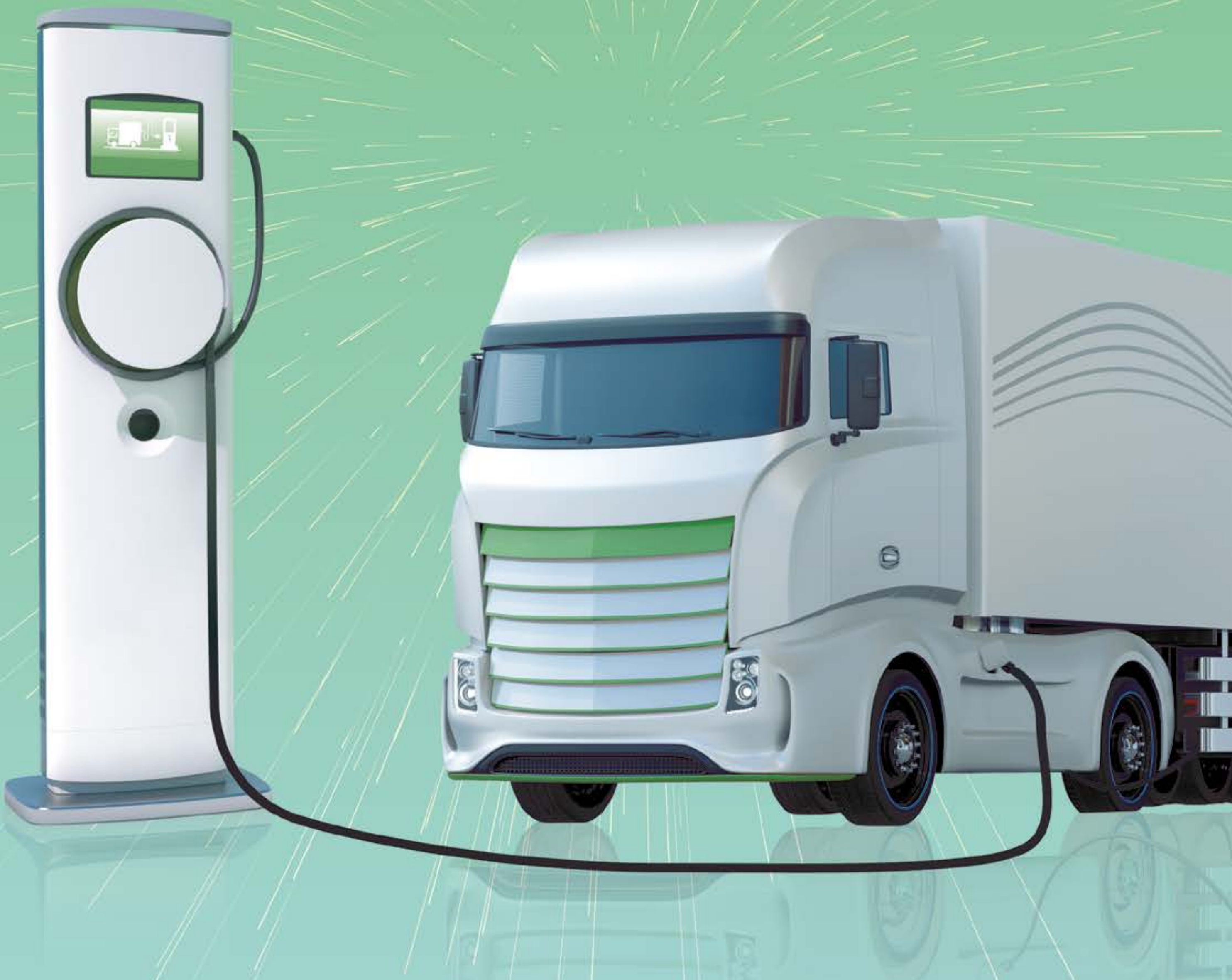
2022［第五届］铌在电池中应用国际研讨会文集

2022 | International Conference on Niobium Based Batteries

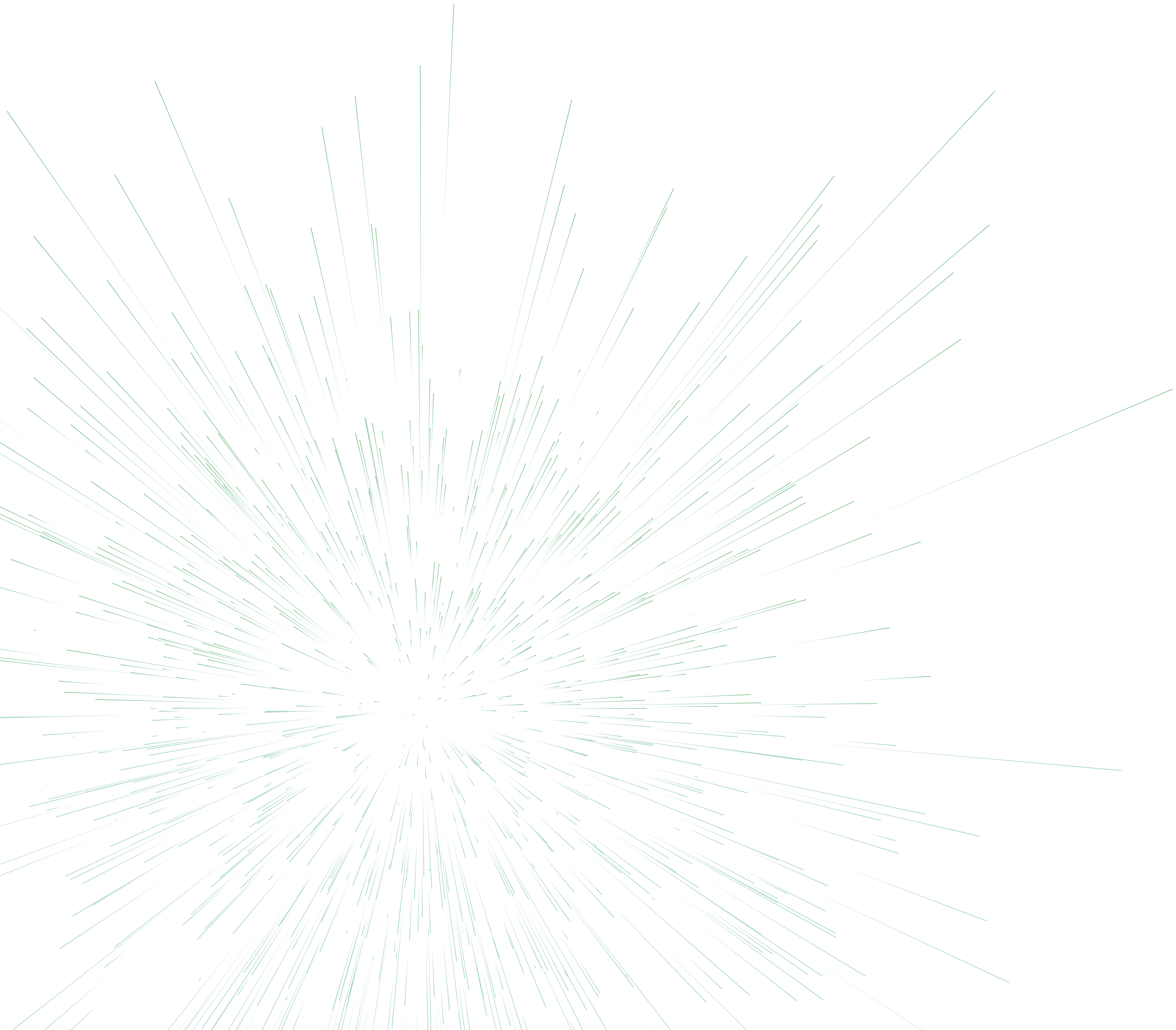
The 5th Edition

Nanning - China | September 15th



中信金属股份有限公司
CITIC Metal Co., Ltd

CBMM | Niobium



2022［第五届］铌在电池中应用国际研讨会文集

2022 International Conference on Niobium Based Batteries

Date: September 15th, 2022
Hybrid Event

主办单位 / Organized by

中信金属股份有限公司 CITIC Metal Co., Ltd

CBMM | Niobium Nb

支持单位 / Partners

- China Nonferrous Metals Industry Association
- China Industrial Association of Power Sources
- China Industry Technology Innovation Strategic Alliance for Electric Vehicle
- The Chinese Society of Electrochemistry
- Institute of Physics, Chinese Academy of Sciences
- Songshan Lake Materials Laboratory
- South Manganese Group Limited

