.

Figure 4.5. HRXPS spectra of (a). Mo-3d, (b). W-4f, (c). Nb-3d and (d). O-1s for MWNO material.

Figure 4.6. NPD Rietveld refinement of MWNO.

Figure 4.7. The proposed lattice structure of MWNO based on NPD analysis.

Figure 4.8. AC-STEM studies of MWNO material. (a). HAADF image along zone axis of [001]. (b and c). Local lattice structure model of the MoO$_4$ tetrahedral site and the corresponding HAADF simulation image. (d). HAADF image along zone axis of [100].

Figure 4.9. Electron microscopy studies of MWNO. (a-c). SEM, TEM and HRTEM images, respectively. (d). SAED pattern (from the selected area in b)). (e-i). HAADF image and its corresponding EDX elemental mapping images.

Figure 4.10. CV profile of MWNO at a scan rate of 0.05 mV/s.

Figure 4.11. Galvanostatic discharge/charge curves of MWNO at a current rate of 0.1 C.

Figure 4.12. Rate performance study of MWNO, MNO and WNO.

Figure 4.13. Plot of $(a\nu)^2$ versus $\nu$.

Figure 4.14. Projected density of states obtained from the DFT computation. The Fermi level is represented by the gray line at energy of 0 eV.

Figure 4.15. EIS Nyquist plot of MWNO.

Figure 4.16. MWNO GITT study. (a-c). GITT discharge/charge curve, its zoomed-in plot and the corresponding Li$^+$ insertion/extraction diffusivity plot, respectively.
Figure 4-17. Contour plot of the operando XRD pattern of MWNO along with the corresponding voltage profile of the initial discharge/charge cycle. .......... 137
Figure 4-18. The evolution of the refined lattice parameters for MWNO unit cell obtained from the operando XRD experiment. .......................................................... 138
Figure 4-19. (a and b). Demonstrations of the Li$^+$ diffusion paths. The NbO$_6$ and WO$_6$ octahedra are shown in green and gray, respectively, and MO$_6$ octahedra and MO$_4$ tetrahedra are shown in purple. The blue arrows indicate possible Li$^+$ diffusion paths, named as Path I, II, III and IV. The black balls indicate Li$^+$ at the initial and final sites for Li$^+$ diffusion. (c-f). The DFT study of the energy barriers of the Li$^+$ diffusion paths along Path I, II, III and IV, respectively. ................................................................................................................. 138
Figure 4-20. Cyclic performance study of MWNO, MNO and WNO. ................. 139
Figure 4-21. Studies of cycling effect for the MWNO electrode. a) XRD patterns of an uncycled MWNO electrode and the cycled MWNO electrode. Copper foil appears two sharp diffraction peaks at 43.3 and 50.4 °, corresponding to the (111) and (200) crystallographic planes, respectively. b) Zoomed-in XRD patterns of an uncycled MWNO electrode and the cycled MWNO electrode as the illustration of tiny shifts of peaks. c) SEM images of the cycled MWNO electrode and the uncycled MWNO electrode: I and II — broad view and zoomed-in view of the cycled MWNO electrode, respectively; III and IV — broad view and zoomed-in view of the uncycled MWNO electrode, respectively. d-h) HRXPS spectra of Mo, W, Nb, C, O and F elements for the 2000-cycled MWNO electrode, respectively. ................................................................. 140
Figure 4-22. Electrochemical performance studies of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-MWNO full-cells in the voltage window of 1.5 – 3.5 V. a). The galvanostatic charge/discharge profiles at 1 C. b). Rate performance and Coulombic efficiency at multiple current rates with discharge current rate fixed at 1 C (except the discharge/charge profiles at 0.5 C) c). Cyclic performance and Coulombic efficiency at a constant current rate of 2 C after aging at 0.1, 0.5 and 1 C. ...................................................................................................................... 141
Figure 4-23. HNMR spectra of the synthesized [BMIm]Br and [BMIm][NTf$_2$] in DMSO. .......................................................................................................................... 142
Figure 4-24. CNMR spectrum of the synthesized [BMIm][NTf$_2$] in DMSO. ........ 142
Figure 4-25. Digital images of the obtained samples. ........................................ 143
Figure 4-26. The vanadium can (sample holder) for neutron powder diffraction experiment at Oak Ridge National Laboratory Spallation Neutron Source on the POWGEN BL-11A. ........................................................................................................... 143
Figure 4-27. Normalized (a) XRD patterns, (b) FTIR spectra and (c) Raman spectra of MWNO. MNO and WNO materials. ................................................................. 144
Figure 4-28. Rietveld refinements of the XRD patterns of (a) MNO and (b) WNO. ......................................................................................................................... 144
Figure 4-29. Broad XPS spectrum of MWNO. ..................................................... 145
Figure 4-30. Broad XPS spectrum of MNO. ....................................................... 145
Figure 4-31. Broad XPS spectrum of WNO. ....................................................... 146
Figure 4-32. (a-c). HRXPS spectra of MNO for Mo, Nb and O, respectively. (d-e). HRXPS spectra of WNO for W, Nb and O, respectively. 146
Figure 4-33. NPD patterns of MWNO, MNO and WNO. 147
Figure 4-44. Rietveld refinement of the NPD pattern of WNO. 147
Figure 4-45. Full-sized image of the crystal structure of MWNO. The red, green, grey (in the faint-green octahedra) and purple spheres correspond to the O, Nb, W and Mo atoms in the unit cell, respectively. The structure consists of 4 × 4 ReO₃ blocks intersected with crystallographic shear planes. 148
Figure 4-46. (a and b). Crystal structures of MNO along the c axis and b axis, respectively. (c and d). Crystal structures of WNO along the c axis and a axis, respectively. 149
Figure 4-47. ACSTEM HAADF with atom assignments of MWNO along the [001] projection (yellow: Nb/W/Mo; blue: Mo). 149
Figure 4-48. The corresponding FFT pattern of Figure 2k for MWNO along the [001] projection. 150
Figure 4-49. The corresponding FFT pattern of Figure 2l for MWNO along the [010] projection. 150
Figure 4-50. AC-STEM HAADF images of MNO and WNO materials at atomic-resolution. (a and b). MNO. (c and d). WNO. 151
Figure 4-51. (a-d). SEM, TEM, HRTEM images and SAED pattern of MNO, respectively. (e-h). SEM, TEM, HRTEM images and SAED pattern of WNO, respectively. 151
Figure 4-52. SEM EDX spectrum of MWNO. 152
Figure 4-53. SEM EDX spectrum of MNO. 153
Figure 4-54. SEM EDX spectrum of WNO. 154
Figure 4-55. Images of SEM EDX elemental mapping of MWNO. 155
Figure 4-56. Images of SEM EDX elemental mapping of MNO. 155
Figure 4-57. Images of SEM EDX elemental mapping of WNO. 155
Figure 4-58. STEM-HAADF and EDX elemental mapping images of MNO. 156
Figure 4-59. STEM-HAADF and EDX elemental mapping images of MNO. 156
Figure 4-60. (a and b). N₂ adsorption isotherms BET curves and BJH plots of MWNO, MNO and WNO materials, respectively. 157
Figure 4-61. (a-c). CV cycles at a scan rate of 0.05 mV/s, galvanostatic discharge/charge profiles at a current rate of 0.1 C and initial EIS impedance spectrum of MNO, respectively. (d-f). CV cycles at a scan rate of 0.05 mV/s, galvanostatic discharge/charge profiles at a current rate of 0.1 C and initial EIS impedance spectrum of WNO, respectively. 157
Figure 4-62. (a). UV-vis DRS spectra of MWNO, MNO and WNO. (b). Determination of the transition type for MWNO. (c and d). Determination of the transition type and measurement of bandgap for MNO, correspondingly. (e and f). Determination of the transition type and measurement of bandgap for WNO, correspondingly. 158
Figure 4-63. (a and b). Projected density of states for MNO and WNO, respectively. 159
Figure 4-64. GITT results of MNO and WNO electrodes. (a and b). GITT discharge/charge curve and the corresponding Li$^+$ insertion/extraction diffusivity plot of MNO, respectively. (c and d). GITT discharge/charge curve and the corresponding Li$^+$ insertion/extraction diffusivity plot of WNO, respectively.

Figure 4-65. Contour plot of the operando XRD patterns of MNO.

Figure 4-66. Evolution of lattice parameters of MNO obtained from Rietveld refinement.

Figure 4-67. Contour plot of the operando XRD patterns of WNO.

Figure 4-68. Evolution of lattice parameters of WNO obtained from Rietveld refinement.

Figure 4-69. (a and b). Demonstrations of the Li$^+$ diffusion paths. The NbO$_6$ and WO$_6$ octahedra are shown in green and gray, respectively, and MO$_6$ octahedra and MO$_4$ tetrahedra are shown in purple. The blue arrows indicate possible Li$^+$ diffusion paths, named as Path I, II and III. The black balls indicate Li$^+$ at the initial and final sites for Li$^+$ diffusion. (c-e). The DFT study of the energy barriers of the Li$^+$ diffusion paths along Path I, II and III, respectively.

Figure 4-70. Rietveld refinement of the XRD pattern of the 2000-cycled MWNO electrode.

Figure 4-71. SEM and EDX elemental mapping images of the 2000-cycled MWNO electrode.

Figure 4-72. EDX spectrum and elemental composition report of the 2000-cycled MWNO electrode.

Figure 4-73. SEM and EDX elemental mapping images of the uncycled MWNO electrode.

Figure 4-74. EDX spectrum and elemental composition report of the uncycled MWNO electrode.

Figure 4-75. XPS broad spectra of the 2000-cycled and uncycled MWNO electrodes.

Figure 4-76. (a-f) Mo, W, Nb, C, O and F HRXPS spectra of the uncycled MWNO electrode, respectively.

Figure 4-77. Galvanostatic charge/discharge of an assembled full-cell at a current rate of 0.5 C.

Figure 4-78. Cyclic performance of an assembled full-cell at a high current rate of 10 C.
CHAPTER 1

Introduction
1.1 Lithium-ion Batteries: Solution to CO₂ Emission

Modern human society uses non-renewable fossil fuels as the primary energy sources, particularly, the transportation of cargos and people heavily relying on gasoline and diesel, which directly causes the global warming effect, due to the tremendous emission of CO₂. Owing to the economic growth induced increase in energy demands, although scientists have developed several renewable energy sources, such as solar, wind and tide, the efficient storage of those energy sources is still challenging and becomes urgently needed. Therefore, developing high-performance energy storage devices is the key to the reduction of CO₂ emission.

Lithium-ion batteries (LIBs), which reversibly interconverts chemical and electrical energy through the lithium-ion (Li⁺) insertion/extraction mechanism (Figure 1-1 in the Appendix), are often regarded as the best option to store energy and to replace the gasoline and/or diesel-based engine on vehicles.¹ Noticeably, LIBs are already commercialized in many fields, including cell phones, laptops and electrical vehicles (EVs), indicating the promising property of LIBs.

1.2 Challenges of Current Lithium-ion Batteries

Although LIBs have shine light on EVs so far, their further development and commercialization still face several challenges, including the fast-rechargeability,
capacity shortage and safety concerns, which are mainly rooted from the anode materials.

Graphite, as the most commonly used anode material, has a high thermotical capacity of 372 mAh/g and an extremely low operation voltage plateau at 0.1 V vs Li/Li\(^+\). Thereby, the Li\(^+\) insertion of graphite also causes the formation of SEI, which exhibits insufficient Li\(^+\) transport kinetics and thus results in the growth of undeniable Li dendrites during fast-charging. Such phenomenon also can damage the separator and cause short-circuit in the cell and safety issues, impeding the development of graphite in fast-rechargeable LIBs.

To avoid the SEI issues, scientists propose that spinel Li\(_4\)Ti\(_5\)O\(_{12}\) with open Li\(^+\) diffusion channels, excellent structural stability indeed exhibits and high operation voltage of 1.55 V vs Li/Li\(^+\), is potentially fast-rechargeable. However, spinel Li\(_4\)Ti\(_5\)O\(_{12}\) only delivers a low theoretical capacity of 175 mAh/g, which cannot fulfill the practical requirement of high energy density for the next-generation LIBs.

Recently, scientists found the Wadsley–Roth phased niobium-based oxides with crystallographic shear structure, such as TiNb\(_2\)O\(_7\), Mo\(_3\)Nb\(_{14}\)O\(_{44}\) and W\(_3\)Nb\(_{14}\)O\(_{44}\), can perfectly suit the fast-rechargeable LIBs, due to three main aspects. Firstly, these typed materials exhibit slightly higher operation voltage plateaus than spinel Li\(_4\)Ti\(_5\)O\(_{12}\) does (for example, 1.68, 1.68 and 1.57 V for TiNb\(_2\)O\(_7\), Mo\(_3\)Nb\(_{14}\)O\(_{44}\) and W\(_3\)Nb\(_{14}\)O\(_{44}\), respectively), avoiding the safety concerns during fast-charging; secondly, the abundant and reversible Nb\(^{3+}/Nb^{4+}/Nb^{5+}\) redox couples within the materials directly ensure a high theoretical capacity over 250
mAh/g, unchaining the limits of energy density; last but not the least, those materials present open frameworks that is structured by corner-shared octahedral blocks connected with edge-shared octahedral joints (Figure 1-2 in the Appendix), forming three-dimensional interconnected highways and thus ensuring the unhindered electrochemical kinetics in fast-rechargeable LIBs. Therefore, exploiting an effective preparation route of the Wadsley–Roth phased niobium-based oxides is essential to their future commercialization.

1.3 Traditional Preparations of Transition Metal Oxide Anode Materials

1.3.1 Solid-state Mechanochemical Synthesis

As shown in Figure 1-3 a in the Appendix, solid-state mechanochemical synthesis, as a solvent-free preparation method, typically uses mechanical force as the driving force to directly enable chemical transformations via improving the successful collisions and localized temperature, which involves milling and grinding solid-state chemicals without the dissolution process. However, solid-state mechanochemical synthesis often causes heterogeneous morphology, large particle size distribution and low surface area (Figure 1-3 b in the Appendix), impeding the high-rate energy storage.
1.3.2 Hydrothermal and Solvothermal Syntheses

Hydrothermal and solvothermal syntheses refer to the preparations of materials in sealed and heated aqueous or organic solutions at high temperature and high pressure, respectively. As displayed in Figure 1-4 in the Appendix, during the preparation, at high temperature and high pressure, the reactants are well dissolved, dispersed, transferred and coordinated in water and organic solvents that act as the host.5 Thereby, the crystallinity, morphology and particle size of the prepared materials can be well-controlled via these synthesis routes, especially applying templating agents. However, hydrothermal and solvothermal syntheses are time-consuming and complicated.5-6

1.3.3 Hard and Soft Templates

The soft templates are supramolecular entities like self-assembled arrangements of structure-directing molecules (surfactants, block-copolymers are the common choice, such as F127 and P123). The soft template-based preparation involves the co-assembly of surfactant molecules and guest species through electrostatic forces and/or hydrogen bonding into a highly ordered structure.7 To form the final mesoporous materials, calcination has to be performed (burns and removes the used soft templates), which unfortunately leads to the huge environment-unfriendly CO2 emission.8-9 Thereby, the soft-templating approach cannot fit the future large-scale preparation of high-performance transition metal oxide anode materials for the commercialization fast-rechargeable LIBs on EVs.
Hard templates are solid-state templating materials, such as silica and aluminia materials, which rigidly direct the morphology and particle size of the materials.\textsuperscript{10-11} To remove the templates, some highly toxic and caustic etching chemicals have to be used, namely NaOH and HF,\textsuperscript{7} which concurrently causes the potential safety concerns and environmental problems and thereby cannot fulfill the requirement of the future pollution-free industrialization of transition metal oxide-based high-performance LIBs.

1.4 Ionothermal Synthesis

Ionothermal synthesis refers to the material preparation that uses ionic liquids (ILs) as the solvent and/or structure directing template for the formation of solid-state materials.\textsuperscript{12}

Typically, ILs are organic-based liquid-state salts at below 100 °C or even at room temperature.\textsuperscript{13} Owing to the strong Coulombic interactions between the constituent bulky ions of ILs (the delocalization and screening of charges and leading to the reduction of the lattice energy and the melting point) and the vast possible cation and anion combinations, ILs present desirable unique chemical and physical properties, including the tunable polarity, the hydrophobicity, the solvent miscibility, the non-flammability and the thermal stability, and thereby ILs are generally considered as an environmentally benign reaction media.\textsuperscript{14} Additionally, as shown in Figure 1-5 in the Appendix, the templating effect of ILs is based on the hydrogen bonding between the anions of ILs and precursors and
the \( \pi-\pi \) stack interaction between the neighboring imidazolium rings. Notably, the proposed alignment of the positively charged neighboring imidazolium rings is mainly attributed to the hydrogen bonding between the metal-oxo-metal framework and the anions of ILs, which leads to the oriented arrangement of anions and thereby causes the aligned imidazolium rings with \( \pi-\pi \) stacking.\textsuperscript{15-16} Those effects above eventually results in the formation of a wormlike mesoporous frameworks.\textsuperscript{15, 17-18} Furthermore, thanks to the excellent compatibility of ILs with organic solvents, the templated ILs can easily be recycled to avoid the potential environmental issues.\textsuperscript{19-20}

Therefore, ionothermal synthesis with promising properties should be regarded as a highly facile, safe, and eco-friendly preparation method for the syntheses of high-performance anode materials.

In this dissertation, the employed ionothermal syntheses adapt the nonhydrolytic sol-gel method, which is based on the hydrolysis and polycondensation reactions (shown in Figure 1-6 in the Appendix) in non-aqueous condition. Comparing the hydrolytic route with uncontrollable hydrolysis rates that lead to heterogeneous forms and phase separation, the nonhydrolytic sol-gel method is advantageous in the uniform reaction rates and desirable homogeneous dispersions of metal cations in mixed oxides were achieved.\textsuperscript{21} Typically, the chemical reactions involves non-aqueous conditions and oxygen donors other than water, such as alcohols and carboxylates, which exhibit high compatibility with the used hydrophobic IL, 1-butyl-3-methylimidazolium
bis(trifluoromethanesulfonyl)imide ([BMIm][NTf₂]), leading to the homogenous metal oxo matrix around [BMIm][NTf₂] due to the controllable hydrolysis of the metal precursors on the surface of “IL supramolecular network” via electrostatic interaction.¹⁸

1.5 Typical Characterizations of Ionothermally Prepared Anode Materials

1.5.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

To verify the success of the preparation of ILs, the ¹H and ¹³C NMR spectra of the synthesized ILs were recorded on a JEOL 400 MHz YH spectrometer using deuterated dimethyl sulfoxide. Typically, as shown in Figure 1-7 in the Appendix, applying an external magnetic field either aligns the nuclei spin with or against the external magnetic field. Nuclei absorb radio-wave to move to a higher spin energy state, and NMR occurs as the nuclei resonate between their spin energy states, causing the variation of resonance frequency, which thereby enables the determination of the functional groups and the electronic structure of a molecule.

1.5.2 X-ray and neutron powder Diffractions (XRD and NPD) and Raman Spectroscopy

To confirm the identities of the prepared TMOs, XRD was applied. Typically, as shown in Figure 1-8 in the Appendix, the constructive X-ray Bragg diffraction (Bragg's Law: nλ = 2d sin θ, where n and λ are the integer determined by the order
given and the X-ray wavelength, respectively) reveals the lattice structure, which is based on the wavelength of X-ray to the diffraction angle and the lattice spacing in a crystal.

To further confirm the study the doped structure of the prepared TMOs, NPD experiment was carried out. Typically, as shown in Figure 1-9 in the Appendix, the principle of NPD is identical to XRD, which is based on the constructive Bragg diffraction, while neutron beam is employed. Owing to the interaction between the incident neutrons and atomic nuclei, the diffraction is advantageous for the localization of atoms.

XRD and/or NPD Rietveld refinement reveal the crystal information of the materials, including the fundamental six lattice parameters (a, b, c, α, β and γ), lattice volume, strain, atomic arrangement, bond length, crystallite size and crystallinity. This method is based on the nonlinear least squares method and requires the reasonable initial approximation of many free parameters, including unit cell dimensions and coordinates of all atoms in the crystal structure. The peak position shifting corresponds to the lattice parameters variation induced distortion crystallographic planar. Peak intensity is directly ascribed to the atomic parameter, such as atomic coordinates. Based on the aforementioned two aspects, the determination of the positions of dopants in the lattice can be achieved. Additionally, the peak shape reflects the crystallinity, disorder and defect of the material.
To further study the structure of the prepared TMOs, Raman spectroscopy was used. Typically, as shown in Figure 1-10 in the Appendix, Raman spectroscopy is based on the inelastic photon scattering, named as Raman scattering. Typically, a monochromatic light interacts with molecular vibrations, phonons, or other excitations in the molecular, which lead to the photon energy shifts, thereby providing the vibrational mode information.

1.5.4 Scanning and Transmission Electron Microscopies (SEM and TEM)

To understand the morphology and microstructure of the prepared anode materials and the estimate the templating effect of IL, SEM and TEM were used. In a SEM, the incident electrons with high kinetic energy are dissipated into a variety of signals, which mainly includes the secondary electrons (morphology and topography) and backscattered electrons (contrasts in composition), due to the deceleration of the incident electrons induced the electron-sample interactions. In a TEM, the incident electrons with ultra-high kinetic energy directly transmit through the thin specimen to form images on a fluorescent screen.

1.5.5 X-ray Photoelectron Spectroscopy (XPS)

To study the elemental compositions and valance states of the prepared anode materials, XPS was used. The XPS spectra were collected on a Thermo scientific model K-alpha instrument with a monochromated Al Kα X-ray source (1486.6 eV). Based on the photoemission effect, as shown in Figure 1-11 in the Appendix, X-ray is irradiated on a solid surface to emit electrons with characteristic kinetic energy, which enables the identification and quantification of surface elements.
Specifically, as shown Figure 1-12 in the Appendix, the intersection of the semi-cycle on the horizontal axis in the high frequency region indicates the typical Ohmic impedance of the electrode. The only difference of the composition of our electrodes (70 wt.% active material: 20 wt.% conductive carbon: 10 wt.% binder) is the active materials, and thereby it is valid to make an approach to demonstrate the reduced Ohmic resistance of our doped material. Additionally, the intersection of the semi-cycle on the horizontal axis in the mid-high frequency region reveals the charge transfer impedance.

1.6.2 Galvanostatic Intermittent Titration Technique (GITT)

The GITT contains repeating current pulse duration and relaxation (Figure 1-13 in the Appendix), which reveals the Li\(^+\) diffusion coefficient \((D)\) and electrochemical process of an active material. This method is based on a few assumptions: uniform electrode, current and Li\(^+\) diffusion flux (Fick’s law); no volume variation and structural evolution. Noticeably, for the phase-transition-based electrode material, Li\(^+\) transport in the electrode involves both movement of an interphase boundary and ionic diffusion, which breaks the aforementioned assumption and thereby leads to an apparent \(D\) rather than a true \(D\).

Specifically, when applying a current pulse, the potential initially presents a rapid variation, due to the \(iR\) drop, where \(R\) is the sum of the uncompensated resistance and the charge transfer resistance. Subsequently, the potential slowly varies, which is rooted from the galvanostatic charge or discharge pulse, leading to a deposition of small amount of Li\(^+\) onto the electrode surface. Afterwards, during
the following relaxation, the Li$^+$ diffusion equalizes the composition in the electrode, which consequently causes a sudden $iR$-based potential variation followed by a slow decrease until reaching the equilibrium state. Afterwards, the Li$^+$ The following equation was used to calculate the $D$ values for different anode materials, $D = \frac{4}{\pi \tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2$, where $\tau$, $n_m$, $V_m$, $S$, $\Delta E_s$, $\Delta E_t$ are the duration of the current pulse (s), the number of moles (mol), the molar volume of the active material (cm$^3$/mol), the electrode/electrolyte contact area (cm$^2$), the equilibrium potential change induced by current pulse and the potential change during the constant current pulse (neglecting the $iR$ drop), respectively.
CHAPTER 2

Ionic Liquid-Directed Nanoporous TiNb$_2$O$_7$ Anodes with Superior Performance for Fast-Rechargeable Lithium-ion Batteries
2.1 Publication Statement

A version of this chapter was originally published by Runming Tao, Guang Yang, Ethan C. Self, Jiyuan Liang, John R. Dunlap, Shuang Men, Chi-Linh Do-Thanh, Jixing Liu, Yiman Zhang, Sheng Zhao, Hailong Lyu, Alexei P. Sokolov, Jagjit Nanda, Xiao-Guang Sun, and Sheng Dai:


Runming Tao provided major contribution and authorship to this publication. He completed all the syntheses and characterizations of the materials, except the XPS data collection. The contributions of co-authors are as follows: Guang Yang, Ethan C. Self, Jiyuan Liang, John R. Dunlap, Shuang Men, Chi-Linh Do-Thanh, Jixing Liu, Yiman Zhang, Sheng Zhao, Hailong Lyu, Alexei P. Sokolov, Jagjit Nanda, Xiao-Guang Sun, and Sheng Dai discussed the results and suggested the manuscript revisions.

2.2 Abstract

Four novel ionic liquid-directed nanoporous TiNb₂O₇ (NPTNO) materials and a bulk TiNb₂O₇ baseline-material are prepared and studied to investigate their
electrochemical performance in lithium-ion batteries (LIBs). The typical characterizations reveal the successes of material preparation and indicate the relationship among crystallinity, porosity and calcination temperature. The LIB half-cell tests suggest that the NPTNO material calcinated from 700 °C (denoted as TNO700) exhibits the best cyclability and rate-capability, and the LIB full-cell experiments illustrate the practicality of TNO700. To further characterize the origin of the superb electrochemical performance of TNO700, a series of studies were carried out. The X-ray diffraction, scanning electron microscope and X-ray photoelectron spectroscopy tests elucidates the excellent structural robustness and electrochemical stability of TNO700, which dramatically benefits the long-term cyclability. The galvanostatic intermittent titration technique confirms the high Li$^+$ diffusivity of TNO700, which directly enables an unhindered Li$^+$ transfer process and thereby ensures the sensational rate-capability of TNO700. Therefore, this work establishes the potential of ionothermal syntheses in the preparation of energy storage materials and demonstrates the advantages of TNO700 as a promising anode material candidate for fast-rechargeable LIBs.

2.3 Introduction

Lithium-ion batteries (LIBs) are a type of promising power source of electric vehicles (EVs), which can alleviate the global warming issues due to their avoidance of CO$_2$ emission, unlike the traditional diesel and gasoline vehicles. However, the current anode materials cannot satisfy the future requirements of
high-performance and safety. Specifically, graphite with a high theoretical specific capacity of 372 mAh/g is the most common anode material, while graphite suffers from its low operating potential of 0.1 V versus Li/Li⁺ and low Li⁺ diffusivity, causing the safety concerns of solid electrolyte interface (SEI) and the formation of lithium dendrites, which dramatically restrict the future application in fast-rechargeable LIBs.²³-²⁷ Although, as the other widely used anode material, Li₄Ti₅O₁₂ (LTO) with high operating potential of 1.55 V vs Li/Li⁺ and zero-strain property does not exhibit SEI issue and thereby is suitable for fast-charging, the low specific capacity (about 160 mAh/g) of LTO deeply impedes its competitiveness as a fast-rechargeable anode material for high-performance LIBs.²⁴, ²⁷-²⁹ Therefore, developing a promising anode material with excellent rate-capability, high capacity, promising cyclability and reliable safety is urgently needed for the future fast-rechargeable LIBs in EVs.

In 2011, Goodenough’s research group first proposed that Wadsley–Roth phased TiNb₂O₇ (TNO) with three promising redox couples (Ti⁺⁴/Ti⁺³, Nb⁺⁵/Nb⁺⁴ and Nb⁺⁴/Nb⁺³) delivers a high specific capacity of 388 mAh/g.³⁰ Moreover, the operating voltage of TNO is 1.66 V vs Li/Li⁺, which can effectively avoid the SEI issues and thereby ensures the safety.³¹ In addition, TNO presents layered monoclinic structure based on the metal-oxygen octahedra, stabilizing intercalated Li⁺ and achieving excellent cyclability. With the aforementioned promising properties, TNO is considered to be a promising candidate for the next-generation anode material, while the intrinsic electrochemical kinetic issues of poor electrical and ionic conductivities still restrict the future practical applications of TNO.⁶, ²⁶
Therefore, exploiting a new strategy to resolve the discussed electrochemical kinetic limitations above is the key to fast-rechargeability. As an important kinetic characteristic of Li\(^+\) insertion–extraction, the solid phase Li\(^+\) diffusivity determines the rate-capability of TNO-based cells. To improve the electrochemical kinetics of TNO material, shortening the Li\(^+\) diffusion distance by nanosizing the material is a highly effective route, which directly reduces the Li\(^+\) diffusion time \(t\) based on the correlation: \(t \sim L^2/D\), where \(L\) and \(D\) correspond to the Li\(^+\) diffusion length and the Li\(^+\) diffusion coefficient in solid material, respectively.\(^{26, 32-33}\) Meanwhile, another useful approach for enlarging the Li\(^+\) diffusion kinetics is to improve the contact area between the electrode and electrolyte via preparing porous anode materials due to the dependence of \(D\) on the structure of the material,\(^6\) and thereby porous structure with large and open surface area can vastly enhances the Li\(^+\) diffusion efficiency.\(^{34}\) More interestingly, porosity also offers extra free space to relieve the structural strain and to alleviate the volume fluctuation caused by the repeating Li\(^+\) insertion–extraction processes, which maintains the mechanical stability and structural integrity, ensuring the excellent long-term cyclability.\(^{26, 35-37}\) Therefore, synthesizing nanoporous TNO (NPTNO) with abundant “highways” for Li\(^+\) diffusion should be regarded as the key to fast-rechargeable LIBs.

Traditionally, TNO is synthesized via mechanochemical methods, while the involved ball milling and high temperature treatment inevitably cause heterogeneous morphology, large particle size and low surface area, resulting to poor rate-capability.\(^{38-39}\) Zhang and his co-workers prepared nano-TNO by
solvothermal method, which is highly complicated and time consuming. In 2014, although our group obtained NPTNO through a block copolymer assisted sol-gel route, the burning of the involved block copolymer during the calcination causes the safety concerns of huge volume expansion and leads to the large eco-unfriendly CO₂ emissions, thereby failing to achieve the future large-scale industrial production. Therefore, developing a novel alternative preparation method to facilitate and eco-friendly prepared NPTNO is highly urgent.

Ionic liquids (ILs) with some promising properties, such as the negligible volatility and versatile solvation, are applied in multiple fields, including being solvents and/or templates in material syntheses and electrolytes in energy storage devices. Particularly, Zhou et al. synthesized mesoporous silica by 1-butyl-3-methylimidazolium ([BMIm]⁺) -based ILs as porous structure directing templates and suggested that the mechanisms of the formation of mesoporous oxide frameworks are based on the ILs anions-precursors hydrogen bonding and the neighboring imidazolium rings’ \( \pi-\pi \) stacking. ILs not only act as the templates in porous silica preparation but also can exhibit templating effects in the syntheses of porous carbonaceous and metal oxides, which is attributed to the facilitation of the sol-gel hydrolysis and polycondensation of metal precursors on the surface of IL “super-molecular” networks. Inspired by the aforementioned work and with the avoidance of templating block polymer, we propose that a [BMIm]⁺-based IL can serve as the porous structure directing template to synthesize NPTNO as a promising anode material for fast-rechargeable LIBs.
Moreover, owing to the excellent solubility and compatibility of IL in organic solvents,\textsuperscript{19-20} enabling the recycling of ILs, our synthesis method thereby holds great potential.

Herein, a facile and novel IL-templating preparation strategy of fast-rechargeable NPTNO anode material for LIBs is reported, revealing the templating potential of ILs in the syntheses of energy storage materials. In this work, we comprehensively characterized the structure and electrochemical performance of the obtained NPTNO materials. In brief, the prepared NPTNO anodes indeed exhibit sensational rate-capability, high specific capacity and excellent cyclability, which can be regarded as a promising candidate for realizing future fast-rechargeable LIBs. Furthermore, the superb rate-performance is demonstrated the galvanostatic intermittent titration technique (GITT) tests, illustrating the enhanced Li\textsuperscript{+} diffusion kinetics via the short Li\textsuperscript{+} diffusion distance and the large NPTNO-electrolytes contact area, and the desirable cyclability is studied by the X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy analyses of the long-term cycled electrode, confirming the good structural and electrochemical stabilities of the NPTNO material.

2.4 Experimental

2.4.1 Ionic Liquids Syntheses

Solvents, reagents, and chemicals were purchased from commercial vendors and used without further purification. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were
recorded at ambient temperature on a JEOL 400YH spectrometer, and $^1$H and $^{13}$C NMR chemical shifts were referenced to the residual solvent.

As shown in **Figure 2-1 a** in the **Appendix**, 1-Butyl-3-methylimidazolium bromide ([BMIm]Br) synthesis: 1-Bromobutane (14.83 mL, 134.71 mmol) was slowly added to 1-methylimidazole (9.76 mL, 122.46 mmol) under stirring at 0 °C. The mixture was allowed to continue stirring at room temperature for 3 days after which it was washed with diethyl ether (3 x 20 mL) and dried under vacuum at room temperature to give the product as a tan solid (26.81 g), which was carried on to the next step. As shown in Fig. **Figure 2-1 b** in the **Appendix**, 1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ([BMIm]NTf$_2$) synthesis: The obtained [BMIm]Br was dissolved in water (140 mL) and decolorized by adding activated coconut charcoal (3.30 g), followed by stirring at 70 °C for 16 h. After cooling down to room temperature, the mixture was filtered and washed with water. The filtrate was then added to a solution of lithium bis(trifluoromethanesulfonyl)imide (38.67 g, 134.71 mmol) in water (70 mL), and the reaction was stirred at room temperature overnight, forming a visible bottom liquid layer. Dichloromethane (150 mL) was added to the mixture, and the resulting bottom organic layer was separated, washed with water (4 x 150 mL), dried with magnesium sulfate, filtered, concentrated, and finally stirred at 65 °C under vacuum for 24 h to yield the product as a colorless liquid (46.23 g, 90% over 2 steps). $^1$H NMR (DMSO-$d_6$, 400 MHz): $\delta$ 9.29 (s, 1H), 7.83 (s, 1H), 7.76 (s, 1H), 4.18 (t, $J = 7.2$ Hz, 2H), 3.86 (s, 3H), 1.82–1.70 (m, 2H), 1.31–1.18 (m, 2H), 0.88
(t, J = 7.4 Hz, 3H) (as shown in Figure 2-2 in the Appendix). $^1$H NMR (DMSO-$d_6$, 400 MHz) $\delta$ 9.10 (s, 1H), 7.76 (s, 1H), 7.69 (s, 1H), 4.15 (t, J = 7.1 Hz, 2H), 3.84 (s, 3H), 1.82–1.71 (m, 2H), 1.32–1.20 (m, 2H), 0.90 (t, J = 7.3 Hz, 3H) (as shown in Figure 2-3 in the Appendix). $^{13}$C NMR (DMSO-$d_6$, 101 MHz) $\delta$ 136.5, 123.6, 122.3, 119.5 (q, $J_{C-F}$ = 321.9 Hz, NTf$_2$), 48.5, 35.7, 31.4, 18.8, 13.2 (as shown in Figure 2-4 in the Appendix).

2.4.2 Materials Syntheses

Reagents and solvents were purchased from commercial vendors and used without further purification.

As presented in Figure 2-5 in the Appendix, NPTNO was prepared via a facile IL-assisted sol-gel method. Typically, 25 mmol of Ti(OC$_4$H$_9$)$_4$ and 50 mmol of NbCl$_5$ were mixed with 15 mmol of [Bmim][NTf$_2$] in ethanol and were stirred for 12 h. Afterwards, the mixture was transferred into a Petri dish and was gelled at 50 °C followed by a 2 h aging at 200 °C. Subsequently, the [Bmim][NTf$_2$] was extracted and recycled from sample by ethanol wash and rotary evaporation. Lastly, the as-obtained sample was calcined at different temperatures (400, 600, 700 and 850 °C) in air for 3 h (ramp rate 2 °C/min) to obtain the final NPTNO materials (denoted as TNO400, TNO600, TNO700 and TNO850, respectively).

As shown in Figure 2-6 in the Appendix, equimolar (5mmol) of Nb$_2$O$_5$ (1.329 g) and anatase-type TiO$_2$ (0.3994 g) were loaded into a commercially available 25 mL screw-capped stainless-steel reactor and ball milled along with 3 diameter of 10 mm steel balls for 2 h at a vibrational frequency of 30 Hz on a
planetary ball mill (Retsch, Mixer Mill MM400). The resulting white powders were then calcinated at 1000 °C for 20 h in air (ramp rate 10 °C/min).

2.4.3 Typical Characterizations

Powder X-rays diffraction (XRD) patterns were collected on a Panalytical Empyrean diffractometer at conditions of 45 kV and 40 mA. The obtained XRD patterns were analyzed by Jade 6. N\textsubscript{2} isothermal adsorption–desorption tests were performed on a TriStar 3000 volumetric adsorption analyzer from Micromeritics Instrument Corp. Scanning electron microscope (SEM) imaging was carried on a Carl Zeiss Auriga 40 SEM microscope, and the samples were coated with Iridium on a sputter coater from Structure Probe Inc.. SEM element mapping was performed on a Carl Zeiss EVO MA15. Transmission electron microscope (TEM) images were collected on a Carl Zeiss Libra 200 MC TEM microscope. Raman spectra were acquired from a WITec GmnmbH Alpha 300 confocal Raman microscope with a solid-state 532 nm excitation laser for 60 s. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific X-ray photoelectron spectrometer with a monochromated Al K\textalpha\ (1486.6 eV) X-ray source focused to a 400-micron spot under a pressure below 1×10\textsuperscript{-7} mbar. The energy calibration and deconvolution of XPS peaks were conducted by CasaXPS (Casa Software Ltd).

2.4.4 Electrode Fabrication

The sample electrodes were prepared with the TNO active materials, Super C65\textsuperscript{TM} carbon black and polyvinylidene fluoride (PVDF) at a mass ratio of 70:20:10.
The slurry was casted onto a Cu foil and dried under an infrared lamp, followed by an 120 °C vacuum oven drying for 12 h. The weight loading of the active material on the fabricated electrodes was 1.3 - 2.3 mg/cm².

**2.4.5 Electrochemical Property Studies**

The CR2032-type coin cells were prepared in an argon-filled glove box with H₂O and O₂ contents less than 1 ppm. The half-cells were assembled by pairing the as-prepared electrode to lithium counter electrode, and the full-cells were assembled by using LiNi₀.₅Mn₁.₅O₄ cathodes. Celgard 2500 was used as the separator. Gen2 electrolyte was used (consisting of 1.2 M of LiPF₆ in ethylene carbonate (EC)/ ethyl methyl carbonate (EMC) with a weight ratio of 3/7 from Tomiyama Pure Chemical Industries, LTD). The half-cells and full-cells galvanostatic charge-discharge tests were carried out at various C-rates in the voltage range of 1.0 - 3.0 V and 1.5 - 3.5 V on a Maccor Series 4000 tester, correspondingly. Cyclic Voltammetry (CV) tests with potential range of 1.0 - 3.0 V were performed on a BioLogic MPG2 system at a scan rate of 0.05 mV/s by using half-cells. Half-cells' Galvanostatic Intermittent Titration Technique (GITT) studies were conducted on a BioLogic MPG2 system by employing a constant 0.05 C current pulse for 200 s followed by an 1 h rest within potential range of 1.0 - 3.0 V.
2.5 Results

2.5.1 Structural Characterizations

Figure 2-7 a and b in the Appendix present the X-ray diffraction (XRD) patterns of NPTNO and bulk TNO (BTNO) materials annealed at different temperatures, which is directly consistent with the standard XRD pattern (JCPDS #77-1374). The typical diffraction peaks of (002), (110), (003), (-602), and (-512) can be assigned to the ReO₃-type structure with a space group of C2/m.⁶⁰-⁶¹ Furthermore, the obtained crystal structures of NPTNOs are attributed to monoclinic system with prismatic shape and have the point group of C₂h.²⁶, ³⁸, ⁶⁰ The XRD patterns suggest that the materials calcinated at higher temperatures are more crystalized. Noticeably, TNO material crystallizes at around 600 °C. The calculated crystallite sizes of TNO700 and TNO850 by Scherrer equation are about 17.5 and 25.6 nm, respectively. Such difference can be ascribed to the crystal growth at higher temperature. As shown in Figure 2-7 c in the Appendix, the Rietveld refinement suggests that TNO700 exhibits lattice parameters of a = 20.351 Å, b = 3.801 Å, c = 11.882 Å, α = 90.0 °, β = 120.19 ° and γ = 90.0 °.

Figure 2-8 in the Appendix presents the Raman spectra of NPTNO materials in range. Particularly, the peaks at 1005 and 901 cm⁻¹ correspond to the metal–oxygen stretching of edge/corner-shared NbO₆ octahedra, respectively.⁵¹ The three peaks at 650, 535 and 398 cm⁻¹ are assigned to the metal–oxygen stretching of TiO₆ octahedra.⁵¹, ⁵² The peaks around 274 cm⁻¹ are attributed to the
symmetric and antisymmetric bending vibrations of O–Ti–O and O–Nb–O.[51] The sharp peak at 147 cm\(^{-1}\) belong to the external models based on the cation-oxygen stretching.[51, 53, 54] Noticeably, the Raman spectra also reveal that TNO850 has higher crystallinity than TNO700 does, which is in good agreement with their XRD patterns (Figure 2-7 b in the Appendix).

The nitrogen adsorption-desorption isotherms Brunauer–Emmett–Teller (BET) plots shown in Figure 2-9 a in the Appendix, presents the typical IUPAC H4-type loops, indicating that the IL-templated NPTNO materials have internal porosity with three-dimensional intercrystalline mesopores,\(^{62}\) which leads to large surface area and can facilitate the Li\(^+\) diffusion kinetics in the LIB cells. Specifically, TNO400, TNO600, TNO700 and TNO850 materials have high specific surface area of 169, 101, 72 and 38 m\(^2\)/g, respectively. Noticeably, the higher calcination temperatures can reduce the specific surface areas of the NPTNO materials, which is due to the collapse of porous structure at high temperature. Figure 2-9 b in the Appendix exhibits the Barrett-Joyner-Halenda (BJH) pore size distribution plots. The amorphous TNO400 material has a wide range of pore size, while the crystallized NPTNO materials present mesopores with size of 23.1 nm. The formation of pores is attributed to the occupied space of the templating IL due to the IL anions-precursors hydrogen bonding effects and the neighboring imidazolium rings’ \(\pi-\pi\) stack interactions.\(^{15}\)

To obtain a direct view of the mesoporous structure, scanning electron microscopy (SEM) was applied. As shown in Figure 2-10 a and c in the Appendix,
TNO700 and TNO850 materials present three-dimensionally porous structure, conforming to the observation of the aforementioned Nitrogen adsorption-desorption tests. Noticeably, such morphology can directly lead to a high contact area between electrolytes and electrode and thereby enables the fast \( \text{Li}^+ \) diffusion in the LIB cells. Furthermore, as shown in Figure 2-10 b and d in the Appendix, the SEM element mapping suggest that the NPTNO materials have homogeneous element distribution of Ti, Nb and O in (Figure S1 b and d in the Appendix).