大会主席 /Chairman

- Dr. Aimin Guo, Vice President of CITIC Metal Co., Ltd, China

组织委员会 /Organizing Committee:

- Mr. Ricardo Lima, President of CBMM, Brazil
- Dr. Aimin Guo, Vice President of CITIC Metal Co., Ltd, China
- Mr. Weijian Li, President of South Manganese Group Limited, China
- Mr. Debing Duan, Deputy President, China Nonferrous Metals Industry Association
- Mr. Yanlong Liu, General Secretary, China Industrial Association of Power Sources
- Prof. Dr. Xuejie Huang, Institute of Physics, Chinese Academy of Sciences, China
- Prof. Dr. Yongyao Xia, Fudan University, China
- Mr. Lijing Zhao, Assistant of General Secretary, China SAE, China
- Mr. Rogerio Ribas, Executive Manager of Battery Products, CBMM, Brazil
- Dr. Robson Monteiro, Sr. Market Development Specialist, CBMM, Brazil
- Dr. Zhongzhu Liu, Senior Engineer, CITIC Metal Co., Ltd, China
- Dr. Luanna Parreira, Senior Engineer of Battery Products, CBMM, Brazil

秘书长 /General Secretary

- Dr. Zhongzhu Liu, Senior Engineer, CITIC Metal Co., Ltd, China
- Dr. Luanna Parreira, Senior Engineer of Battery Products, CBMM, Brazil

Dear guest,

On behalf of the board of CBMM, I would like to thank you for participating in the 5th Edition of the International Conference on Niobium Based Batteries, held in hybrid mode on September 15th, in Nanning, China.

On this year's conference, we've brought together guest speakers from all over the world to contribute to developing niobium technology in electrochemical energy storage related to lithium-ion batteries. In the first session, our guest speakers will approach the next generation of applications of niobium in doping and coating for active cathode materials. The second session will introduce the development of niobium's role in active anode materials to evidence application for high-power technologies for industrial, commercial, and heavy-duty applications. And this year, CBMM and CITIC Metal introduced the Excellent Paper Award, a recognition for researchers on niobium batteries in China. This initiative aims to recognize the excellence of the production of knowledge and scientific contribution from the Chinese researchers and academics of the future in this important area of advancement in niobium based batteries and to speed up the technical development in this field.

This event is happening thanks to the strong alliance between CITIC Metal and CBMM. It's a long-term partnership, and our friends from CITIC Metal make us happy to be able to share this additional activity with them. We're very proud to have such a relevant and important partner in this event and new initiative. Furthermore, on behalf of Ricardo Lima, president of CBMM, and Dr. Aimin Guo, vice president of CITIC Metal in China, we would like to express our sincere appreciation to all the speakers, attendees, and organizers for being here and for sharing with us some more fresh and new information on the advanced battery materials using niobium.

Yours sincerely,

João Fernando
Board Member, CBMM

The rapid development of electric vehicles and energy storage technologies has fast-tracked the urgent requirements for high-performance batteries. The 2022 International Conference on Niobium Based Batteries will present the significant advantages of niobium technology in lithium-ion batteries, including heavy-duty vehicle applications, which have attracted extensive attention from the global market and academia. This year's conference specially invited experts from the United States, the UK, Brazil, Korea, Japan and China to exchange insights on the market development and application of advanced energy storage.

2022 International Conference on Nioibum Based Batteries Programme

Opening Session and Excellent Paper Award Ceremony

08:30 - 08:35	VIP Introduction	Dr. Zhongzhu Liu, CITIC Metal Co., Ltd
08:35 - 08:50	Opening Address	• Prof. Dr. João Fernando, CBMM Board Member • Mr. Debing Duan, Vice President of China Nonferrous Metals Industry Association • Mr Yanlong Liu, Generay Secretary of China Industrial Association of Power Sources • Dr. Aimin Guo, VP CITIC Metal Co., Ltd
08:50 - 09:00	Excellent Paper Award Ceremony	