To further investigate the morphology and microstructure of the obtained NPTNO materials, transmission electron microscopy (TEM) was employed. In Figure 2-11 a and c in the Appendix, the measured average crystallite sizes of TNO700 and TNO850 are around 18.4 and 29.2 nm, respectively, which is in good agreement with the estimated crystallite sizes from XRD patterns. Noticeably, the difference of sizes is mainly attributed to the crystal growth during the higher temperature calcination. Moreover, the selected area electron diffraction (SAED) patterns in Figure 2-12 in the Appendix further indicate that TNO850 has a higher crystallinity than TNO700, conforming to the discussed XRD patterns below. The measured d-spacings in Figure 2 b and d in the Appendix are 0.370 and 0.341 nm, corresponding to the (110) and (003) crystallographic planes, respectively.

2.5.2 Electrochemical Performance Studies

To characterize the electrochemical performance of the IL-templated NPTNO materials, half-cells were assembled with Li metal as the counter electrodes and were tested between 1.0 to 3.0 V. As the cyclic voltammetry (CV)
curves shown in Figure 2-13 in the Appendix, the huge redox peaks at around 1.60 and 1.72 V are ascribed to Nb\(^{5+}/Nb^{4+}\) redox couple and the small peaks at around 1.73 and 2.00 V to the Ti\(^{4+}/Ti^{3+}\) redox pair.\(^{[13, 22, 55]}\) Noticeably, the reduction peak position between the first cycle and the following cycles is different, which is mainly attributed to the Fermi level migration, metal-oxygen octahedra distortion caused by the initial Li\(^+\) insertion and the potential formation of SEI layer.\(^{[12, 13, 55]}\) More interestingly, the highly overlapped CV profiles after the first cycle suggest that the IL-directed TNO700 anode exhibits excellent electrochemical and cycling stability.\(^{[55]}\) Noticeably, with similar active material loading, the shape of the three CV profiles below are obviously different. This is mainly due to the double-layer effect (charge build-up on the large surface area of the porous structure: the chemical interactions between the surface molecule and the first layer ions and corresponding Coulomb force between the first layer ions and compositely charged ions).\(^{[63]}\) Noticeably, such phenomenon is also observed in a previous study of TNO material with large surface area, which clearly indicates the positive effect of the surface capacitance-controlled capacity, ensuring abundant active sites for the Li\(^+\) storage.\(^{[60]}\) Thereby, TNO700 with the highest specific surface area presents the bulkiest CV profile.

As presented in Figure 2-14 a in the Appendix, TNO700 delivers an initial discharge (Li\(^+\) insertion) and charge (Li\(^+\) extraction) capacities of 316 and 276 mAh/g with a high Coulombic efficiency of 87.7\%. For TNO850, the initial discharge and charge capacities are 306 and 279 mAh/g with a Coulombic
efficiency of 91.1% (Figure 2-14 b in the Appendix). For comparison, the initial cycle’s discharge, charge capacities and calculated Coulombic efficiency of BTNO are 325, 302 mAh/g and 93.0%, respectively (Figure 2-14 c in the Appendix). The reversible capacities of TNO700, TNO850 and BTNO are 281, 280 and 275 mAh/g. Obviously, the specific capacity of TNO700 are distinctively higher than that of LTO, and it’s almost comparable to some commercial graphite anodes (300 - 330 mAh/g). The obtained operation voltage of the three materials are observed at 1.66 V. In addition, the higher irreversible capacities of NPTNO materials mainly stem from the potential side reactions between electrolytes and NPTNO’s numerous active sites on the large surface, reducing the initial Coulombic efficiency.

To investigate the rate-capability of the prepared materials, several C rates were applied. As shown in Figure 2-15 in the Appendix, TNO700 exhibits the best performance. Particularly, the average reversible discharge capacities of TNO700 over 10 cycles at 10, 20 and 50 C are 235, 218 and 210 mAh/g, respectively. TNO850 exhibits average discharge capacities of 209, 203 and 194 mAh/g at 10, 20 and 50 C, correspondingly. TNO700 delivers higher capacity than TNO850 does, which is mainly due to the relatively smaller particle sizes and relatively higher porosity of TNO700. In sharp contrast, BTNO only has 76, 131 and 58 mAh/g at 10, 20 and 50 C, respectively. Therefore, the distinctive difference of rate-performance among the three materials indicates the superiority of the
nanocrystal composed mesoporous structure, which is directed by IL, dramatically benefiting the rate-capability.

Besides excellent rate-capability, a superb cyclability is also required for the next-generation high-performance LIBs with fast-rechargeability. Interestingly, as shown in Figure 2-16 in the Appendix, NPTNO delivers sensational long-term cycle life at a high C rate, especially TNO700. Specifically, the reversible capacities of the first cycle and the 1000\textsuperscript{th} cycle of the nano-porous TNO700-based half-cell are 243 and 180 mAh/g, respectively, corresponding to a promising capacity retention of 74\%. For TNO850, owing to its low porosity, the cell does not perform like TNO700, which only exhibits 241 and 112 mAh/g in the first and the 1000\textsuperscript{th} cycles, respectively, leading to a capacity retention of 46\%. Noticeably, the NPTNO materials present low Coulombic efficiencies in the initial cycles, causing by the side reactions on the large surface area, in good agreement with 0.1 C discharge-charge tests above. In sharp contrast, the BTNO-based cell only presents a low capacity retention of 28\%, failing to fulfill the practical requirements, which is attributed to unfavorable volume fluctuation during the repeating Li\textsuperscript{+} insertion-extraction processes. Therefore, such obvious difference of cyclability among TNO700, TNO850 and BTNO indicates that the IL-templated porosity with extra free space can significantly relieve the structural strain from Li\textsuperscript{+} insertion-extraction and can maintain the mechanical stability and structural integrity, which leading to extraordinary cyclic performance.\textsuperscript{26, 35-37, 60}

To further demonstrate the practicality of the IL-directed TNO700 material,
LiNi_{0.5}Mn_{1.5}O_4 (LNMO) cathodes were coupled with TNO700 anodes to assemble full-cells. As shown in **Figure 2-17 a** and **c** in the **Appendix**, TNO700 anodes exhibit high reversible capacities of 252 and 203 mAh/g and excellent capacity retentions of 81% and 87% at C rates of 1 and 2 C over 1000 cycles with Coulombic efficiency of above 99.9%. Furthermore, **Figure 2-17 b** and **d** in the **Appendix** suggest that the operation voltage of full-cells stables at 3.0 V. Noticeably, such cyclability of the IL-templated TNO700 is superior or comparable to that of our group's previous copolymer-directed NPTNO material (a reversible capacity of 220 mAh/g with a capacity retention of 82% over 1000 cycles at 1 C).\(^{26}\)

To the best of our knowledge, the TNO700 in this work achieves the best full-cell cyclability in TNO materials. In brief, such promising performance of the LNMO-TNO700 full-cells implies the great potential of ionothermal syntheses and indicates the promising practicality of the IL-templated TNO700 for future application on EVs.

To fully uncover the long-term cycling stability of TNO700, an 1000 cycled TNO700 half-cell was dissembled and characterized. As shown in **Figure 2-18 a** in the **Appendix**, the XRD pattern of cycled TNO700 is highly similar with that of the pristine TNO700 powder, which reveals the promising stability and robustness of the crystal structure of the IL-templated NPTNO.\(^{38}\) As the SEM images presented below (**Figure 2-19** in the **Appendix**), the uncycled and the 1000 cycled electrodes share parallel morphology, implying the excellent structural integrity of the TNO700 material. No obvious SEI can be found after the long-term cycling.
Additionally, the EDS elemental mappings show even distributions of Ti, Nb, O, C and F elements.

To further study the cycling induced potential chemical composition variations, X-ray photoelectron spectroscopy (XPS) was applied. As shown in Figure 2-18 b in the Appendix, the broad XPS spectra of the uncycled and the 1000 cycled TNO700 electrodes are similar, which both contain Ti, Nb, O, C and F elements, being in good agreement with the SEM EDS element mapping results above. Particularly, as displayed in Figure 2-20 in the Appendix, the cycled and uncycled TNO700 electrodes have highly similar high-resolution XPS (HRXPS) spectra for Ti and Nb, which is attributed to the excellent electrochemical stability of TNO700.\(^{60,66-67}\) To determine the existence of the potential side reactions during the cycling, the C, O and F HRXPS were further collected. As shown in Figure 2-18 c and d in the Appendix, the variations of chemical compositions of C, O and F elements suggest that side reactions indeed occur during the long-term cycling. Figure 2-18 d in the Appendix presents C=O group and C-OH/C-O-C groups at 287.8 and 286.2 eV,\(^{62,68}\) which correspond to the decomposition of carbonates during the cycling and can be further seen in the O HRXPS.\(^{59,62,64-65}\) Moreover, the appeared LiF peak at 686.1 eV on the F HRXPS is due to the side reaction of LiPF\(_6\) salt.\(^{62}\)

To understand the excellent rate-capability of the TNO700, galvanostatic intermittent titration technique (GITT) was used to measure the Li\(^+\) diffusion coefficients (\(D\)). The apparent Li\(^+\) diffusion coefficients of TNO anodes are
calculated by the following Equation derived from Fick’s second law,\textsuperscript{[21, 68]} $D = \frac{4}{\pi \tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2$, where $\tau$, $n_m$, $V_m$, $S$, $\Delta E_s$, $\Delta E_t$ are the duration of the current pulse (s), the number of moles (mol), the molar volume of the active material (cm$^3$/mol), the electrode/electrolyte contact area (cm$^2$), the equilibrium potential change induced by current pulse and the potential change during the constant current pulse (neglecting the $iR$ drop), respectively. As shown in Figure 2-21 a in the Appendix, the measured GITT profiles of the three TNO electrodes present identical voltage plateaus in the galvanostatic discharge-charge processes, corresponding to the same structural evolution of TNO crystal caused by the Li$^+$ insertion and extraction. The inset in Figure 2-21 a in the Appendix indicates two typical discharge steps for the TNO700 half-cell. Particularly, the cell potential rapidly decreases resulted from the $iR$ drop, followed by a relatively slow potential decrease due to the galvanostatic discharge current pulse. Afterwards, during the relaxation time, the potential immediately increases due to the $iR$, and then slowly increases until stabilizing at an equilibrium potential.

As presented in Figure 2-21 b in the Appendix, during the discharge process, when potential is above 1.70 V, unlike BTNO anode having a stable $D$ value because of its very little surface area, the rapid decreases of $D$ values of NPTNO electrodes are attributed to the quick filling of Li$^+$ on their nanocrystal composed mesoporous structures’ large surface areas. The decrements of $D$ values within the voltage range of 1.70 to 1.65 V correspond to the transformation from solid-solution phase (SS1) to two-phase coexistence (SS1 and SS2), and the
rapid $D$ value increments from 1.65 to 1.60 V are assigned to the transition from two-phase coexistence (SS1 and SS2) to solid-solution phase (SS2).\cite{26, 39, 69}

Subsequently, the $D$ values stabilize between 1.60 and 1.00 V. Noticeably, the observed Li$^+$ diffusion coefficients of the Li$^+$ extraction process are generally higher than those of the Li$^+$ insertion process, indicating Li$^+$ insertion is the rate-limiting step during the cycling. To the best of our knowledge and conjecture, this observation may be attributed to the inflexible volume expansion due to the metal-oxygen octahedra distortion induced by the irreversibly inserted Li$^+$ in the crystal lattice, which may also relates to the irreversible capacity decay in the 0.1 C galvanostatic discharge-charge plots and the positional shift of the reduction peaks between the first cycle and following cycles in Figure 2-13 and Figure 2-14 in the Appendix.\cite{38, 60, 64} The Li$^+$ diffusion coefficients of NPTNO electrodes are obviously greater than those of BTNO electrode ($D_{TNO700} > D_{TNO850} > D_{BTNO}$), implying that the Li$^+$ diffusion coefficients of the NPTNO electrodes heavily rely on the nanocrystal and porosity induced large surface area. As shown in Table 2-2 in the Appendix, the calculated $D$ of the NPTNO materials remarkably surpass those of other ReO$_3$-type M-Nb-O anode materials.\cite{69-74} According to the relationship of $t \sim L^2/D$, the IL-templated NPTNO materials indeed have faster Li$^+$ insertion-extraction kinetics than BTNO anode due to the shorter diffusion distance and larger Li$^+$ diffusion coefficients induced by the nanocrystal composed mesoporous structure (Table 2-1 in the Appendix). To the best of our knowledge, the as-prepared
NPTNO materials achieve superior rate-capability in the titanium-based oxide materials (Table 2-3 in the Appendix).

2.6 Discussion

In view of the aforementioned results, NPTNO materials with the open and interconnected mesoporous framework composed of TNO nanocrystals indeed exhibit excellent electrochemical performance in LIB cells, which can be ascribed to the three aspects below. Firstly, the IL-templated TNO nanocrystals facilitate the electrochemical reactions on the surface and near the surface regions of electrode, enabling fast Li$^+$ insertion-extraction kinetics, and thereby the rate-capability is fully unchained from the Li$^+$ diffusion. Secondly, the open mesoporous structure with large surface area leads to a high contact between electrolytes and electrode, vastly benefitting the Li$^+$ transport and further ensuring the excellent rate-capability. Lastly, the IL-templated highly mesoporous framework with huge free internal space alleviates the mechanical stress and volume fluctuation caused by the repetitive Li$^+$ insertion-extraction processes, ensuring the long-term cyclability.

2.7 Summary

NPTNO materials are successfully prepared via ionothermal synthesis, which uses an IL as the nanoporous structure directing template. The IL-templated
NPTNO materials with mesoporous frameworks composed of nanocrystals indeed exhibits a superb rate-capability and high specific capacity in the titanium-based oxide materials with the best full-cell cyclic performance in the TNO materials. Such excellent electrochemical performance suggests that the IL templating effect is essential, opening a novel era for the syntheses of energy storage materials. The IL-directed TNO700 should be considered as a highly promising anode material candidate of fast-rechargeable LIBs, which shines new light on the future EVs.

2.8 Acknowledgements

The research at Oak Ridge National Laboratory and the University of Tennessee at Knoxville was supported by the U.S. Department of Energy’s Office of Science, Office of Basic Energy Science, Division of Materials Sciences Engineering under contract No. DE-AC05-00OR22725.
CHAPTER 3

Ionothermally Synthesized Nano-porous Ti$_{0.95}$W$_{0.05}$Nb$_2$O$_7$ as a Novel High-Rate Anode Material for Lithium-Ion Batteries
3.1 Abstract

A new type of $W^{6+}$-doped TiNb$_2$O$_7$ material with nano-porous structure is synthesized by ionothermal synthesis. The nitrogen sorption isotherm and the electron microscopies analysis confirm that the obtained nano-porous Ti$_{0.95}$W$_{0.05}$Nb$_2$O$_7$ (NPTWNO) material has mesoporous structure composed of nanocrystals, leading to a relatively large specific surface of 55 m$^2$/g. The obtained NPTWNO indeed delivers a slightly improved capability (203 mAh/g at 50 C) and cyclability (77 % capacity retention over 1000 cycles at 5 C), which is attributed to the excellent Li$^+$ diffusion kinetics and enhanced electrical conductivity. Such tiny electrochemical improvement. Therefore, this study successfully indicates the potential of ionothermal synthesis in energy storage materials and opens a new era for primarily improving the high-rate capability of material.

3.2 Introduction

Lithium-ion batteries (LIBs) have increasingly employed in electric vehicles (EVs) as the power sources based on the global warming concern of the CO$_2$ emission from the gas-powered vehicles.$^{22}$ Unfortunately, the broadly used graphite-based LIBs cannot fulfill the requirement of the high-rate charging. Graphite’s low operation potential (0.1 V vs. Li/Li$^+$) with the generation of passivating solid-electrolyte interphase (SEI) dramatically impedes its future application in EVs due to the unsafe Li-plating during fast charging.$^{23, 26, 60}$ Spinel
Li$_4$Ti$_5$O$_{12}$ (LTO) with a high working potential of 1.55 V vs. Li/Li$^+$ and zero-strain property has been proposed to be an excellent material for fast-charging, but its low specific capacity (175 mAh/g) cannot fit the crucial needs of the large-scale energy storage.$^{60,67}$

A few years ago, Goodenough et al. proposed TiNb$_2$O$_7$ (TNO) as a promising candidate to substitute LTO.$^{26,30,40,70}$ Because TNO with a safe operation voltage of 1.66 V vs Li/Li$^+$ and three redox couples Ti$^{4+}$/Ti$^{3+}$ and Nb$^{5+}$/Nb$^{4+}$/Nb$^{3+}$ can deliver a higher specific capacity (388 mAh/g) than graphite (372 mAh/g) and LTO.$^{26,60}$ However, similar to other metal oxides, the intrinsically low ionic diffusivity and poor electronic conductivity restrict the commercial applications of TNO materials.$^{26,60,67,70}$ On the one hand, to address the limit of ionic diffusivity, one strategy is to reduce the particle size based on the correlation of $t \sim L^2/D$, where $t$ represents the Li$^+$ diffusion time, $L$ means the diffusion length, and $D$ indicates the diffusion coefficient for Li$^+$ in the solid,$^{26,71}$ and the other strategy is to introduce porosity into the active material to enhance the contact between electrode and electrolytes.$^{26}$ For instance, our group applied ionic liquids (ILs) in synthesis of multiple materials, such as porous carbonaceous and metal oxides.$^{18,41,55-59}$ Recently, we novelly combined those two pre-mentioned strategies together to synthesize a nano-porous TNO material with superior electrochemical properties by applying an IL as the template based on the IL anions-precursors hydrogen bonding effects and the neighboring imidazolium rings’ $\pi-\pi$ stack interactions.$^{4,15}$ On the other hand, to overcome the disadvantage
of electronic conductivity, high valence transition metal ion doping is an effective method due to the bandgap reduction of the material’s conduction-valence bands by the impurity band formation.\textsuperscript{31, 70, 72-73} For example, although a few groups previously used mechanochemical approach to develop doped TNO materials,\textsuperscript{31, 70, 74} the large and unfavorable particle sizes of products couldn’t be avoided. As far, to the best of our knowledge, very limited work has been done to combine those pre-mentioned strategies above to resolve the fundamental disadvantages of TNO material.

Herein, we report a novel type of tungsten doped nano-porous TiNb\textsubscript{2}O\textsubscript{7} material by ionothermal synthesis. The obtained nano-porous Ti\textsubscript{0.95}W\textsubscript{0.05}Nb\textsubscript{2}O\textsubscript{7} (NPTWNO) with the simultaneously improved ionic diffusivity and electronic conductivity achieves high reversible capacity at high rates and displays an excellent cyclability, respectively. We believe that the IL templated nano-porous structure can effectively boost the Li\textsuperscript{+} diffusion kinetics,\textsuperscript{4, 26, 75} and the doped W\textsuperscript{+6} has higher valence than Ti\textsuperscript{4+}, thereby greatly enhancing the electronic conductivity based on the effect of charge redistribution.\textsuperscript{31, 72}

\section*{3.3 Experimental Section}

\subsection*{3.3.1 Synthesis of nano-porous Ti\textsubscript{0.95}W\textsubscript{0.05}Nb\textsubscript{2}O\textsubscript{7} (NPTWNO) material}

Starting reagents 3.2333 g of Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}, 0.1983 g of WCl\textsubscript{6} and 5.4034 g of NbCl\textsubscript{5} were dissolved in [BMIm][NTf\textsubscript{2}] and ethanol and vigorously stirred for 12 h. Subsequently, the solution was gelled in a Petri dish at 50 °C followed by a 2 h
aging at 200 °C. Next, the templating [Bmim][NTf₂] was extracted and recycled from sample by ethanol wash and rotary evaporation. Lastly, the washed sample was calcined at 700 °C in air for 3 h (ramp rate 2 °C/min) to obtain the NPTWNO material.

3.3.2 Synthesis of bulk TiNb₂O₇ (TNO) material

Starting reagents 3.4035 g of Ti(OC₄H₉)₄ and 5.4034 g of NbCl₅ were dissolved in ethanol and vigorously stirred for 12 h. Afterwards, the solution was transferred into a Petri dish and gelled at 50 °C followed by a 2 h aging at 200 °C. Lastly, the as-prepared sample was calcined at 700 °C in air for 3 h (ramp rate 2 °C/min) to obtain the bulk TNO material.

3.3.3 Typical Characterizations

The crystal structures of the obtained materials were characterized by powder X-ray diffraction (XRD, Panalytical Empyrean diffractometer at conditions of 45 kV and 40 mA). The recorded XRD patterns were analyzed by High Score Plus. Raman spectra were acquired from a WITec GmbH Alpha 300 confocal Raman microscope with a solid-state 532 nm excitation laser. The energy calibration and deconvolution of XPS peaks were carried out by CasaXPS (Casa Software Ltd). Nitrogen isothermal adsorption–desorption isotherm was measured on a TriStar 3000 volumetric adsorption analyzer from Micromeritics Instrument Corp. Scanning electron microscope (SEM) imaging was conducted on a Carl Zeiss Auriga 40 SEM microscope. SEM energy dispersive X-ray spectroscopy (EDX) studies were performed on a Carl Zeiss EVO MA15. Transmission electron
microscope (TEM) images were collected on a Carl Zeiss Libra 200 MC TEM microscope.

3.3.4 Electrochemical property studies

The sample electrodes were prepared with the obtained anode materials, Super C 65TM carbon black and polyvinylidene fluoride (PVDF) at a mass ratio of 70:20:10. The slurry was casted onto a Cu foil and dried under an infrared lamp to remove the solvent, followed by an 120 °C vacuum oven drying for 12 h. The weight loading of the active material on the fabricated electrodes was 1.5 – 1.8 mg/cm². The CR2032-type coin cells were assembled by pairing the as-prepared electrode to lithium counter electrode inside an argon-filled glove box with H₂O and O₂ contents less than 1 ppm. Celgard 2500 was used as the separator. Gen2 electrolyte was used (consisting of 1.2 M of LiPF₆ in ethylene carbonate (EC)/ ethyl methyl carbonate (EMC) with a weight ratio of 3/7 from Tomiyama Pure Chemical Industries, LTD). The LIB cells galvanostatic discharge-charge tests were carried out at various C-rates in the voltage range of 1.0 - 3.0 V on a Maccor Series 4000 tester. Cyclic Voltammetry (CV) tests with potential range of 1.0 - 3.0 V were carried on a BioLogic MPG2 system.

3.4 Results

In the ionothermal synthesis, titanium (IV) n-butoxide (Ti(OBu)₄), niobium (V) chloride (NbCl₅), tungsten (VI) chloride and nano-porous structure directing template IL [BMI]=NTf₂] were mixed and gelled as the precursor, followed by an
air-calcination (more details can be found in the supporting information). Figure 3
1 in the Appendix presents the synthesis schematic diagram of NPTWNO material.

3.4.1 Structural Characterizations

As shown in Figure 3-2 in the Appendix, the obtained X-ray diffraction
(XRD) of patterns of NPTWNO and TNO conform to the standard XRD pattern
(ICDD 01-085-7298), and the indicated crystal structure of NPTWNO is the same
as that of TNO, which belongs to monoclinic system with prismatic shape and has
the point group of C2/m.23, 26, 38 Furthermore, the XRD Rietveld refinements
indicate the differences of lattice parameters and unit cell volumes between TNO
and NPTWNO, which is mainly attributed to the W6+ doping. Particularly, NPTWNO
has lattice parameters of a= 20.575 Å, b= 3.803 Å, c= 12.169 Å, α= 90.0 °, β=
121.47 ° and γ= 90.0 ° with the calculated unit cell volume of 812.1 Å³. Compared
with TNO, which owns the standard lattice parameters of a= 20.555 Å, b= 3.802
Å, c= 12.16 Å, α= 90.0 °, β= 121.45 ° and γ= 90.0 ° with the estimated unit cell
volume of 811.0 Å³, the tiny variations of lattice parameters and unit cell volume of
NPTWNO are due to the W6+ doping.31, 72, 74, 76-77 Although all the prementioned
XRD features of the obtained NPTWNO material demonstrate that the W6+ is
successfully doped into the TNO crystal lattice, the negligible volume variations of
the unit cells suggest that the effect of lattice size won’t play a significant role in
the Li⁺ diffusion kinetics.31
To determine the templating effect of IL, N\textsubscript{2} adsorption/desorption study was carried out. As shown in Figure 3-3 a in the Appendix, the obtained NPTWNO material exhibits a mesoporous-featured isotherm profile with a large specific area of 55 m\textsuperscript{2}/g. Noticeably, such specific area of NPTWNO is relatively smaller than that the undoped NPTNO material from the previous study (72 m\textsuperscript{2}/g). This further confirms the successful doping of W\textsuperscript{6+} into the lattice because of its large atomic mass. As displayed in Figure 3-3 b in the Appendix, the Barrett–Joyner–Halenda (BJH) pore size distribution plot further indicates the mesoporous nature of NPTWNO material, presenting a main pore size distribution of 30.1 nm, which confirms the promising templating effect of IL.

To further reveal the crystallite sizes, morphologies and microstructures of the synthesized materials, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were employed. The SEM image displayed in Figure 3-4 a in the Appendix shows the three-dimensionally porous structure of the obtained NPTWNO. Additionally, NPTWNO material presents a typical secondary structure, containing micrometer-scale particles agglomerated by NPTWNO nanocrystallites. Additionally, the SEM EDX analysis reveal the existences and even distributions of Ti, W, Nb and O elements on NPTWNO material (Figure 3-9 in the Appendix). Figure 3-4 b in the Appendix reveals the size distribution of NPTWNO nanocrystallites is relatively homogenous. As shown in Figure 3-4 c in the Appendix, the obverse lattice fringes on the NPTWNO nanocrystallite indicate the appearance of a well-defined crystal structure.
Particularly, the measured lattice fringe space is about 0.340 nm, which is assigned to the crystallographic planar of (003), sharing coherence with the aforementioned XRD results.

### 3.4.2 Electrochemical Performance Studies

To investigate the electrochemical performance of the synthesized NPTWNO material, LIB half-cells were assembled and tested. As shown in Figure 3-5 in the Appendix, cyclic voltammetry was conducted to study the electrochemical properties of NPTWNO electrode. The broad peaks at 1.0–1.4 V are ascribed to the Nb$^{4+}$/Nb$^{3+}$ redox couple. The large redox at 1.73 and 1.62 V are attributed to Nb$^{5+}$/Nb$^{4+}$ redox couple. The two small sharp peaks at 1.92 and 1.74 V are assigned to the reaction of Ti$^{4+}$/Ti$^{3+}$. Noticeably, no W$^{6+}$/W$^{5+}$ peak is found at 2.01 and 2.06 V, suggesting that the little capacity contribution of W$^{6+}$-dopant, which may be due to its limited apperancy in the lattice. Furthermore, the overlapped CV profiles after the first cycle suggest that the obtained NPTWNO has excellent electrochemical and cycling stability. Notably, the slight reduction peak shift after the first cycle corresponds to the migration of the Fermi level and major distortion of the metal-oxygen octahedra during the Li$^+$ insertion process.

Figure 3-6 a in the Appendix presents the galvanostatic discharge-charge curves of NPTWNO at 0.1 C (38.7 mA/g). A discharge plateau appears around 1.65 V, correlating to a solid-solution phase transition process (the transformation from solid-solution phase (SS1) to two-phase coexistence (SS1 and SS2)) occurs.
within voltage range from 1.70 to 1.65 V, and the transition from two-phase coexistence (SS1 and SS2) to solid-solution phase (SS2) happens within voltage range from 1.65 to 1.60 V). The initial discharge (Li\textsuperscript{+} insertion) and charge (Li\textsuperscript{+} extraction) capacities are 309 mAh/g and 275 mAh/g, corresponding to a coulombic efficiency of 89.0 %. Moreover, unlike TNO only delivering a reversible capacity of 245 mAh/g (Figure 3-5 b in the Appendix), NPTWNO achieves a reversible capacity of 283 mAh/g, which is close to that of graphite and is significantly higher than that of LTO.

Figure 3-7 a in the Appendix shows the rate performance of the prepared TNO and NPTWNO electrodes. The obtained average discharge capacities of TNO at 20 and 50 C are 167 and 97 mAh/g, respectively. However, the obtained NPTWNO indeed presents a much better performance at high rates. It delivers average discharge capacities of 222 and 203 mAh/g at 20 and 50 C, respectively. Compared to TNO with poor high-rate capability induced by its bulk feature, the extraordinary high-rate performance of NPTWNO can be attributed to the enhanced Li\textsuperscript{+} diffusivity and improved electronic conductivity. To investigate the cyclability of the obtained TNO and NPTWNO materials, 1000 cycling tests at 5 C were performed (Figure 3-7 b in the Appendix). For TNO, the obtained capacities of the first and 1000th cycle are 144 and 99 mAh/g, respectively, reflecting a capacity retention of 69 %. In sharp contrast, NPTWNO performs high capacities of 218 and 167 mAh/g in the first and 1000th cycle with a capacity retention of 77 %, correspondingly. The enhanced cyclability of NPTWNO is due to the excellent
structural integrity and stability of its nano-porous architecture. Noticeably, comparing to the undoped NPTNO material from the previous work, which exhibits a large specific surface area of 72 m$^2$/g with excellent rate-capability (203 and 194 mAh/g at 20 and 50 C, respectively) and cyclability (capacity retention of 74 % over 1000 cycles), the aforementioned electrochemical performance of this doped NPTWNO material with a relatively smaller specific area of 55 m$^2$/g is due to the enhanced Li$^+$ diffusivity and improved electronic conductivity, confirming the advantages of our ionothermal-synthesis-assisted doping strategy.

### 3.5 Discussion

In light of the pre-mentioned electrochemical results, the origins of excellent rate-capability of the obtained NPTWNO material can be attributed to two aspects: the unhindered Li$^+$ diffusion kinetics induced by the nano-porous structure and the improved electronic conductivity based on the charge redistribution effect of doping W$^{6+}$. Firstly, the mesoporous structure composed of TWNO nanocrystallites from IL templating can significantly reduce the Li$^+$ diffusion distance and also can improve the electrode-electrolytes contact, benefitting the Li$^+$ insertion-extraction kinetics. Secondly, doping W$^{6+}$ into the TNO crystal lattice generates an impurity band between the conduction and valence bands, and consequently the electronic conductivity is dramatically boosted due to the bandgap narrowing induced by charge redistribution. Furthermore, the nano-porous structure can benefit the cyclability based on the alleviation of the repetitive mechanical stress and volume
fluctuation from the Li\(^{+}\) insertion-extraction processes. Additionally, it’s important to note that W\(^{6+}\)-dopant with high atomic mass in the lattice indeed significantly reduces the porosity, which does not dramatically enhance the Li\(^{+}\) diffusion kinetics and thereby only can lead to a tiny improvement of the electrochemical performance.

### 3.6 Summary

In summary, this study indicates the potential of ionothermal synthesis in energy storage materials, which enables the concurrent improvements of the electronic and ionic conductivities. Accordingly, the novel W\(^{6+}\)-doped nano-porous TiNb\(_2\)O\(_7\) material achieves a slightly improved rate performance of 222 and 203 mAh/g at 20 and 50 C, respectively. Moreover, besides owing high rate-capability, the synthesized NPTWNO also delivers an excellent cyclability at high rate (77 % capacity retention over 1000 cycles at 5 C). Such promising performance is mainly corresponded to the improved electronic conductivity due to the charge redistribution effect of doping W\(^{6+}\) and the enhanced Li\(^{+}\) diffusion kinetics induced by the IL templated nano-porous structure. Noticeably, although W\(^{6+}\)-dopant with high atomic weight can enhance the electronic conductivity, W\(^{6+}\)-dopant also present negative effect on the porosity, which fails to dramatically improve the rate-capability. Based on the pre-mentioned investigations and analyses, we believe that this ionothermal synthesis strategy may be more applicable to other anode
materials. Therefore, more efforts need to be taken in the future to develop more novel anode materials.

3.7 Acknowledgements

The research at Oak Ridge National Laboratory and the University of Tennessee at Knoxville was supported by the U.S. Department of Energy's Office of Science, Office of Basic Energy Science, Division of Materials Sciences Engineering under contract No. DE-AC05-00OR22725. The electron microscopy work was performed at Joint Institute for Advanced Materials Microscopy Center by Dr. John R. Dunlap. The synthesis of ionic liquids was partially assisted by Dr. Chi-Linh Do-Thanh. This manuscript has been authored by UT-Battelle, LLC under contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.
CHAPTER 4

Comprehensively Revealing Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$: A Novel High-performance Anode Material for Fast-rechargeable Lithium-ion Batteries
4.1 Publication Statement

A version of this chapter will be originally published by Runming Tao, Xiao-Guang Sun, Susheng Tan, Charl J. Jafta, Tianyu Zhang, Cheng Li, Tao Wang, Juntian Fan, Xian Suo and Sheng Dai.

Runming Tao provided major contribution and authorship to this publication. He completed all the syntheses and the most characterizations of the materials, expect the NPD measurement, AC-STEM operation, computational study and operando XRD data collection, which were performed by Dr. Cheng Li, Prof. Susheng Tan, Dr. Tianyu Zhang and Dr. Charl J. Jafta, respectively. The contributions of co-authors are as follows: Xiao-Guang Sun, Susheng Tan, Charl J. Jafta, Tianyu Zhang, Cheng Li, Tao Wang, Xian Suo and Sheng Dai discussed the results and suggested the manuscript revisions.

4.2 Abstract

Wadsley-Roth phased niobium-based oxides with open and interconnected crystallographic shear structures are promising anode materials for lithium-ion batteries (LIBs), while the inherently low electrical conductivity still limits their rate-capability. Herein, a novel doped Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ material is facilely prepared via an ionothermal-synthesis-assisted doping strategy. The detailed crystal structure of Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ is studied by NPD and AC-STEM, unveiling the full occupation of Mo$^{6+}$-dopant at the t1 tetrahedral site. In half-cells, Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ exhibits
superior fast-rechargeability (92.1 mAh/g at 100 C and 81.7% capacity retention over 2000 cycles at 10 C). The origin of such sensational performance is characterized by UV-vis, DFT and EIS, revealing that bandgap narrowing improves the electrical conductivity of Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$. Furthermore, operando XRD elucidates that Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ presents the typical solid-solution phase conversion-based lithium-ion insertion/extraction mechanism with reversible structural evolution during the electrochemical reaction. The boosted lithium-ion diffusivity of Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ is confirmed by GITT and DFT, due to the Mo$^{6+}$/W$^{6+}$ doping effect. With the simultaneously enhanced electrical conductivity and lithium-ion diffusivity, Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ successfully achieves promising practicality and desirable fast-rechargeability as the high-performance anode material in the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-coupled full-cells. Therefore, this work demonstrates the potential of ionothermal synthesis in energy storage materials and provides mechanistic understanding of the doping effect to primarily improving material’s electrochemical performance.

4.3 Introduction

To resolve the environmental and energy crises caused by the CO$_2$ emission from fossil fuel vehicles, lithium-ion batteries (LIBs) have been being regarded as the essential energy storage devices in electric vehicles (EVs). However, graphite, as a common anode material with high theoretical storage capacity of 372 mAh/g in LIBs, cannot meet the future requirement of fast-
rechargeability on EVs due to the formation of a passivating solid-electrolyte interphase (SEI) rooted from its low lithium-ion (Li$^+$) insertion potential (~0.2 V vs Li/Li$^+$),$^{30, 78, 81-82}$ which dramatically increases the energy barrier for Li$^+$ to cross the SEI and causes the sluggish electrochemical kinetics, thereby impeding the future application of graphite in fast-rechargeable LIBs. Another common anode material of LIBs is spinel Li$_4$Ti$_5$O$_{12}$ (LTO). Owning to its high operation voltage of 1.55 V vs Li/Li$^+$, LTO doesn’t suffer from the SEI issues and exhibits good structural stability. Its low theoretical capacity (175 mAh/g) deeply plagues the future application of EVs.$^{83-84}$

Recently, niobium-based oxides with Wadsley-Roth phase, like W$_3$Nb$_{14}$O$_{44}$ (WNO) and Mo$_3$Nb$_{14}$O$_{44}$ (MNO), both denoted as M$_3$Nb$_{14}$O$_{44}$, have been shining new light on the intercalation mechanism of Li$^+$ due to their open and interconnected crystallographic shear structures and thereby are considered as promising candidates of anode materials for fast-rechargeable LIBs.$^{78-80, 85-87}$ The abundant Nb$^{5+}$/Nb$^{4+}$/Nb$^{3+}$ redox couples with high reversibility ensure the high theoretical capacities ($374 \sim 403$ mAh/g).$^{78, 81, 88}$ Additionally, the operation voltages of M$_3$Nb$_{14}$O$_{44}$ materials are slightly higher than that of LTO (around 1.6 V), which are indeed above the formation potential of SEI layer and thereby successfully avoid the pre-mentioned SEI issues, enhancing the safety of LIBs during fast-charging. Despite the aforementioned advantages, a facile synthesis method with excellent safety is never exploited. Since the second-half of 2019, a few studies reported the preparation of micron-scaled and nano-wired WNO and
MNO materials through solution combustion and electrospinning routes, involving complicated open-flame burning and high voltage usage, respectively,\textsuperscript{78, 81, 89} which can potentially cause safety issues and thereby cannot be applied in the future large-scale commercialization.\textsuperscript{82, 90-91} Noticeably, no study has solved the low electrical conductivity of those Wadsley-Roth phased niobium-based oxide materials due to their inherent insulator property of metal oxides,\textsuperscript{79} which can significantly restrict their rate-capability in LIBs.\textsuperscript{26, 31, 72} Therefore, a facile and effective synthesis strategy with the ability to concurrently improve the electrical conductivity and the Li\textsuperscript{+} diffusivity (doping induced bandgap narrowing with potentially alleviated structural disorder and templating effect induced nano-scale crystallites) of M\textsubscript{3}Nb\textsubscript{14}O\textsubscript{44} material is highly desirable. More importantly, resolving the limited understanding of the doping effect on M\textsubscript{3}Nb\textsubscript{14}O\textsubscript{44} is also essential and transferrable for the future research and development of Wadsley-Roth phased niobium-based oxides, including the occupational status of the dopant in the lattice structure and the potential influence on the bandgap and the transport path of Li\textsuperscript{+} storage mechanism.

Herein, for the first time, a novel doped Mo\textsubscript{1.5}W\textsubscript{1.5}Nb\textsubscript{14}O\textsubscript{44} (MWNO) with Wadsley-Roth phase was prepared through a facile ionothermal-synthesis-assisted doping strategy (\textbf{Figure 4-1} in the \textbf{Appendix}). Specifically, an ionic liquid (IL), 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([BMIm][NTf\textsubscript{2}]), was used as the solvent and/or templating agent to dissolve the metal chlorides because of the solvent miscibility and electrostatic interaction of ILs (the hydrogen
bonding between the anions of ILs and precursors and the $\pi-\pi$ stacking between the neighboring imidazolium rings). After the mixture being gelled, the applied IL was simply extracted and recycled by ethanol wash. Lastly, the obtained precursor was calcinated in air to form the desired nanostructured MWNO material with Wadsley-Roth phase (more details can be found in the Supporting Information), which indeed exhibits superb fast-rechargeability and high specific capacity in LIB half-cells and full-cells. More impressively, the doping effect on MWNO and the origin of its sensational electrochemical performance with the Li$^+$-storage mechanism are first exploited by several in-depth analyses, including NPD, AC-STEM, UV-vis, EIS, DFT, operando XRD and GITT, revealing that the concurrently improved the electrical conductivity and Li$^+$ diffusivity assure the excellent electrochemical performance of MWNO in LIBs, which demonstrates the promising advantage of the ionothermal-synthesis-assisted doping strategy.

4.4 Experimental

4.4.1 Preparation of ionic liquid: 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

An ionic liquid, 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[\text{BMIm}][\text{NTf}_2]$), was synthesized as described in the previous literatures.$^4$ In brief, 1-butyl-3-methylimidazolium bromide ($[\text{BMIm}]\text{Br}$) was firstly synthesized through a nucleophilic substitution reaction between 1-methylimidazole and 1-bromobutane. Afterwards, $[\text{BMIm}][\text{NTf}_2]$ was
prepared by an ion exchange reaction between the obtained [BMIm]Br and lithium bis(trifluoromethanesulfonyl)imide (LiNTf₂).

4.4.2 Synthesis of M₃Nb₁₄O₄₄ materials

Three nanostructured M₃Nb₁₄O₄₄ (M = Mo and/or W) materials with Wadsley-Roth phase were prepared by ionothermal synthesis. Typically, a desired stoichiometry amount of NbCl₅, MoCl₅ and/or WCl₆ were dissolved in [BMIm][NTf₂], and a fixed amount of anhydrous ethanol was applied to adjust the viscosity of the mixtures. For Mo₃Nb₁₄O₄₄ (MNO), 1.8912 g of NbCl₅ and 0.4099 g of MoCl₅ were dissolved in 12 g of [BMIm][NTf₂] and 10 mL of ethanol; for Mo₁.₅W₁.₅Nb₁₄O₄₄ (MWNO), 1.8912 g of NbCl₅, 0.2050 g of MoCl₅ and 0.2974 g of WCl₆ were dissolved in 12 g of [BMIm][NTf₂] and 10 mL of ethanol the liquid mixture; for W₃Nb₁₄O₄₄ (WNO), 1.8912 g of NbCl₅ and 0.595 g of WCl₆ were dissolved in 12 g of [BMIm][NTf₂] and 10 mL of ethanol. After an overnight stirring, the obtained liquid mixtures were gelled at 50 °C. Subsequently, the gelled precursors were aged in an oven at 200 °C for 2 hours and then were washed by ethanol to extract the used [BMIm][NTf₂]. Lastly, the obtained MNO, MWNO and WNO precursors are air-calcinated at 700, 800 and 1200 °C to obtain the final products, respectively.