Session 01: Next Generation of Niobium Containing Cathode Materials

09:00 - 09:25	Role of Niobium in Nickel-rich Layered Oxide Cathodes for Lithium-ion Batteries	Prof. Stanley Whittingham, 2019 Nobel Prize in Chemistry Laureate and 2022 Charles Hatchett Award Winner
09:25 - 09:50	Reducing the Surface Reactivity of High-nickel Cathodes with Niobium	Prof. Arumugam Manthiram, The University of Texas at Austin
09:50 - 10:15	High Cycling Stability and Mechanism Analysis of High-nickel Ternary Cathode Materials Modified by Nb	Prof. Dr. Xuejie Huang, Songshan Lake Materials Lab
10:15 - 10:25	Q&A Session	
10:25 - 10:45	Group Photo and Tea Break	
10:45 - 11:10	Development of Cobalt-free or Cobalt-less Li[NixCoyMnzNb1-x-y-z]O2	Prof. Yang-Kook Sun, Hanyang University
11:10 - 11:35	The Role of Nb in Single Crystal Spinel-structure Lithium Manganese Oxides (LMO & LNMO)	Prof. Dr. Yongyao Xia, Fudan University
11:35 - 12:00	Niobium-doped Layered Cathode Material for High-power and Low-temperature Sodium-ion Batteries	Prof. Dr. Yufeng Zhao, Shanghai University
12:00 - 12:10	Q&A Session	

Session 02: High-power Battery Technologies for Industrial, Commercial and Heavy-duty Applications

13:30 - 13:55	Role of Niobium for High Power, Fast Charging and Long Life Li-ion Batteries	Dr. Kent Griffith, CBMM Consultant
13:55 - 14:20	Defect and Wire Modulated Nb-Based Oxide Anodes for Durable and Fast-Charging Li-ion Batteries	Prof. Dr. Chilin Li, Shanghai Institute of Ceramics, Chinese Academy of Sciences
14:20 - 14:45	High Power Energy Storage Applications and Requirements	Dr. Sebastian Pohlmann, Skeleton Technologies
14:45 - 15:10	Current Status of Niobium Titanium Oxide (NTO) Cell Development for Commercialization	Dr. Yasuhiro Harada, Toshiba Corporation
15:10 - 15:35	Commercialization of Next-gen Batteries Based on Niobium Based Chemistries	Dr. Rahul Fotedar, Morrow Batteries
15:35 - 15:50	Q&A Session	
15:50 - 16:00	Tea Break	

Session 03: Excellent Paper Award - Recognition for Research on Niobium Based Batteries

16:00 - 16:20	Winning Paper Presentation Ultrafast and Stable Li-(De)intercalation in a Large Single Crystal H-Nb_2O_5 Anode via Optimizing the Homogeneity of Electron and Ion Transport	Zihan Song, Hui Li, Wei Liu, Hongzhang Zhang, Jingwang Yan, Yongfu Tang, Jianyu Huang, Huamin Zhang, Xianfeng Li
16:20 - 16:40	2nd Place Paper Presentation Engineering the Conductive Network of Metal Oxide-Based Sulfur Cathode Toward Efficient and Longevous Lithium-Sulfur Batteries	Jiayi Wang, Gaoran Li, Dan Luo, Yonggang Zhang, Yan Zhao, Guofu Zhou, Lingling Shui, Xin Wang, Zhongwei Chen
16:40 - 17:00	3rd Place Paper Presentation Rational Design and Synthesis of Nickel Niobium Oxide with High-Rate Capability and Cycling Stability in a Wide Temperature Range	Changpeng Lv Chunfu Lin S. Zhao
17:00 - 17:10	Q&A Session	
17:10 - 17:15	Closing Speech	Mr. Jefferson Vieira, CBMM

目录 Summary

Next Generation of Niobium Containing Cathode Materials

High-power Battery Technologies for Industrial, Commercial and Heavy-duty Applications

Prof. Stanley Whittingham

FRS Chemistry Department - Binghamton University

M. STANLEY WHITTINGHAM 是纽约州立大学宾汉姆顿分校化学和材料科学与工程杰出教授，2019年诺贝尔化学奖获得者。他在牛津大学获得化学学士和博士学位，是牛津新学院的荣誉研究员。自1971年以来，他一直活跃于锂电池领域，当时他因在β-氧化铝方面的工作获得了电化学学会的青年作家奖。1972年，他加入了Exxon公司，发现了插层在电池反应中的作用，这产生了Exxon公司制造的第一批商用锂可充电电池。1988年，他回到了纽约州立大学宾厄姆顿分校的学术界，开始了材料化学项目。2018年，他被选为国家工程院院士，并获得了TURNBULL奖。他是皇家学会、MRS、ECS、ISE和ICDD的研究员。