4.4.3 Typical characterizations

Powder X-rays diffraction (XRD) patterns were collected on a Panalytical Empyrean diffractometer at an operation voltage of 45 kV and a current of 40 mA, and the obtained XRD patterns were analyzed by HighScore Plus from Malvern...
Panalytical. Fourier-transform infrared spectroscopy (FTIR) tests were performed on a Thermo Scientific™ Nicolet™ iS50 FTIR spectrometer. Raman spectra were acquired from a Raman model HORIBA microscope with an edge violet laser with wavelength of 405 nm for 60 s. N₂ isothermal adsorption tests were carried on a Micromeritics Gemini VII adsorption analyzer. Scanning electron microscope (SEM) analysis was carried out on a Carl Zeiss Auriga 40 SEM microscope, and SEM energy dispersive X-ray (EDX) element mapping was conducted on a Carl Zeiss EVO MA15. Before the transmission electron microscope (TEM) studies, the powders were well-dispersed in isopropanol, then a 10 ul of the dispersions were drop-casted on TEM Cu grid with ultrathin carbon supporting films followed by an ambient condition drying and plasma cleaning. TEM images were recorded on a Carl Zeiss Libra 200 MC TEM microscope and JEOL JEM2100F TEM operated at 200 kV and equipped with Oxford AZtec EDS with windowless SDD detector. X-ray photoelectron spectra (XPS) were obtained on a Thermo Scientific X-ray photoelectron spectrometer with a monochromated Al Kα (1486.6 eV) X-ray source focused to a 400-micron spot under a pressure below 1×10⁻⁷ mbar, and the energy calibration and deconvolution of XPS peaks were analyzed by CasaXPS (Casa Software Ltd). UV-vis diffuse reflectance spectroscopy (UV-vis DRS) studies were performed on a Shimadzu UV-2450 Ultraviolet-visible spectrophotometer equipped with an integrated sphere.
4.4.4 Neutron powder diffraction experiments

Time-of-flight room-temperature neutron powder diffraction (NPD) data was collected by the Powder Diffractometer instrument (POWGEN BL-11A) within a neutron wavelength between 0.3 and 1.3 Å, at Spallation Neutron Source (SNS), Oak Ridge National Laboratory. The samples were loaded into 6-mm diameter vanadium cans with sample heights of 20 mm. The peak-shape was described with a convolution of the moderator induced asymmetrical shape function and a pseudo-Voigt function. The instrument parameters were obtained by refining the NIST standard LaB6 powder (SRM 660c). The Rietveld refinement analyses were carried out using academic TOPAS 6.93

4.4.5 Aberration-corrected scanning transmission electron microscope analysis

Ultrathin lamellar specimens with thicknesses of 32 nm were prepared using focused ion beam (FIB) to enable the lattice structure analyses at atomic resolution on a 70-pm resolution Ultra-STEM (Thermo Fisher Scientific Titan Themis G2 200 probe Cs aberration-corrected scanning transmission electron microscope (AC-STEM) with SuperX EDX) at 200 kV.

Quantitative STEM image simulations with Dr. Probe simulation software apply the multi-slice method to calculate the quasi-elastic forward scattering of the incident high-energy electron probes by the sample.94-95 While scanning an electron probe over positions distributed equidistantly in a rectangular frame, multi-slice electron-diffraction calculations are performed independently for each position, and the fractions of probe intensity falling into detector areas are
registered. Atomic structure models are input to the simulations and provided by CIF structure files.

4.4.6 Electrode fabrication and electrochemical performance studies

The three types of working electrodes were prepared by mixing the synthesized metal oxides, Super C45 conductive carbon black and polyvinylidene fluoride (PVDF) at a mass ratio of 70:20:10, respectively. Subsequently, after casting the slurries onto Cu foils and drying under an infrared lamp, the electrodes were further dried in an 120 °C vacuum oven for 12 h. The obtained weight loading of the active material on the fabricated electrodes was 1.5 – 1.7 mg/cm².

For lithium-ion battery (LIB) cells, the CR2032-type coin cells were assembled by using Gen2 electrolytes (consisting of 1.2 M of LiPF₆ in ethylene carbonate / ethyl methyl carbonate with a weight ratio of 3/7 from Tomiyama Pure Chemical Industries, LTD) inside an argon-filled glove box with H₂O and O₂ concentrations lower than 1 ppm. For LIB tests, the half-cells were assembled by pairing the as-prepared electrode to lithium foil counter electrode, and the full-cells were assembled by using LiNi₀.₅Mn₁.₅O₄ cathode. Celgard 2500 was used as the separator. The LIB half-cells and LIB full-cells (N:P ratio is around 0.77) were all tested in voltage ranges of 1.0 – 3.0 V and 1.5 – 3.5 V vs. Li/Li⁺, respectively. The galvanostatic discharge-charge and charge-discharge tests were carried out at various current rates on a Neware 4000 tester. Cyclic Voltammetry (CV) tests were carried on a BioLogic MPG2 system at a scan rate of 0.05 mV/s by using half-cells in a voltage range of 1.0 – 3.0 V vs. Li/Li⁺. Half-cells' galvanostatic intermittent
titration technique (GITT) studies were performed on a BioLogic MPG2 system by employing a constant 0.1 C current pulse for 200 s followed by an 1 h rest within potential range of 1.0 – 3.0 V vs. Li/Li⁺. Electrochemical impedance spectroscopy (EIS) data were acquired on a BioLogic MPG2 system within a frequency range between 0.01 Hz and 20 kHz, and the Nyquist plots were fitted by Z-view software based on equivalent circuit models. Before the cell dissembling, the cell was charged back to 3 V (at charge state: delithiated); then the electrode was retrieved and carefully rinsed twice by dimethyl carbonate.

4.4.7 Operando XRD experiments

To perform the operando XRD measurements, three different working electrodes (MNO, WNO, MWNO) were prepared by mixing the active material, Super C45 conductive carbon black and PVDF at a mass ratio of 70:20:10, respectively. Afterwards, the obtained slurries were casted onto polytetrafluoroethylene (PTFE) coated Al foils, followed by overnight vacuum oven drying. Then, the electrodes were peeled off from the PTFE coated Al foils and cut into 10-mm diameter discs that acted as the current collector-free working electrodes. Commercial El-Cells with a beryllium window were used and assembled by lithium disc anodes, glassy fiber separators and working electrodes. To ensure the good electrical contact between the electrodes and the pins that connect to the potentiostat, thin Al meshes were placed on the top of the working electrodes. Thin Kapton film were placed between the Al mesh and the beryllium window to avoid any reactions. Before sealing the cell, it was completely wetted
with Gen2 electrolyte. The assembled El-Cells were discharged/charged with simultaneous operando XRD measurement. The galvanostatic measurements were carried out on a LAND potentiostat and the XRD patterns were collected by a PANalytical Empyrean X-ray diffractometer with Cu Kα radiation.

**4.4.8 Density functional theory (DFT) computational quantum mechanical modelling studies**

All the computational studies were performed with the generalized gradient approximation (GGA) of the Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional as implement in the Ab-Initio Simulation Package (VASP). The projected augmented wave (PAW) pseudopotentials were utilized to describe the core and valence electrons using a plane-wave kinetic energy cut-off of 500 eV. For The Brillouin zone integration, a Monkhorst−Pack scheme mesh $1 \times 1 \times 5$ was used. The modeling structure is mainly based on the results of NPD and ACSTEM. In these results, the $t_1$ tetrahedral site in MWNO is fully occupied by Mo atom. Additionally, Mo atom can also occupy the $o_1$ octahedral site, which we are interested. W atom has very small chance to occupy the octahedral sites $o_2$ - $o_4$ and prefers to occupy the $o_1$ octahedral site. The structures were allowed to relax with the force convergence criteria of $0.02$ eV/Å, and the convergence criteria for the energy was set as $10^{-5}$ eV. The lattice parameters of layered MWNO were calculated to be $a = 21.19$ Å, $b = 21.19$ Å, $c = 3.85$ Å, in a good agreement with experimental values. The energy paths of Li$^+$ diffusion were using the climbing
image nudged elastic band (CI-NEB) method by relaxing the force below 0.05 eV/Å.

### 4.5 Results

#### 4.5.1 Structural Characterizations

The crystal structure of as-synthesized MWNO material was studied by powder X-ray diffraction (XRD) analysis (Figure 4-2 in the Appendix). The collected diffraction pattern conforms to the standard XRD pattern of tetragonal W₃Nb₁₄O₄₄ with space group of I-4 (ICDD # 04-009-3726) without any hetero-phased peak, possessing consecutive edge-shared MO₆ (M = Nb, Mo and/or W) octahedral blocks attached with corner-shared MO₄ (M = Mo and/or W) tetrahedra, which ensures the excellent structural stabilities of crystals.⁷⁸ Consequently, the formed shear ReO₃-type structure with A-B-A layers can stabilize and storage the inserted Li⁺ ions.⁷⁸, ⁸¹ Noticeably, the diffraction patterns of MWNO, WNO and MNO indeed appear little shifts, which is ascribed to the successful Mo⁶⁺/W⁶⁺ doping in the lattice, due to their highly similar ionic sizes.⁹⁶ The refined lattice parameters of three materials are listed in Table 4-1 in the Appendix, showing that MWNO has a = b = 20.998(1) Å, c = 3.819(1) Å and α = β = γ = 90 ° with a unit cell volume of 1683.9 Å³. As expected, the variances of those unit cell lattice parameters of the three materials elucidate the existences of distortions in the lattices based on the Mo⁶⁺/W⁶⁺ doping. Additionally, the estimated crystallite size of MWNO from the Scherrer equation are 96.4 nm (Table 4-1 in the Appendix).
As a complement to XRD, Raman spectroscopy was employed to verify the structural information of the synthesized materials. As shown in Figure 4-3 in the Appendix, four apparent peaks are observed on the Raman spectrum. The two obvious peaks at around 258 and 631 cm\(^{-1}\) are attributed to the metal-oxygen and metal-oxygen-metal bonds, respectively.\(^{78,97}\) The M-O vibrations of the MO\(_6\) (M = Mo and/or W) octahedra occurs at 899 cm\(^{-1}\).\(^{78,98}\) Lastly, the sharp peak at 989 cm\(^{-1}\) is rooted from the NbO\(_6\) octahedra.\(^{78}\) Therefore, based on the above studies, the formation of Wadsley-Roth phased MWNO material is well-confirmed.

To investigate the valence states of the elements in the prepared MWNO material, X-ray photoemission spectroscopy (XPS) analysis was conducted. As shown in Figure 4-4 in the Appendix, the broad spectra of the materials are highly similar, confirming the existances of Nb, Mo, W and O elements in the obtained materials. Figure 4-5 a in the Appendix presents the high-resolution XPS (HRXPS) spectrum of Mo in MWNO material, which suggests that the two peaks at 232.7 and 235.8 eV are assigned to Mo-3d\(_{5/2}\) and Mo-3d\(_{3/2}\), respectively. Noticeably, the splitting of 3.1 eV in the core levels uncovers the normal oxidation state of Mo\(^{6+}\) in the obtained oxide.\(^{81,99}\) As shown in Figure 4-5 b in the Appendix, the peaks of W at 35.7 and 37.8 eV with a splitting of 2.1 eV correspond to W-4f\(_{7/2}\) and W-4f\(_{5/2}\), indicating the appearance of the valence state of W\(^{6+}\) in the material.\(^{78}\)\(^{100}\) The HRXPS spectrum of Nb element in Figure 4-5 c in the Appendix shows two peaks centered at 207.2 and 209.9 eV, which are respectively attributed to the Nb-3d\(_{5/2}\) and Nb-3d\(_{3/2}\), elucidating the Nb\(^{5+}\) oxidation state.\(^{4}\) Lastly, Figure 4-5 d
in the Appendix exhibits a main peak of O-1s and a small peak of hydroxyl group at 530.2 and 531.6 eV that are rooted from the oxygen species in the MWNO and the tiny amount of trace water, respectively.\textsuperscript{60, 78, 101-102}

To further understand the Mo\textsuperscript{6+}/W\textsuperscript{6+} doping effect in the lattice, neutron powder diffraction (NPD) experiments were carried out at Oak Ridge National Laboratory Spallation Neutron Source. The NPD Rietveld refinements of MWNO and WNO patterns are presented in Figure 4-6 and Figure 4-44 in the Appendix, respectively. The pristine WNO belongs to a family of niobium tungsten oxides that is formed with 4 × 4 ReO\textsubscript{3}-type blocks with edge-shared octahedron, which extends along c axis (Figure 4-7, Figure 4-45 and Figure 4-46 in the Appendix). The ReO\textsubscript{3} blocks intersect with each other via the linkage of edge sharing octahedra and tetrahedra (marked as \textit{t}1) and present a crystallographic shear plane.\textsuperscript{103-104} Of the four octahedral positions (\textit{o}1 – \textit{o}4, following the notion of Roth et al.),\textsuperscript{103} the \textit{o}1 is closest to an ideal octahedron whereas the octahedra on the edge of the blocks, namely the \textit{o}2 – \textit{o}4 sites, are deformed (i.e. larger deviation of the O-Nb-O away from 180 °). The 2c position of WNO at (0, ½, ¼) is fully occupied with W, whereas the rest of W and Nb randomly distribute in the octahedral sites (Figure 4-46 c and Table 4-2 in the Appendix), consistent with previous report.\textsuperscript{103} As expected, the size of the \textit{t}1 tetrahedron site of MWNO is considerably smaller than those of the rest of the cation positions, implying the only possible occupation of W or Mo. Particularly, the NPD refinement suggests that the Mo has a strong tendency to locate at the \textit{t}1 with a Mo-occupancy of 100%. Although, owing to the
highly similar coherent scattering lengths of Nb and Mo, the exact occupational statuses of the o1 – o4 sites cannot be directly distinguished by neutron scattering, the inspection of the Fourier map ($F_{obs}$) successfully uncovers that the o1 site has the lowest nuclear density, thereby indicating the higher occupancy of W. Moreover, the o2 – o4 sites present comparable observed nuclear densities, reflecting the equal restricted site occupancy (Table 4-2 in the Appendix). Accordingly, in MWNO, W tends to prefer the center of the ReO$_3$ blocks whereas Nb has higher occupancy at the blocks on the edge. Interestingly, as shown in Table 4-3 in the Appendix, the Mo$^{6+}$ dopant indeed leads to a slight increase in transition metal-oxygen bond lengths, potentially indicating a less disordered local cation arrangement that may benefit the Li$^+$ diffusion kinetics, which also appears in other metal oxide anode materials, including Wadsley-Roth phased TiNb$_2$O$_7$, spinel-structured Li$_4$Ti$_5$O$_{12}$ and rock-salt-structured NiO.$^{31, 72, 105}$ To further confirm the aforementioned observations, several early studies were reviewed. In 1965, Roth and Wadsley’s research proposes the equal W distribution amongst the o1 – o4 sites in WNO material.$^{103}$ Later, in the consideration of electrostatic interaction, Cheetham and Allen suggest that W exhibits the highest concentration (about 40%) at the Nb1 site, at the center of the ReO$_3$ block; noticeably, their work also indicates the high W occupancy at o2 site, despite the o2 – o4 sites sharing the very similar bonding environment.$^{106}$ Fortunately, our NPD refinement is in line with a recent computation study, which investigates the energy landscape of a full enumeration of cation distribution in WNO and reveals that the system is most
stable when W is at the center of the block due to electrostatic repulsion.\(^7\) In addition, it is interesting to note that various WO\(_3\) compounds have the corner-sharing octahedra motif,\(^7\),\(^1\) whereas the most commonly encountered H-Nb\(_2\)O\(_5\) contains edge-sharing polyhedra;\(^1\) these are consistent with the pre-mentioned results as well. Therefore, to the best of our knowledge and conjecture, the majority of the doped Mo\(^{6+}\) fully occupies the \(t1\) site, and the remaining Mo\(^{6+}\)-dopant may also likely reside on the \(o1 – o4\) sites due to the similar sizes of Mo\(^{6+}\) and W\(^{6+}\) (the crystal ionic radii of Mo\(^{6+}\) and W\(^{6+}\) are 73 and 74 pm, respectively).\(^9\)

As a verification, an aberration-corrected scanning transmission electron microscope (AC-STEM) was applied to directly observe the Mo\(^{6+}\)/W\(^{6+}\) doping effect in the MWNO lattice. On the collected high-angle annular dark-field (HAADF) images of the atomic arrangements of the obtained MWNO material, the white dots are assigned to metal atoms because of their high electron scattering density, and thereby oxygen atoms are basically concealed in the dark regions. As shown in Figure 4-8 a in the Appendix, the typical \(4 \times 4 \times \infty\) shear ReO\(_3\)-type blocks along the [001] crystallographic direction can be clearly observed, displaying corner-sharing octahedra with edge-sharing octahedra in a-b plane that forms nine ordered tunnels along the c axis in each block, which is identical to the a-b plane lattice structure in Figure 4-7 in the Appendix. Noticeably, the round-like dots in the octahedra with bright white color and the cross-like dots in on the tetrahedra with faint white color are highly distinguishable. Such obvious contrast indicates the doped Mo\(^{6+}\) fully occupies the cross-like tetrahedral sites that are only occupied
by W$^{6+}$ in WNO; thereby the round-like dots in the octahedra with bright white color are mainly attributed to the Nb$^{5+}$ and W$^{8+}$ with possible Mo$^{6+}$ because of similar proton number ($Z$) of Nb and Mo ($Z$ values of Nb, Mo and W are 41, 42 and 74, respectively, and the corresponding average $Z$ of Nb-W and Nb-Mo are 57.5 and 58, which are significantly higher than the $Z$ of Mo). Additionally, based on the proposed local lattice structure of the MoO$_4$ tetrahedron (Figure 4-8 b in the Appendix), a HAADF image stimulation was performed, which also further confirms the occupation of Mo$^{6+}$ at the tetrahedral sites (Figure 4-8 c in the Appendix). As expected, the aforementioned observation is obviously different from the previously reported WNO HAADF image with similar brightness and little contrast between the octahedral and tetrahedral sites,$^{78}$ further implying the lower electron density of $t1$ site in MWNO due to the occupation of Mo$^{6+}$. Therefore, the ACSTEM study above is in line with the NPD refinement results, confirming the exact lattice structure of MWNO, which present that the majority of the Mo$^{6+}$-dopant fully occupies the $t1$ site, and the remaining Mo$^{6+}$ cations may possibly reside on the $o1$ – $o4$ sites. In addition, as shown in the HAADF image along [010] zone axis (Figure 4-8 d in the Appendix), the shown structure is similar to the b-c plane lattice demonstration in Figure 4-7 in the Appendix, featuring the typical $I-4$ symmetry. The main fringe distance is measured to be 0.470 nm, which corresponds to the (420) crystallographic plane. Those pre-mentioned HAADF images display highly ordered atomic arrangement. This suggests that the
ionothermally prepared MWNO material is well crystallized, benefitting the rapid Li\(^+\) transport in the MWNO anode.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to observe the microstructure and morphology of the obtained materials. The SEM images in Figure 4-9 a in the Appendix indicates that MWNO has a typical secondary structure. Those micrometer-scaled particles are composed of the agglomerated MWNO nano-crystallites, which are formed from the templating effect of IL. As comparisons, the morphology of MNO is similar to MWNO, while WNO exhibits brick-like structured particles within a size range of 1 – 1.6 μm, which is due to the high temperature calcination. The SEM energy dispersive X-ray spectroscopy (EDX) elemental mapping images (Figure 4-55 in the Appendix) indicate the existences of Nb, Mo and/or W and O elements, sharing good agreement with the broad XPS spectra of MWNO material (Figure 4-29 in the Appendix). Additionally, the mapping results confirm the homogenous distribution of all elements among the materials. As the TEM images shown in Figure 4-9 b in the Appendix, the average crystallite size of MWNO material is at nano-scale. In the high-resolution TEM (HRTEM) image of MWNO (Figure 4-9 c in the Appendix), the estimated d-spacing of the main lattice fringe of MWNO is about 0.360 nm, potentially implying the (530) crystallographic plane of the tetragonal MWNO lattice. The selected-area electron diffraction (SAED) pattern of MWNO in Figure 4-9 d in the Appendix is rhombus-symmetrical, which is consistent with the observed I-4 Wadsley-Roth phased crystallographic structure.
from XRD experiment and simultaneously reveals the good single-crystal appearance and high crystallinity of the primary MWNO nanocrystallite.\textsuperscript{78,81,99,109} Moreover, as the high-angle annular dark-field scanning TEM (HAADF-STEM) EDX elemental mapping images displayed in Figure 4-9 e-i in the Appendix, the even distribution of Mo, W, Nb, and O elements along the whole MWNO single-crystallite is further confirmed, in good agreement with the aforementioned SEM EDX elemental mappings. This uncovers that MWNO has identical composition at micron-scale and nano-scale, which may benefit the electrochemical stability.

4.5.2 Electrochemical Performance Studies

To reveal the electrochemical performance of the three prepared materials in LIBs, half-cells were assembled with lithium foil counter electrodes and cycled in the range of 1.0 – 3.0 V. As shown in Figure 4-10 in the Appendix, cyclic voltammetry (CV) test with a scan rate of 0.05 mV/s was conducted to study the electrochemical behaviors of the obtained MWNO. The intensive redox peak-pair within 1.1 – 1.4 V is ascribed to the W\textsuperscript{5+/4+} and Nb\textsuperscript{4+/3+} couples.\textsuperscript{78,81} The broad peak-pair within 1.4 – 2.1 V can be attributed to the W\textsuperscript{6+/5+}, Mo\textsuperscript{5+/4+} and Nb\textsuperscript{5+/4+} couples.\textsuperscript{60,78,89,99,110} Lastly, the small peak-pair within 2.2 – 2.3 V is assigned to the Mo\textsuperscript{6+/5+} couple.\textsuperscript{99,110} The presences of redox of molybdenum and tungsten cations in MWNO further confirms the success of our ionothermal-synthesis-assisted doping strategy. Moreover, some small shifts of the reduction peaks can be observed after the initial CV cycle, which may mainly correspond to the Fermi level migration and the MO\textsubscript{6} (M = Nb, Mo and/or W) octahedra distortion.
rooted from the Li\textsuperscript{+} insertion\textsuperscript{4, 60}. Additionally, comparing to MNO and WNO materials (Figure 4-61 a and d in the Appendix), MWNO exhibits the tiniest polarization of 0.05 V. Such phenomenon foresees the unhindered electrochemical kinetics of MWNO\textsuperscript{78}. Noticeably, after the initial cycles, the highly overlapped CV curves of the subsequent cycles reveal the excellent electrochemical and cyclic stabilities of MWNO\textsuperscript{4, 111-112}.

**Figure 4-11** in the Appendix displays the galvanostatic discharge/charge curves of assembled MWNO-based half-cells at a current rate of 0.1 C (37.6 mA g\textsuperscript{-1}). The initial discharge and charge capacities are 284.9 and 270.2 mAh/g with a Coulombic efficiency of 94.7\%. An overall voltage plateau is observed at 1.63 V, and the reversible capacity is 269.1 mAh/g. As shown in **Figure 4-61 b** in the Appendix, for MNO, the initial cycle's discharge capacity, charge capacity and calculated Coulombic efficiency of MNO are 300.7, 281.6 mAh/g and 93.6\%, respectively. The measured voltage plateau and reversible capacity of MNO are 1.67 V and 283.6 mAh/g. As shown in **Figure 4-61 e** in the Appendix, for WNO, the initial discharge (Li\textsuperscript{+} insertion) and charge (Li\textsuperscript{+} extraction) capacities are 261.9 and 225.9 mAh/g, respectively, corresponding Coulombic efficiency is 86.3\%, and the obtained reversible capacity is 227.9 mAh/g. The observed voltage plateau appears at 1.57 V. Noticeably, such calculated initial Coulombic efficiencies of MNO and WNO are in line with the previous studies\textsuperscript{78, 81}. Additionally, MWNO displays the highest initial Coulombic efficiency among the three M\textsubscript{3}Nb\textsubscript{14}O\textsubscript{44} materials, which is comparable to that of the commercial graphite (~90\% to 95\%).
implying its good practicality.\textsuperscript{113} Moreover, the acquired reversible capacity of MWNO is significantly higher than that of LTO,\textsuperscript{4, 26} further indicating the promising potential of MWNO material. In view of the above results, MWNO indeed presents desirable theoretical and practical capacities and initial Coulombic efficiency because Mo\textsuperscript{6+} cation has lower atomic weight and smaller ionic radius than those of W\textsuperscript{6+}, leading to cation redistribution in the lattice and thereby possibly improving its structural stability during the Li\textsuperscript{+} insertion/extraction processes.\textsuperscript{72, 96}

To exploit the fast-rechargeability of the obtained MWNO material with nanostructure feature and Wadsley-Roth phase, multiple current rates were applied. As shown in Figure 4-12 and Table 4-4 in the Appendix, MWNO exhibits the best rate performance among the three materials. Reversible capacities as high as 191.2 and 154.6 mAh/g are achieved at charge rates of 20 and 50 C, respectively. Noticeably, even at an extremely high charge rate of 100 C, the prepared MWNO can still deliver an extraordinarily high reversible capacity of 92.1 mAh/g. More impressively, after fast-charging at 100 C for 10 cycles, MWNO successfully recovers back to a high reversible capacity of 219.2 mAh/g at a small returning current rate of 1 C, which is pretty comparable to the obtained capacity of 220.0 mAh/g from the initial 1 C cycling, illustrating the excellent electrochemical reversibility of the MWNO electrode. As expected, the rate performance of MWNO is significantly superior to those of its parent-materials (MNO and WNO) from this study and the previous work.\textsuperscript{78, 81, 86-87, 114} Thereby, such sharp contrast can be
attributed to the doping effect that may potentially improve the electrical conductivity and Li⁺ diffusivity.

On the one hand, to confirm the electrical conductivity improvement of MWNO due to the doping, several in-depth experiments and analyses were performed. As shown in Figure 4-25 in the Appendix, MWNO has obviously darker color than its parent materials, implying that the doping induces bandgap narrowing, which leads to the reflection of visible light with energy less than the bandgap energy and absorption of the remaining visible light; in brief, this is the reason why the colors of insulative materials with broad bandgap are generally lighter than those of conductive materials.³¹ As shown in Figure 4-62 a in the Appendix, the ultraviolet-visible absorption spectra are collected by a ultraviolet-visible diffuse reflectance spectrometer (UV-vis DRS) to verify the observation above. Noticeably, owing to the formed impurity band based on the doping induced charge redistribution, the doped MWNO material indeed exhibits a higher absorbance band than MNO and WNO do in the visible light region, which is in good agreement with the observed colors of the materials discussed above. Displayed in Figure 4-13 and Figure 4-62 in the Appendix, the estimations of band edge and semiconductor type of the three materials are performed through the following equation from the Tauc method, \( a\nu = A(h\nu-E_g)^n/2 \), where \( a \), \( h \), \( \nu \), \( A \), \( E_g \) and \( n \) are the absorption coefficient, the Planck constant, the light frequency, the proportionality constant, the bandgap energy and the electron transition factor (1 for the direct absorption and 4 for the indirect absorption), respectively.¹¹⁵-¹²²
Figure 4-62 b, c and e in the Appendix suggest that the three materials may have direct transitions. Accordingly, as shown in Figure 4-13 and Figure 4-62 d and f in the Appendix, the determined bandgap of MWNO is 2.82 eV, which is significantly less than the those of MNO, WNO and Nb$_2$O$_5$ (3.16, 3.03 and 3.5$^{123}$ eV, correspondingly), reflecting that electrons can be easily excited from the valence band to the conduction band. Additionally, a pre-edge band is observed on the plot of MWNO, which does not appear on the plots of the parents. The extra band may indicate the existence of defects on the MWNO structure, which may facilitate the electron transfer process. More importantly, such observation implies that MWNO has enhanced electrical conductivity with the facilitated electrochemical kinetics, which is attributed to the new crystal structure and energy band structure resulted by the Mo$^{6+}$/W$^{6+}$ doping.$^{72}$

To further understand the doping effect in the MWNO, due to considerable influence of the co-doped Mo$^{6+}$ and W$^{6+}$ in the electronic structure of MWNO that plays a crucial role on the rate-capability of MWNO electrode, a set of bandgap modelling studies based on the density-functional theory (DFT) computational quantum mechanical calculation were carried out. As shown in Figure 4-63 in the Appendix, the valence and conduction bands of MNO and WNO are mainly contributed by O-2p, Nb-4p/4d and Mo-4p/4d and O-2p, Nb-4p/4d and W-5p/5d, correspondingly. The calculated values of bandgaps for MNO and WNO are about 1.9 and 1.8 eV, respectively. Interestingly, as revealed by the highly overlapped bands among the Mo-4p/4d, W-5p/5d, Nb-4p/4d and O-2p in Figure 4-14 in the
Appendix, the co-existences of Mo$^{6+}$ and W$^{6+}$ cations in MWNO material lead to an enhanced hybridizations of Mo$^{6+}$ and W$^{6+}$ in MWNO material, due to the formation of strong metal-oxygen bonds in the lattice,\textsuperscript{72} sharing good agreement with the XRD, FTIR, Raman, NPD and AC-STEM results above. As a result, MWNO presents a narrowed bandgap of 1.0 eV, obviously smaller than those of parent oxides. Additionally, it is also worthy to note that the final electrode indeed contains 20 wt.% of highly porous conductive carbon. To the best of our knowledge, those aforementioned aspects may directly overcome the tiny electron thermal energy at room temperature and make the MWNO electrode more electrically conductive than the parents electrode, thereby benefitting the rate-capability.

Furthermore, the enhancement on electrical conductivity is electrochemically verified by an electrochemical impedance spectroscopy (EIS) experiment. As shown in Figure 4-15 and Figure 4-62 c and f in the Appendix, the estimated intrinsic impedances (the intercepts of the curves in the high-frequency regions of the Nyquist plots) of MWNO, MNO and WNO are 3.56, 15.41 and 8.85 $\Omega$. With the consideration of the identical electrolyte used in the cells, the differences among the intrinsic impedances are mainly attributed to the differences among the ohmic resistances of the electrodes, which uncovers the benefit of the Mo$^{6+}$/W$^{6+}$ doping in improving the electrical conductivity of the electrodes.\textsuperscript{31} The charge transfer impedance (the approximated diameter of the semicircle in the high-medium-frequency region) of MWNO electrode is 41.77 $\Omega$, which is distinctively lower than those of MNO and WNO electrodes (230.2 and 241.5 $\Omega$,}
respectively), suggesting that MWNO electrode presents an unhindered charge transfer kinetics enabled by the ionothermal-synthesis-assisted doping strategy (the improved electrical conductivity and the IL-templated nanoporous architecture with large surface area).\textsuperscript{86, 124-125} In the low-frequency region, the steep linear fitting of MWNO reveals its unhindered interfacial Li\textsuperscript{+} diffusion kinetics, which is due to the observed nanoporous structure of MWNO and the potentially facilitated Li\textsuperscript{+} diffusivity induced by the doping.\textsuperscript{31, 72, 125-128} Therefore, based on the aforementioned studies and analyses of UV-vis DRS, DFT and EIS, it is confirmed that the Mo\textsuperscript{6+}/W\textsuperscript{6+} doping indeed optimize the electrical conductivity of MWNO material, facilitating the electrochemical kinetics and improve the rate-capability.

On the other hand, to investigate the enhanced Li\textsuperscript{+} diffusion kinetics and storage mechanism of MWNO due to the doping, galvanostatic intermittent titration technique (GITT), operando XRD and computational studies were conducted. \textbf{Figure 4-16 a} and \textbf{Figure 4-16 b} in the \textbf{Appendix} present the typical GITT discharge steps of the MWNO half-cell. In brief, the rapid potential decreases and increases are mainly due to the \textit{iR} drops; the relatively slow potential decays and potential growths are attributed to the galvanostatic discharge current pulse and the relaxation, respectively. The 1 h relaxation after 200 s discharge pulse is long enough to allow the MWNO electrode to reach the equilibrium statues. The measured GITT profile of the MWNO electrode in \textbf{Figure 4-16 a} in the \textbf{Appendix} are different from those of MNO and WNO electrodes (\textbf{Figure 4-64 a} and \textbf{c} in the \textbf{Appendix}), implying the different structural variations of the three crystals during
the Li$^+$ insertion/extraction processes, which is further elucidated by the operando experiments below. Accordingly, the Li$^+$ diffusion coefficients are calculated by the following equation derived from Fick’s second law, 

$$D_{Li^+} = \frac{4}{\pi \tau} \left( \frac{n_m V_m}{S} \right)^2 \left( \frac{\Delta E_s}{\Delta E_t} \right)^2,$$

where $D_{Li^+}$, $\tau$, $n_m$, $V_m$, $S$, $\Delta E_s$, and $\Delta E_t$ are the Li$^+$ diffusion coefficient (m$^2$/s), the duration of the current pulse (s), the number of mole of MWNO (mol), the molar volume of the MWNO (m$^3$/mol), the electrode-electrolyte contact area (m$^2$), the equilibrium potential change induced by current pulse and the potential variation during the constant current pulse (neglecting the $iR$ drop), respectively. As shown in Figure 4-16 c and Table 4-5 in the Appendix, the obtained $D_{Li^+}$ values in the lithiation and delithiation vary between $3.00 \times 10^{-18}$ to $1.47 \times 10^{-17}$ m$^2$/s and $3.57 \times 10^{-17}$ to $1.56 \times 10^{-18}$ m$^2$/s, corresponding averages of at $7.70 \times 10^{-18}$ and $2.01 \times 10^{-17}$ m$^2$/s, correspondingly. Noticeably, the obtained average $D_{Li^+}$ value from lithiation is less than that from delithiation, suggesting that lithiation is the rate-limit step in the whole electrochemical kinetics. More interestingly, MWNO electrode exhibits significantly higher $D_{Li^+}$ values of than those of the parents (Figure 4-16 b, d and Table 4-5 in the Appendix), especially MNO with higher surface area and smaller crystallite sizes, indicating that the doping strategy can also facilitate the Li$^+$ insertion/extraction processes in the lattice structure, which may be attributed to the mediated structural disorder in the lattice and the enhanced Li$^+$ diffusion pathways. Moreover, the trends of $D_{Li^+}$ values of MWNO electrode is also slightly different from those of MNO and WNO electrodes, which is consistent with the observation from the acquired GITT profiles discussed above. Noticeably,
unlike WNO exhibiting a typical solid-solution phase transition within the voltage range of 1.5 to 1.75 V, the phase transitions of MWNO and MNO may occur at around 2.0 V, due to the presences of rapid \( D_{Li^+} \) variations at around 2.0 V. To further analyze these results, a set of operando XRD studies were performed to characterize the \( Li^+ \) storage mechanisms of the three prepared materials.

As the operando XRD patterns of MWNO shown in Figure 4-17 in the Appendix, the diffraction peaks continuously migrate during the entire discharge/charge process, which implies the shrinkage and/or expansion of the interplanar distance in the lattice, uncovering the typical solid-solution phase-transition-based intercalation nature of MWNO material. Specifically, when the cell is discharged from 3.0 to 2.0 V, the (420), (101), (530), (431), (521) and (280) peaks at 18.8, 23.6, 24.7, 31.6, 32.8 and 35.2 °, respectively, present lower-angle shifts. From 2.0 to 1.47 V, the (420), (530) and (280) peaks show high-angle shifts, while the (101), (431) and (521) peaks still exhibit lower-angle shifts. Noticeably, the intensities of (530) and (280) peaks gradually weaken along with the decrease of potential. Within a voltage range of 1.47 to 1.0 V, all the peaks display lower-angle shifts. Such observation corresponds to the continuous solid-solution phase transitions from SS1 to two-phase coexistence (SS1 + SS2) then to SS2, which is also reflected by the aforementioned variation of \( D_{Li^+} \) (Figure 4-16 c in the Appendix). Particularly, the rapid \( D_{Li^+} \) drop at above 2.0 V is ascribed to the quick filling of \( Li^+ \) in the MWNO lattice induced transformation from the first solid-solution phase (SS1) to two-phase coexistence (SS1 and SS2), probably leading to the
transition from Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ to Li$_4$Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$; between 2.0 and 1.5 V, the quick $D_{Li^+}$ value increase is attributed to the transition from two-phase coexistence (SS1 and SS2) to solid-solution phase (SS2), likely due to the evolution from Li$_4$Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ to Li$_{15}$Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$; from 1.5 to 1.0 V, the second solid-solution phase (SS2) is completed formed along with the continuous lithiation of Li$_{15}$Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$ to Li$_{26}$Mo$_{1.5}$W$_{1.5}$Nb$_{14}$O$_{44}$, causing the gradual decrease of $D_{Li^+}$. Notably, such typical solid-solution phase transition mechanism can also be observed in other niobium-based oxide materials with Wadsley–Roth phases, such as MNO, WNO, TiNb$_2$O$_7$, Nb$_{16}$W$_5$O$_{55}$ and Nb$_{18}$W$_{16}$O$_{93}$.$^{4, 26, 39, 80-81}$ Additionally, it is interest to note that the XRD peaks indeed recover to the original position after fully charged to 3.0 V, indicating the excellent electrochemical reversibility and structural stability of the MWNO material. In view of the operando XRD patterns of MWNO, MNO (Figure 4-65 in the Appendix) and WNO (Figure 4-67 in the Appendix), it can be conjectured that MWNO exhibits a raised potential of the two-phase coexistence region, which can be also observed in the CV and GITT studies, potentially suggesting that the Mo$^{6+}$/W$^{6+}$ doping may facilitate the Li$^+$ diffusion and storage in the MWNO lattice.

To further unveil the Li$^+$ insertion induced structural evolution of MWNO, the operando XRD patterns were refined to study the lattice parameters. As shown in Figure 4-18 in the Appendix, during the discharge process (Li$^+$ insertion), the lattice parameters a and c and the corresponding unit cell volume V present increasing trends within a potential range from 3.0 to 2.0 V (0 – 0.7 h), which are
well reflected by the discussed low-angle shifts above; afterwards, discharging from 2.0 to 1.47 V (0.7 – 4.2 h), a rapidly shrinks while c and V continue their expansions, corresponding to the aforementioned co-existing solid-solution phases, SS1 and SS2; then, a, c and V exhibit steady growth until the potential reaching to 1.0 V (4.2 – 7.8 h), leading to a V expansion of 9.0% (from 1683.9 to 1838.3 Å³), which is obviously smaller than that of graphite (13.2%). Noticeably, the anisotropic evolution trends of the lattice parameters share similarities among the prepared MWNO, MNO and WNO materials and are in line with the computational study from Morris et. al, further confirming the typical three-region solid-solution phase evolution mechanism.

Furthermore, inspired by the enhanced electrochemical kinetics (including Li⁺ diffusivity and electrical conductivity) and the uncovered Li⁺ storage mechanism of MWNO discussed above, a series of DFT quantum mechanical computational studies were performed to further obtain in-depth insights of the comprehensive three-dimension Li⁺ diffusion behaviors in MWNO structure. As shown in Figure 4-19 a and b in the Appendix, the possible Li⁺ diffusion paths to adjacent sites on the plane layer (Path I, II and IV) and path between neighboring layers (Path III) are displayed, which present Li⁺ migration energy barriers of 0.17, 0.22, 0.047 and 0.060 eV (Figure 4-19 c-f in the Appendix), respectively. In comparison, as shown in Figure 4-69 c-e in the Appendix, the Li⁺ migration energy barriers of WNO material are 0.13 eV (Path I), 0.15 eV (Path II) and 0.069 eV (Path III). Obviously, the Li⁺ diffusion energy barrier of Path IV of MWNO is much less than those of the
Path II of MWNO and WNO, suggesting that Li⁺ prefers an off-center site that is closer to the Mo⁶⁺ and has coordination with the four neighboring bridge O atoms. Additionally, MWNO exhibits a significantly reduced Li⁺ diffusion energy barrier of Path III, which indicates that the Mo⁶⁺/W⁶⁺ doping can benefit the Li⁺ diffusion between layers. Therefore, these results share coherence with the GITT test and clearly reveal that Li⁺ can transport easily and rapidly in MWNO, benefitting its rate-capacity.

To further characterize the origin of doping effect on Li⁺ diffusivity, the electronic structures MWNO and WNO were obtained from DFT simulation. The total valance charge of the centered Mo site in MWNO is +2.425, while that of the W at the same site in WNO is +2.723. As mentioned in the previous study, such n-type doping charge redistribution behavior is similar to what happened in the lithiation negative-electrode,⁷⁹ which causes the reduction of the covalency between Mo and O in the MWNO, compared with the covalency between W and O in WNO. This may elongate the interatomic distance of the cation-oxygen bond and the leads to the swing of the oxygen ions, potentially offering some extra space for the Li⁺ in the lattice.⁷² Indeed, at o1 site, the simulated average bond length of Mo-O in MWNO (1.96 Å) is slightly greater than that of the W-O in and WNO (1.94 Å). Thereby, the doping results the expansion of cation-oxygen bond and induces the rearrangement of the lattice structure of MWNO material, which may eventually benefit the Li⁺ diffusion kinetics.
Besides the enhanced Li$^+$ diffusivity and the improved electrical conductivity co-induced excellent rate-capability of MWNO, long-term cyclability is another key feature of a reliable electrode material. As shown in Figure 4-20 in the Appendix, MWNO exhibits the best cyclic performance with the highest capacity among the three prepared electrodes at a large current rate of 10 C, achieving specific capacities of 125.5 and 111.7 and 105.5 mAh/g in the first, 1500th and 2000th cycles, respectively. Such results reflect excellent capacity retentions of 89.0% and 84.1% over 1500 and 2000 cycles, correspondingly. Moreover, the calculated Coulombic efficiency of each cycle is above 99.9%. For MNO and WNO, their specific capacity obtained from the first and 1500$^{th}$ cycles are 81.0 and 73.0 mAh/g and 98.6 and 79.8 mAh/g, implying capacity retentions of 90.1% and 80.1% over 1500 cycles, respectively. Noticeably, the capacity retentions of MWNO and MNO are better than that of WNO, which can be mainly attributed to their nanoporous structures, alleviating the volume fluctuation resulted from the repetitive Li$^+$ insertion/extraction processes.$^4,26,60$ In brief, such aforementioned superb cyclic performance of MWNO is mainly due to its structural and excellent electrochemical stabilities.

To better demonstrate the concluded origin of the sensational cyclability, a 2000-cycled MWNO half-cell at charge state was dissembled and analyzed by a series of characterizations, including XRD, SEM, SEM EDX elemental mapping and XPS. As shown in Figure 4-21 a in the Appendix, the uncycled and 2000-cycled MWNO electrodes share similar XRD patterns, indicating the excellent
crystal structural stability. As expected, the XRD peaks of the cycled MWNO electrode indeed exhibits some tiny shifts (Figure 4-21 b in the Appendix), corresponding to the inevitably irreversible volume variation caused by the repetitive Li$^+$ insertion/extraction processes. This is further exploited through the Rietveld refinement (Figure 4-70 in the Appendix), which suggests that the unit cell is only enlarged by about 0.23% (Table 4-1 and Table 4-6 in the Appendix). Noticeably, such a sight volume expansion reflects the highly reversible Li$^+$ storage performance and also confirms the excellent crystal structural stability, directly leading to the promising cyclability observed above. As the SEM images presented in Figure 4-21 c in the Appendix, the morphology of the cycled electrode (I and II in Figure 4-21 c in the Appendix) is parallel with that of the uncycled electrode (III and IV in Figure 4-21 c in the Appendix), appearing no obvious SEI layer. Additionally, the SEM EDX elemental mapping images of the cycled and uncycled electrodes exhibit homogeneous distributions of all the existing elements (Figure 4-71 and Figure 4-73 in the Appendix). Such well-maintained structural integrity reflects the good robustness of MWNO electrode, which also reflects the excellent cyclability observed above. Moreover, as shown in Figure 4-72 and Figure 4-74 in the Appendix, the EDX elemental composition analyses show that the relative Mo:W:Nb ratios of the cycled and uncycled electrodes stay around 1.5:1.5:14, which implies the desirable electrochemical stability of MWNO material, in line with the pre-mentioned XRD study. However, the atomic percentages of C, O and F do exhibit some considerable changes after the long-term cycling, indicating the
existences of side reactions. To further study such phenomenon, XPS was applied. As shown in Figure 4-75 in the Appendix, the broad spectra of the cycled and uncycled electrodes both contain Mo, W, Nb, O, C and F, in good agreement with the SEM EDX results. As expected, the 2000-cycled and uncycled MWNO electrodes indeed present highly similar Mo-3d, W-4f and Nb-3d HRXPS data (Figure 4-21 d-f and Figure 4-76 in the Appendix), elucidating the desirable electrochemical stability of MWNO material. Comparing Figure 4-21 g with Figure 4-76 d in the Appendix, the C HRXPS spectrum of the cycled electrode contains a C=O peak at 286.6 eV and a C-C and/or C-H peak with reduced relative intensity at 285.0 eV, which suggests that the decomposition of carbonates indeed exists during the cycling. Such phenomenon is also revealed by the O HRXPS spectrum of the cycled MWNO electrode because of the appearance of the obvious C=O peak at 532.1 eV (Figure 4-21 h in the Appendix). Comparing the F HRXPS spectra in Figure 4-21 i and Figure 4-76 f in the Appendix, besides the observation of the polyvinylidene fluoride induced C-F peak at 687.8 eV, a LiF-corresponded peak at 685.4 eV is found after cycling, corresponding to the degradation of lithium hexafluorophosphate in the electrolyte. Thereby, the side reactions of the electrolyte is confirmed, which may be the main reason of the capacity decay during cycling.

Based on the aforementioned superior electrochemical performance of MWNO, full-cells with LiNi0.5Mn1.5O4 (LNMO) cathodes were further assembled and investigated in voltage range from 1.5 – 3.5 V to verify the practicality of
MWNO. Figure 4-77 and Figure 4-22 a in the Appendix present the galvanostatic charge/discharge curves of the prepared full-cells at 0.5 and 1 C, which show high reversible capacities of 235.5 and 218.1 mAh/g with an operation voltage of 3.0 V, respectively. Additionally, the initial discharge specific capacities are 241.7 and 218.8 mAh/g at 0.5 and 1 C, implying excellent energy densities of 175.8 and 159.1 Wh/kg, correspondingly. To uncover the fast-rechargeability of the full-cells, a series current rates were applied. As shown in Figure 4-22 b in the Appendix, the full-cell delivers average discharge specific capacities of 235.4, 217.4, 203.6, 181.3, 136.2 and 91.5 mAh/g at current rates of 0.5, 1, 2, 5, 10 and 20 C, respectively. Such good capacity retention reflects the promising fast-rechargeability of the full-cell. Noticeably, a high specific capacity of 205.7 mAh/g is obtained at the recovering 1 C, revealing the excellent electrochemical reversibility of the full-cell system. Furthermore, cyclic performance studies at current rates of 2 and 10 C were conducted to investigate the long-term cycling reliability. As shown in Figure 4-22 c in the Appendix, the full-cell delivers a specific capacity of 181.8 mAh/g in the initial cycle with a corresponding high energy density of 132.3 Wh/kg and exhibits a capacity retention of 63.3% over 500 cycles at 2 C. Even at a higher current rate of 10 C, the assembled full-cell can still present capacity retentions of 70.7% and 63.6% over 500 and 1000 cycles (Figure 4-78 in the Appendix), respectively. Such cycling results indicate the successful achievement of long-term cyclability. In brief, the studies of the LNMO-coupled full-
cells above indeed show promising fast-rechargeability, which directly confirms the practical potential of MWNO material.

4.6 Discussion

In the panoramic view of the above results and analyses, the fundamental reasons of the superb rate-capability and cyclability in LIBs can be summarized in six aspects. Firstly, the well-maintained lattice structure of the obtained MWNO material is similar to its parent WNO and MNO materials, which shares open and interconnected crystallographic shear structure for Li\(^+\) storage, presenting the promising potential of fast-charging. Secondly, the co-doped Mo\(^{6+}\) and W\(^{6+}\) cations enhance the electrical conductivity of MWNO material via bandgap narrowing, ensuring straightforward electron transfer pathways.\(^{31}\) Thirdly, the Mo\(^{6+}\) and W\(^{6+}\) may mediate the structural disorder in the lattice and thereby boosts the Li\(^+\) diffusion kinetics of MWNO, further benefitting its rate-capability.\(^{72,79}\) Fourthly, the doped Mo\(^{6+}\) with less atomic weight than W\(^{6+}\) enlarges the theoretical and practical capacities. Next, the excellent structural stability and electrochemical reversibility of MWNO enable the desirable fast-rechargeability in LIBs. Lastly, the ionic liquid-templating effect induced nanoporous feature of MWNO offers free buffering space that alleviates the volume fluctuation caused by the repetitive Li\(^+\) insertion/extraction, ensuring the long-term cyclability. With the aforementioned advantages, MWNO achieves favorable electron transfer kinetics and unhindered Li\(^+\) insertion/extraction mechanism, which lead to the superb electrochemical
performance and realize the fast-rechargeability in the next-generation high-performance LIBs.

4.7 Summary

In summary, we have successfully prepared a novel doped $\text{Mo}_{1.5}\text{W}_{1.5}\text{Nb}_{14}\text{O}_{44}$ with Wadsley-Roth phase through an ionothermal-synthesis-assisted doping strategy, which is highly facile and safe, reaching the requirements of industrialization and commercialization. Owning to the open and interconnected crystallographic architectures with the concurrently improved electrical conductivity and Li$^+$ diffusivity and the nanoporous structure, the prepared $\text{Mo}_{1.5}\text{W}_{1.5}\text{Nb}_{14}\text{O}_{44}$ material exhibits a high capacity of 92.1 mAh/g at 100 C and a desirable capacity retention of 81.7% over 2000 cycles at 10 C. Such excellent fast-rechargeability in LIBs is attributed on the unhindered electrochemical kinetics, demonstrating the promising potential of ionothermal-synthesis-assisted doping strategy in the preparation of high-performance energy storage materials. Therefore, this work not only provides an efficient preparation strategy to optimize electrode materials for fast-rechargeable LIBs, but also establishes an in-depth understanding of the doping effect on the Li$^+$ storage mechanism of Wadsley-Roth phased niobium-based oxides. Furthermore, this study may also enlighten the designing of advanced electrode materials for other high-performance energy storage devices in the future.
4.8 Acknowledgements

The research at Oak Ridge National Laboratory and the University of Tennessee at Knoxville was supported by the U.S. Department of Energy’s Office of Science, Office of Basic Energy Science, Division of Materials Sciences Engineering under contract No. DE-AC05-00OR22725. The neutron diffraction study used resources at the Spallation Neutron Source, a DOE Office of Science User Facility operated by the Oak Ridge National Laboratory. This manuscript has been authored by UT-Battelle, LLC under contract No. DE-AC05-00OR22725 with the U.S. Department of Energy.
CHAPTER 5

Conclusion

5.1 Synopsis

New fast-rechargeable LIB anode materials are essential to realize the future high-performance LIBs in EVs for solving the environmental and energy crises caused by the burning of fossil fuels in vehicles. However, the currently commercialized anode materials, graphite (SEI-induced sluggish electrochemical kinetics and safety issues) and LTO (limited theoretical capacity), cannot fulfill the fast-charging requirement of future EVs. This dissertation novelly provides an ionothermal approach for the preparation of fast-rechargeable anode materials to resolve those aforementioned concerns for the future high-performance LIBs in EVs, due to the desirable templating effect, solvent miscibility, non-flammability and thermal stability of ILs.

In more detail, the great potential of ionothermal synthesis on the preparation of high-performance anode materials is well explored throughout this dissertation. The highly nanoporous structures of the ionothermally prepared anode materials demonstrate the promising templating effect of IL, which dramatically favors the Li\(^+\) diffusion kinetics and thereby achieves fast-rechargeability in LIBs, shining new light on the candidates of the next-generation LIB anode materials for the environmental and energy crises caused by the
burning of fossil fuels in vehicles. Therefore, we believe that ionothermal synthesis is highly suitable for future high-performance LIBs in EVs.

5.2 Outlook

This research dissertation has demonstrated the effectiveness of ionothermal synthesis. However, to realize its industrialization for the preparation of high-performance LIB anode materials, performing more detailed studies are essential.

Firstly, studies on the types of the applied ILs need to be taken. Various ILs with different combinations of cations and anions with tunable polarity can lead to a broad selection of the strength of the intermolecular interaction between IL and precursor molecules, which is directly related to the porosity of materials and their electrochemical performance. Additionally, the cost of the ILs is various due to the difficulty of the synthesis of the reactants. Thereby, it’s highly necessary to select a cost-effective IL for the future large-scale industrialization. Secondly, studies on the durability of ILs are also important since a highly reusable IL is desirable for large-scale preparation of high-performance anode materials. Owing to the good compatibility with organic solvent, excellent thermal stability and high redox robustness of IL, we indeed retrieved the used IL via a simple ethanol wash, which successfully avoids the CO$_2$ emission due to the burning of templates. Noticeably, the retrieved IL does present the identical NMR spectrum with the pristine IL. However, to the best of our knowledge, nobody has performed any durability study
yet. Therefore, to fully illustrate the eco-friendly effect of ionothermal synthesis, understand the property and potential decomposition of each IL during multi-time material syntheses is of interesting, which can establish the durability of ILs for future industrialization.

Accordingly, although this dissertation successfully paves a new avenue to realize the future fast-rechargeable LIBs, the industrialization of ionothermal synthesis for high-performance LIB anode materials still faces challenges, which should be considered and systematically addressed before industrialization, balancing the electrochemical performance of the prepared materials, cost of the preparation and the recyclability of the ILs.
REFERENCES


40. Li, H.; Shen, L.; Pang, G.; Fang, S.; Luo, H.; Yang, K.; Zhang, X., TiNb2O7 nanoparticles assembled into hierarchical microspheres as high-rate
capability and long-cycle-life anode materials for lithium ion batteries. *Nanoscale* 2015, 7 (2), 619-624.


47. Liao, C.; Sun, X.-G.; Dai, S., Crosslinked gel polymer electrolytes based on polyethylene glycol methacrylate and ionic liquid for lithium ion battery applications. *Electrochim. Acta* 2013, 87, 889-894.


74. Lin, C.; Yu, S.; Wu, S.; Lin, S.; Zhu, Z.-Z.; Li, J.; Lu, L., Ru0.01Ti0.99Nb2O7 as an intercalation-type anode material with a large capacity and high rate performance for lithium-ion batteries. *J. Mater. Chem. A* 2015, 3 (16), 8627-8635.


76. Yang, C.; Lin, C.; Lin, S.; Chen, Y.; Li, J., Cu0.02Ti0.94Nb2.04O7: An advanced anode material for lithium-ion batteries of electric vehicles. *J. Power Sources* 2016, 328, 336-344.


122. Lu, Z.; Yu, Z.; Dong, J.; Song, M.; Liu, Y.; Liu, X.; Ma, Z.; Su, H.; Yan, Y.; Huo, P., Facile microwave synthesis of a Z-scheme imprinted ZnFe2O4/Ag/PEDOT with the specific recognition ability towards improving


APPENDIX

Figure 1-1. Working principle of LIBs.$^{133}$

Figure 1-2. Crystal structures of (a). TiNb$_2$O$_7$ $^{134}$ and (b). W$_3$Nb$_{14}$O$_{44}$.

Figure 1-3. (a). Illustration of solid-state mechanochemical synthesis for bulk TiNb$_2$O$_7$ material. (b). TEM image of the corresponding prepared bulk TiNb$_2$O$_7$ material.
Figure 1-4. Schematic of the hydrothermal and solvothermal syntheses.\textsuperscript{5}

Figure 1-5. Schematic demonstration of the hydrogen bonding and $\pi-\pi$ stacking mechanism for the porous structure framework.\textsuperscript{15}
Figure 1-6. Demonstration of hydrolysis (upper) and polycondensation (lower).

Figure 1-7. Scheme of NMR working principle.

Figure 1-8. Scheme of XRD working principle.
Figure 1-9. Scheme of NPD working principle.

Figure 1-10. Scheme of Raman spectroscopy working principle.
Figure 1-11. Scheme of XPS working principle.

Figure 1-13. Scheme demonstration of the typical GITT process.
Figure 2-1. Synthesis scheme of [Bmim][NTf₂].

Figure 2-5. Synthesis scheme of NPTNO material.
Figure 2-6. Synthesis schematic diagram of the bulk TNO.
Figure 2-2. HNMR spectrum of [BMIm][NTf₂] in DMSO.
Figure 2-3. HNMR spectrum of [BMIm][NTf₂] in DMSO.
Figure 2-4. CNMR spectrum of [BMIm][NTf₂] in DMSO.
Figure 2-7. (a and b). XRD patterns of the prepared TNO materials. (c). XRD Rietveld refinement of TNO700. (d). Crystal structure of TNO700.
Figure 2-8. Raman spectra of TNO700 and TNO850 materials within range from 100 to 1100 cm\(^{-1}\).

Figure 2-9. (a and b). Nitrogen adsorption-desorption isotherm curves and their corresponding BJH plots of NPTNO materials, respectively.
Figure 2-10. SEM images and elemental mappings of NPTNO and BTNO materials. (a and b). TNO700. (c and d). TNO850.
Figure 2-11. TEM and HRTEM images of the obtained NPTNO materials at different magnifications. (a and b). TNO700. (c and d). TNO850.

Figure 2-12. SAED patterns of (a). TNO700 and (b). TNO850.
Figure 2-13. CV plots of TNO700 half-cell at a scan rate of 0.05 mV/s. (a) TNO700. (b) TNO850. (c) BTNO.

Figure 2-14. Discharge-charge profiles of the assembled half-cells at a current rate of 0.1 C (38.7 mA/g). (a) TNO700. (b) TNO850. (c) BTNO.

Figure 2-15. Rate performance test of the assembled half-cells within C rate range from 0.5 C to 50 C.
Figure 2-16. Cyclic performance study of the assembled half-cells at a high C rate of 5 C over 1000 cycles.

Figure 2-17. Electrochemical performance study of the assembled full-cells in voltage range from 1.5 to 3.5 V. (a and c). Cyclic performance study at 1 and 2 C over 1000 cycles. (b and d). The corresponding charge-discharge curves at 1 and 2 C.
Figure 2-18. Structural studies of the cycled TNO700. (a). XRD patterns of pristine TNO powder and the cycled TNO electrode at charge state. (b). XPS broad spectra of the uncycled and the cycled TNO electrodes at charge state. (c and d). The HRXPS of C, O, and F elements for the uncycled and the cycled TNO electrodes, respectively.

Figure 2-19. SEM images and SEM-EDS elemental mappings of NPTNO electrodes. (a) SEM image of uncycled TNO700 electrode. (b) Broad view elemental mappings of uncycled TNO700 electrode. (c) SEM image of 1000 cycled TNO700 electrode. (d) Broad view elemental mappings of 1000 cycled TNO700 electrode TNO700.
Figure 2-20. HRXPS of Ti and Nb elements for the uncycled and 1000 cycled TNO700 electrodes. (a and b). HRXPS of Ti and Nb for the uncycled TNO700 electrode, respectively. (c and d). HRXPS of Ti and Nb for the 1000 TNO700 electrode, respectively.

Figure 2-21. GITT Li⁺ diffusivity studies of TNO anodes in half-cells. (a). GITT curves of the TNO electrodes. (b). GITT Li⁺ diffusivity plots of TNO anodes.
Figure 2.22. Pictures of synthesized ILs. (a) Synthesized [BMIm]Br. (b) [BMIm][NTf₂]-water washing process. (c) Synthesized [BMIm][NTf₂]. (d) Recycled [BMIm][NTf₂].

Figure 2.23. Nitrogen adsorption-desorption isotherm Barrett-Joyner-Halenda (BJH) plots of bulk TNO anode.

Figure 2.24. Raman spectra of the synthesized TNO materials.
Figure 2-25. SEM and SEM EDS elemental mapping images of BTNO.

Figure 2-26. TEM images and TEM-SAED pattern of bulk TNO anode. (a) TEM of TNO Bulk. (b) HRTEM of TNO Bulk. (c) TEM-SAED of TNO Bulk.

Table 2-1. Characterization results of the prepared NPTNO and BTNO materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>BET Surface Area (m²/g)</th>
<th>TEM Measured Average Crystallite Size (nm)</th>
<th>GITT measured Li⁺ Diffusion Coefficient (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNO700</td>
<td>72</td>
<td>18.4</td>
<td>8.5 x 10⁻¹³ – 1.2 x 10⁻⁹</td>
</tr>
<tr>
<td>TNO850</td>
<td>38</td>
<td>29.2</td>
<td>2.4 x 10⁻¹⁴ – 1.2 x 10⁻¹⁰</td>
</tr>
<tr>
<td>BTNO</td>
<td>3.1</td>
<td>340.9</td>
<td>1.1 x 10⁻²¹ – 9.4 x 10⁻¹⁹</td>
</tr>
</tbody>
</table>
Table 2-2. Comparison of the measured Li⁺ diffusion coefficient of several ReO₃-type materials.

<table>
<thead>
<tr>
<th>Type of Anode Materials</th>
<th>Measured Li⁺ Diffusion Coefficient (m²/s)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>TNO700</td>
<td>2.4×10⁻¹⁴ – 1.2×10⁻⁹</td>
<td>This study</td>
</tr>
<tr>
<td>BTNO</td>
<td>1.1×10⁻²¹ – 9.4×10⁻¹⁹</td>
<td>This study</td>
</tr>
<tr>
<td>W₅Nb₁⁶O₅₅</td>
<td>5.0×10⁻¹⁷ – 3.8×10⁻¹⁶</td>
<td>J. Mater. Chem. A, 2019, 7, 25537–25547</td>
</tr>
<tr>
<td>WNb₁₂O₅₅ nanowire</td>
<td>8.5×10⁻¹⁶ – 1.1×10⁻¹⁵</td>
<td>J. Mater. Chem. A, 2015, 5, 8972–8980</td>
</tr>
<tr>
<td>WNb₁₂O₅₅ nanorod</td>
<td>7.2×10⁻¹⁶ – 7.7×10⁻¹⁶</td>
<td>J. Mater. Chem. A, 2015, 5, 8972–8980</td>
</tr>
<tr>
<td>Zn₂Nb₃₄O₈₇ bulk</td>
<td>5.0×10⁻¹⁷ – 9.0×10⁻¹⁶</td>
<td>J. Mater. Chem. A, 2019, 7, 25537–25547</td>
</tr>
<tr>
<td>Zn₂Nb₃₄O₈₇ nanofiber</td>
<td>2.0×10⁻¹⁶ – 9.1×10⁻¹⁶</td>
<td>J. Mater. Chem. A 2019, 7, 25537–25547</td>
</tr>
<tr>
<td>MoNb₁₂O₃₃</td>
<td>3.1×10⁻¹⁹ – 1.1×10⁻¹⁷</td>
<td>J. Mater. Chem. A 2019, 7, 6522–6532</td>
</tr>
<tr>
<td>FeNb₁₁O₂₉</td>
<td>8.6×10⁻¹⁶ – 3.4×10⁻¹⁵</td>
<td>ChemElectroChem, 2017, 7, 3171–3180</td>
</tr>
<tr>
<td>CrNb₁₁O₂₉ nanorod</td>
<td>1.5×10⁻¹⁷ – 3.6×10⁻¹⁷</td>
<td>J. Power Sources, 2018, 397, 231-239</td>
</tr>
<tr>
<td>Carbon coated GaNb₁₁O₂₉</td>
<td>4.3×10⁻¹⁷ – 3.7×10⁻¹⁷</td>
<td>Ceram. Int., 2020, 46, 5913–5919</td>
</tr>
<tr>
<td>GaNb₁₁O₂₉</td>
<td>7.9×10⁻¹⁸ – 8.2×10⁻¹⁸</td>
<td>Ceram. Int., 2020, 46, 5913–5919</td>
</tr>
</tbody>
</table>
Table 2-3. Capacity comparison among various anode materials. Theoretical capacities: TNO = 387.6 mAh/g, Li$_4$Ti$_5$O$_{12}$ = 175 mAh/g, TiO$_2$ bronze = 335 mAh/g, and TiO$_2$ anatase = 167.5 mAh/g.

<table>
<thead>
<tr>
<th>Type of Anode Materials</th>
<th>Reversible Capacity at a Low C-rate (mAh/g)</th>
<th>Rate-Capability at a High C-rate (mAh/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano-porous TNO by IL directed</td>
<td>281 at 0.1 C (1.0 – 3.0 V)</td>
<td>218 at 20 C 210 at 50 C (1.0 – 3.0 V)</td>
<td>This study</td>
</tr>
<tr>
<td>Nano-porous TNO by block polymer directed</td>
<td>281 at 0.1 C (1.0 – 3.0 V)</td>
<td>206 at 50 C (1.0 – 3.0 V)</td>
<td>Energy Environ. Sci., 2014, 7, 2220–2226</td>
</tr>
<tr>
<td>Bulk TNO by solid-state synthesis</td>
<td>275 at 0.1 C (1.0 – 3.0 V)</td>
<td>58 at 50 C (1.0 – 3.0 V)</td>
<td>This study</td>
</tr>
<tr>
<td>Mesostructured TNO by block copolymer directed</td>
<td>289 at 0.1 C (1.0 – 3.0 V)</td>
<td>116 at 50 C (1.0 – 3.0 V)</td>
<td>Chemistry of Materials, 2014, 26, 3508–3514</td>
</tr>
<tr>
<td>Porous TNO microsphere</td>
<td>265 at 0.1 C (1.0 – 3.0 V)</td>
<td>165 at 50 C (1.0 – 3.0 V)</td>
<td>Advanced Energy Materials, 2015, 5, 1401945</td>
</tr>
<tr>
<td>TNO nanorods by sol-gel</td>
<td>265 at 0.1 C (1.0 – 3.0 V)</td>
<td>84 at 50 C (1.0 – 3.0 V)</td>
<td>Chemical Communications, 2015, 51, 17293–17296</td>
</tr>
<tr>
<td>Macroporous TNO by polystyrene sphere</td>
<td>212 at 1 C (1.0 – 3.0 V)</td>
<td>120 at 50 C (1.0 – 3.0 V)</td>
<td>Nano Energy, 2017, 2211-2855</td>
</tr>
<tr>
<td>Mo-doped TNO</td>
<td>260 at 0.1C (1.0 – 3.0 V)</td>
<td>208 at 50 C (1.0 – 3.0 V)</td>
<td>Chemical Communications, 2015, 51, 9849–9852</td>
</tr>
<tr>
<td>TNO nanofiber</td>
<td>284 at 0.1C (1.0 – 3.0 V)</td>
<td>85 at 50 C (1.0 – 3.0 V)</td>
<td>Advanced Energy Materials, 2013, 3, 49-53</td>
</tr>
<tr>
<td>Carbon coated-Li$_4$Ti$<em>5$O$</em>{12}$</td>
<td>168 at 0.2 C (1.0 – 3.0 V)</td>
<td>107 at 10 C (1.0 – 3.0 V)</td>
<td>Energy Environ. Sci., 2011, 4, 1345-1351</td>
</tr>
<tr>
<td>Mesoporous Li$_4$Ti$<em>5$O$</em>{12}$ - carbon composite</td>
<td>144 at 0.2 C (1.0 – 2.5 V)</td>
<td>105 at 20 C 85 at 50 C (1.0 – 2.5 V)</td>
<td>Advanced Functional Materials, 2011, 21, 4349-4537</td>
</tr>
<tr>
<td>TiO$_2$ nanodisk (anatase)</td>
<td>191 at 0.2 C (1.0 – 3.0 V)</td>
<td>112 at 20 C (1.0 – 3.0 V)</td>
<td>Energy Environ. Sci., 2013, 6, 2932-2938</td>
</tr>
</tbody>
</table>
Figure 3-1. Schematic illustration of NPTWNO preparation via ionothermal synthesis.

Figure 3-2. (a). XRD patterns and Rietveld refinements of (b). NPTWNO and (c). TNO materials, respectively.
Figure 3-3. (a). nitrogen adsorption/desorption isotherm of NPTWNO and (b). its corresponding BJH plot.

Figure 3-4. (a-c). SEM, TEM and HRTEM images of NPTWNO.
Figure 3-5. CV profiles of the NPTWNO-based LIB cell in the potential window of 1.0–3.0 V at a scan rate of 0.05 mV/s.

Figure 3-6. The initial galvanostatic discharge-charge plots at 0.1 C. (a) NPTWNO. (b) TNO.
Figure 3-7. (a). Rate capability and Coulombic efficiency comparisons between NPTWNO and TNO half-cells at various rates: discharge current rate fixed at 1 C (except the 0.5 C discharge-charge profile). (b). Cyclic performance comparisons between NPTWNO and TNO half-cells at a current rate of 5 C after aging at 0.1 C for 3 cycles.

Figure 3-8. SEM EDX study of NPTWNO material. (a). SEM image and the selected area. (b). EDX spectrum. (c-f). Elemental mappings of Ti, Nb, W and O, respectively.
Figure 3-9. Electron microscopy images of the bulk TNO material. (a). SEM image. (b). TEM image. (c). HRTEM image.

Figure 3-10. Selected area electron diffraction patterns. (a). NPTWNO. (b). TNO.
Figure 3-11. CV profiles of TNO at a scan rate of 0.05 mV/s.

Figure 4-1. Scheme demonstration of the ionothermal synthesis of MWNO material.
Figure 4-2. XRD pattern of MWNO material.

Figure 4-3. Raman spectrum of MWNO material.
Figure 4-4. Broad XPS spectrum of MWNO material.

Figure 4-5. HRXPS spectra of (a) Mo-3d, (b) W-4f, (c) Nb-3d and (d) O-1s for MWNO material.
Figure 4-6. NPD Rietveld refinement of MWNO.

Figure 4-7. The proposed lattice structure of MWNO based on NPD analysis.
Figure 4-8. AC-STEM studies of MWNO material. (a). HAADF image along zone axis of [001]. (b and c). Local lattice structure model of the MoO$_4$ tetrahedral site and the corresponding HAADF simulation image. (d). HAADF image along zone axis of [100].
Figure 4-9. Electron microscopy studies of MWNO. (a-c). SEM, TEM and HRTEM images, respectively. (d). SAED pattern (from the selected area in b)). (e-i). HAADF image and its corresponding EDX elemental mapping images.
Figure 4-10. CV profile of MWNO at a scan rate of 0.05 mV/s.

Figure 4-11. Galvanostatic discharge/charge curves of MWNO at a current rate of 0.1 C.
Figure 4-12. Rate performance study of MWNO, MNO and WNO.

Figure 4-13. Plot of $(a\nu)^2$ versus $\nu$. 
Figure 4-14. Projected density of states obtained from the DFT computation. The Fermi level is represented by the gray line at energy of 0 eV.

Figure 4-15. EIS Nyquist plot of MWNO.
Figure 4-16. MWNO GITT study. (a-c). GITT discharge/charge curve, its zoomed-in plot and the corresponding Li\(^+\) insertion/extraction diffusivity plot, respectively.

Figure 4-17. Contour plot of the operando XRD pattern of MWNO along with the corresponding voltage profile of the initial discharge/charge cycle.
Figure 4-18. The evolution of the refined lattice parameters for MWNO unit cell obtained from the operando XRD experiment.

Figure 4-19. (a and b). Demonstrations of the Li$^+$ diffusion paths. The NbO$_6$ and WO$_6$ octahedra are shown in green and gray, respectively, and MO$_6$ octahedra and MO$_4$ tetrahedra are shown in purple. The blue arrows indicate possible Li$^+$ diffusion paths, named as Path I, II, III and IV. The black balls indicate Li$^+$ at the initial and final sites for Li$^+$ diffusion. (c-f). The DFT study of the energy barriers of the Li$^+$ diffusion paths along Path I, II, III and IV, respectively.
Figure 4-20. Cyclic performance study of MWNO, MNO and WNO.
Figure 4-21. Studies of cycling effect for the MWNO electrode. a) XRD patterns of an unycled MWNO electrode and the cycled MWNO electrode. Copper foil appears two sharp diffraction peaks at 43.3 and 50.4 °, corresponding to the (111) and (200) crystallographic planes, respectively. b) Zoomed-in XRD patterns of an unycled MWNO electrode and the cycled MWNO electrode as the illustration of tiny shifts of peaks. c) SEM images of the cycled MWNO electrode and the unycled MWNO electrode: I and II — broad view and zoomed-in view of the cycled MWNO electrode, respectively; III and IV — broad view and zoomed-in view of the unceded MWNO electrode, respectively. d-h) HRXPS spectra of Mo, W, Nb, C, O and F elements for the 2000-cycled MWNO electrode, respectively.
Figure 4-22. Electrochemical performance studies of the LiNi$_{0.5}$Mn$_{1.5}$O$_4$-MWNO full-cells in the voltage window of 1.5 – 3.5 V. a). The galvanostatic charge/discharge profiles at 1 C. b). Rate performance and Coulombic efficiency at multiple current rates with discharge current rate fixed at 1 C (except the discharge/charge profiles at 0.5 C) c). Cyclic performance and Coulombic efficiency at a constant current rate of 2 C after aging at 0.1, 0.5 and 1 C.
Figure 4-23. HNMR spectra of the synthesized [BMIm]Br and [BMIm][NTf₂] in DMSO.

Figure 4-24. CNMR spectrum of the synthesized [BMIm][NTf₂] in DMSO.
Figure 4-25. Digital images of the obtained samples.

Figure 4-26. The vanadium can (sample holder) for neutron powder diffraction experiment at Oak Ridge National Laboratory Spallation Neutron Source on the POWGEN BL-11A.
Figure 4-27. Normalized (a) XRD patterns, (b) FTIR spectra and (c) Raman spectra of MWNO, MNO and WNO materials.

Figure 4-28. Rietveld refinements of the XRD patterns of (a) MNO and (b) WNO.
Figure 4-29. Broad XPS spectrum of MWNO.

Figure 4-30. Broad XPS spectrum of MNO.
Figure 4-31. Broad XPS spectrum of WNO.

Figure 4-32. (a-c). HRXPS spectra of MNO for Mo, Nb and O, respectively. (d-e). HRXPS spectra of WNO for W, Nb and O, respectively.
Figure 4-33. NPD patterns of MWNO, MNO and WNO.

Figure 4-44. Rietveld refinement of the NPD pattern of WNO.
Figure 4-45. Full-sized image of the crystal structure of MWNO. The red, green, grey (in the faint-green octahedra) and purple spheres correspond to the O, Nb, W and Mo atoms in the unit cell, respectively. The structure consists of $4 \times 4 \text{ReO}_3$ blocks intersected with crystallographic shear planes.
Figure 4-46. (a and b). Crystal structures of MNO along the c axis and b axis, respectively. (c and d). Crystal structures of WNO along the c axis and a axis, respectively.

Figure 4-47. ACSTEM HAADF with atom assignments of MWNO along the [001] projection (yellow: Nb/W/Mo; blue: Mo).
Figure 4-48. The corresponding FFT pattern of Figure 2k for MWNO along the [001] projection.

Figure 4-49. The corresponding FFT pattern of Figure 2l for MWNO along the [010] projection.
Figure 4-50. AC-STEM HAADF images of MNO and WNO materials at atomic-resolution. (a and b). MNO. (c and d). WNO.

Figure 4-51. (a-d). SEM, TEM, HRTEM images and SAED pattern of MNO, respectively. (e-h). SEM, TEM, HRTEM images and SAED pattern of WNO, respectively.
Figure 4-52. SEM EDX spectrum of MWNO.
Figure 4-53. SEM EDX spectrum of MNO.
Figure 4-54. SEM EDX spectrum of WNO.
Figure 4-55. Images of SEM EDX elemental mapping of MWNO.

Figure 4-56. Images of SEM EDX elemental mapping of MNO.

Figure 4-57. Images of SEM EDX elemental mapping of WNO.
Figure 4-58. STEM-HAADF and EDX elemental mapping images of MNO.

Figure 4-59. STEM-HAADF and EDX elemental mapping images of MNO.
Figure 4-60. (a and b). N₂ adsorption isotherms BET curves and BJH plots of MWNO, MNO and WNO materials, respectively.

Figure 4-61. (a-c). CV cycles at a scan rate of 0.05 mV/s, galvanostatic discharge/charge profiles at a current rate of 0.1 C and initial EIS impedance spectrum of MNO, respectively. 
(d-f). CV cycles at a scan rate of 0.05 mV/s, galvanostatic discharge/charge profiles at a current rate of 0.1 C and initial EIS impedance spectrum of WNO, respectively.
Figure 4-62. (a). UV-vis DRS spectra of MWNO, MNO and WNO. (b). Determination of the transition type for MWNO. (c and d). Determination of the transition type and measurement of bandgap for MNO, correspondingly. (e and f). Determination of the transition type and measurement of bandgap for WNO, correspondingly.
Figure 4-63. (a and b). Projected density of states for MNO and WNO, respectively.
Figure 4-64. GITT results of MNO and WNO electrodes. (a and b). GITT discharge/charge curve and the corresponding Li\(^+\) insertion/extraction diffusivity plot of MNO, respectively. (c and d). GITT discharge/charge curve and the corresponding Li\(^+\) insertion/extraction diffusivity plot of WNO, respectively.
Figure 4-65. Contour plot of the operando XRD patterns of MNO.

Figure 4-66. Evolution of lattice parameters of MNO obtained from Rietveld refinement.
Figure 4-67. Contour plot of the operando XRD patterns of WNO.

Figure 4-68. Evolution of lattice parameters of WNO obtained from Rietveld refinement.
Figure 4-69. (a and b). Demonstrations of the Li$^+$ diffusion paths. The NbO$_6$ and WO$_6$ octahedra are shown in green and gray, respectively, and MO$_6$ octahedra and MO$_4$ tetrahedra are shown in purple. The blue arrows indicate possible Li$^+$ diffusion paths, named as Path I, II and III. The black balls indicate Li$^+$ at the initial and final sites for Li$^+$ diffusion. (c-e). The DFT study of the energy barriers of the Li$^+$ diffusion paths along Path I, II and III, respectively.

Figure 4-70. Rietveld refinement of the XRD pattern of the 2000-cycled MWNO electrode.
Figure 4-71. SEM and EDX elemental mapping images of the 2000-cycled MWNO electrode.

Figure 4-72. EDX spectrum and elemental composition report of the 2000-cycled MWNO electrode.
Figure 4-73. SEM and EDX elemental mapping images of the uncycled MWNO electrode.

Figure 4-74. EDX spectrum and elemental composition report of the uncycled MWNO electrode.
Figure 4-75. XPS broad spectra of the 2000-cycled and uncycled MWNO electrodes.

Figure 4-76. (a-f) Mo, W, Nb, C, O and F HRXPS spectra of the uncycled MWNO electrode, respectively.
Figure 4-77. Galvanostatic charge/discharge of an assembled full-cell at a current rate of 0.5 C.

Figure 4-78. Cyclic performance of an assembled full-cell at a high current rate of 10 C.
Table 4-4. Lattice parameters of MWNO, MNO and WNO obtained from powder XRD Rietveld refinements. Crystallite size is abbreviated as C.S..

<table>
<thead>
<tr>
<th>Material</th>
<th>( a = b ) (Å)</th>
<th>( c ) (Å)</th>
<th>( \alpha = \beta = \gamma ) (°)</th>
<th>( V ) (Å(^3))</th>
<th>C.S. (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNO</td>
<td>20.998(1)</td>
<td>3.819(1)</td>
<td></td>
<td>1683.9</td>
<td>96.44</td>
</tr>
<tr>
<td>MNO</td>
<td>21.016(1)</td>
<td>3.811(1)</td>
<td>90</td>
<td>1683.2</td>
<td>74.47</td>
</tr>
<tr>
<td>WNO</td>
<td>20.993(1)</td>
<td>3.822(1)</td>
<td></td>
<td>1684.4</td>
<td>704.36</td>
</tr>
</tbody>
</table>

Table 4-5. The site occupancies of the cations in WNO and MWNO obtained from the NPD Rietveld refinements.

<table>
<thead>
<tr>
<th>WNO</th>
<th>( t1 )</th>
<th>( o1 )</th>
<th>( o2 - o4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% W</td>
<td>80% Nb + 20% W</td>
<td>77% Nb + 23% W</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>MWNO</th>
<th>( t1 )</th>
<th>( o1 )</th>
<th>( o2 - o4 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Mo</td>
<td>49% Nb/Mo + 51% W</td>
<td>95% Nb/Mo + 5% W</td>
<td></td>
</tr>
</tbody>
</table>
Table 4-6. The calculated cation-oxygen bond length in WNO and MWNO from the NPD Rietveld refinements.

<table>
<thead>
<tr>
<th>Site</th>
<th>cation-O bond length in WNO (Å)</th>
<th>cation-O bond length in MWNO (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_1$</td>
<td>1.761(8) $\times$ 4</td>
<td>1.766(7) $\times$ 4</td>
</tr>
<tr>
<td>$o_1$</td>
<td>1.882(2), 1.923(2) $\times$ 2, 1.964(2), 1.970(2), 2.122(2)</td>
<td>1.883(2), 1.9264(2) $\times$ 2, 1.920(2), 2.001(2), 2.132(2)</td>
</tr>
<tr>
<td>$o_2$</td>
<td>1.831(1), 1.907(1), 1.987(4) $\times$ 2, 2.042(2), 2.306(2)</td>
<td>1.808(1), 1.927(1), 1.990(4) $\times$ 2, 2.048(2), 2.277(2)</td>
</tr>
<tr>
<td>$o_3$</td>
<td>1.728(1), 1.929(1), 1.974(3) $\times$ 2, 2.031(1), 2.163(2)</td>
<td>1.762(2), 1.917(1), 1.985(3) $\times$ 2, 2.031(2), 2.261(2)</td>
</tr>
<tr>
<td>$o_4$</td>
<td>1.808(1), 1.849(1), 2.011(4) $\times$ 2, 2.138(1), 2.283(2)</td>
<td>1.819(1), 1.822(1), 1.985(4) $\times$ 2, 2.141(1), 2.238(2)</td>
</tr>
</tbody>
</table>
Table 4-7. Average discharge capacities of MWNO, MNO and WNO at multiple current rates in the rate performance test.

<table>
<thead>
<tr>
<th>C-rate</th>
<th>0.5 C</th>
<th>1 C</th>
<th>2 C</th>
<th>5 C</th>
<th>10 C</th>
<th>20 C</th>
<th>50 C</th>
<th>100 C</th>
<th>1 C</th>
</tr>
</thead>
<tbody>
<tr>
<td>MWNO capacity (mAh/g)</td>
<td>239.1</td>
<td>220.0</td>
<td>213.8</td>
<td>206.4</td>
<td>198.3</td>
<td>191.2</td>
<td>154.6</td>
<td>92.1</td>
<td>219.2</td>
</tr>
<tr>
<td>MNO capacity (mAh/g)</td>
<td>246.1</td>
<td>200.8</td>
<td>189.0</td>
<td>162.2</td>
<td>136.4</td>
<td>79.3</td>
<td>23.0</td>
<td>7.0</td>
<td>200.7</td>
</tr>
<tr>
<td>WNO capacity (mAh/g)</td>
<td>213.7</td>
<td>203.9</td>
<td>194.9</td>
<td>186.7</td>
<td>173.4</td>
<td>159.6</td>
<td>137.5</td>
<td>63.6</td>
<td>191.2</td>
</tr>
</tbody>
</table>

Table 4-8. $D_{Li^+}$ (m$^2$/s) obtained from GITT.

<table>
<thead>
<tr>
<th></th>
<th>MWNO</th>
<th>MNO</th>
<th>WNO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$ insertion (max)</td>
<td>$1.47 \times 10^{-17}$</td>
<td>$1.05 \times 10^{-18}$</td>
<td>$6.99 \times 10^{-18}$</td>
</tr>
<tr>
<td>Li$^+$ insertion (min)</td>
<td>$3.00 \times 10^{-18}$</td>
<td>$1.72 \times 10^{-19}$</td>
<td>$5.58 \times 10^{-19}$</td>
</tr>
<tr>
<td>Li$^+$ insertion average</td>
<td>$7.70 \times 10^{-18}$</td>
<td>$4.88 \times 10^{-19}$</td>
<td>$2.02 \times 10^{-18}$</td>
</tr>
<tr>
<td>Li$^+$ extraction (max)</td>
<td>$3.57 \times 10^{-17}$</td>
<td>$6.64 \times 10^{-17}$</td>
<td>$2.10 \times 10^{-17}$</td>
</tr>
<tr>
<td>Li$^+$ extraction (min)</td>
<td>$1.56 \times 10^{-18}$</td>
<td>$5.02 \times 10^{-17}$</td>
<td>$1.76 \times 10^{-18}$</td>
</tr>
<tr>
<td>Li$^+$ extraction average</td>
<td>$2.01 \times 10^{-17}$</td>
<td>$1.66 \times 10^{-17}$</td>
<td>$1.26 \times 10^{-17}$</td>
</tr>
</tbody>
</table>

Table 4-9. Lattice parameters of the cycled MWNO electrode at charge state (3.0 V) obtained from XRD Rietveld refinement.

<table>
<thead>
<tr>
<th>a = b (Å)</th>
<th>c (Å)</th>
<th>α = β = γ (°)</th>
<th>V (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21.006(1)</td>
<td>3.825(1)</td>
<td>90</td>
<td>1687.8</td>
</tr>
</tbody>
</table>
In 1993, Runming Tao was born in Kunming, Yunnan, China. After completing high school, he came to the USA to pursue better education in 2012. During Runming’s undergraduate career, he was deeply impressed and inspired by the comprehensive opportunities in the study of science. As a result, he realized superb academic achievement at Southern Illinois University Carbondale and graduated with a Degree of Bachelor of Science in Chemistry and a Minor in Mathematics on Calculus-track. Based on the wonderful experience in USA, he then decided to continue and earn a Ph.D. in Chemistry in the lab of Prof. Sheng Dai at the University of Tennessee, Knoxville, and Oak Ridge National Laboratory in 2017. He learned a lot of research skills from Dr. Jiyuan Liang, Dr. Xiao-Guang Sun, Dr. Guang Yang, Dr. Chi-Linh Do-Thanh, Dr. Ethan Self and Dr. Jagjit Nanda. Unfortunately, he couldn’t graduate within four years because of the huge interference and delay caused by COVID-19. In December 2021, he completed the requirements for a Ph.D. in Chemistry and would find another wonderland in his life.