M. Stanley Whittingham is a SUNY distinguished Professor of Chemistry and Materials Science and Engineering at Binghamton, and the 2019 Chemistry Nobel Laureate. He received his BA and D Phil degrees in chemistry from Oxford University, where he is an honorary Fellow of New College. He has been active in Li-batteries since 1971, when he won the Young Author Award of the Electrochemical Society for his work on beta-alumina. In 1972, he joined Exxon and discovered the role of intercalation in battery reactions, which resulted in the first commercial lithium rechargeable batteries that were built by Exxon Enterprises. In 1988, he returned to academia at SUNY Binghamton to initiate a program in materials chemistry. In 2018, he was elected a member of the National Academy of Engineering and received the Turnbull Award from MRS. He is a Fellow of the Royal Society, of MRS, ECS, ISE and ICDD.

2022 International Conference on Niobium Based Batteries

5TH EDITION

Role of Niobium in Nickel-Rich Layered Oxide Cathodes for Lithium-Ion Batteries

M. Stanley Whittingham
Binghamton University,
Binghamton, NY 13902-6000, USA

Abstract

There is an exponentially increasing demand for lithium batteries to enable the electric economy and to combat climate change. At the same time, end-users are demanding higher energy densities and longer lifetimes. This is leading to the use of ever higher nickel layered oxide cathodes, $LiNi_{1-y-z}Mn_yCo_zO_2$. This change is also being driven by the cost of cobalt and its political challenges. However, as the nickel content increases, so does its reactivity with the electrolyte. This limits its lifetime, so approaches have to be found to reduce this reactivity, which may be associated with loss of oxygen and perhaps some dissolution of the transition metals.

Two approaches are being used to minimize reactivity. First, reduce the surface area of the cathode material by switching from the present meatball morphology to small single crystals, around 3 m. This switch also eliminated the interparticle cracking observed on deep cycling of the meatballs. Second, modify the material by either coatings or substitution in the bulk. Such modification might also reduce the 1st cycle loss, that can amount to as much as 15% of the theoretical capacity. Aluminum has been used to stabilize the lattice, such as in NCA.

Our results on using small amounts of niobium to both reduce the 1st cycle loss and to close to eliminating capacity loss on extended cycling will be presented. We used two different approaches to niobium treat the NMC; treatment of commercial meatballs and addition of niobium with the lithium to the hydroxide precursors. The results are strongly dependent on the conditions used.

This work was supported by the US Department of Energy through the Battery500 consortium.

5TH EDITION

Published work

1. Fengxia Xin, Hui Zhou, Xiaobo Chen, Mateusz Zuba, Natasha Chernova, Guangwen Zhou, and M. Stanley Whittingham, "Li–Nb–O Coating/Substitution Enhances the Electrochemical Performance of the LiNi0.8Mn0.1Co0.1O2 (NMC 811) Cathode", ACS Applied Mater & Interfaces, 2019, 11: 34889-34894. DOI: 10.1021/acsami.9b09696.

2. Fengxia Xin, Hui Zhou, Yanxu Zong, Mateusz Zuba, Yan Chen, Natasha A. Chernova, Jianming Bai, Ben Pei, Anshika Goel, Jatinkumar Rana, Feng Wang, Ke An, Louis F. J. Piper, Guangwen Zhou, and M. Stanley Whittingham, "What is the Role of Nb in Nickel-Rich Layered Oxide Cathodes for Lithium-Ion Batteries?", ACS Energy Letters, 2021, 6: 1377-1382. DOI: 10.1021/acsenergylett.1c00190.

3. Fengxia Xin, Anshika Goel, Xiaobo Chen, Hui Zhou, Jianming Bai, Sizhan Liu, Feng Wang, Guangwen Zhou, and M. Stanley Whittingham, "Electrochemical Characterization and Microstructure Evolution of Ni-Rich Layered Cathode Materials by Niobium Coating/Substitution", Chemistry of Materials, 2022. DOI: 10.1021/acs.chemmater.2c01461.

2022 International Conference on Niobium Based Batteries

5TH EDITION

Notes

Notes

Notes

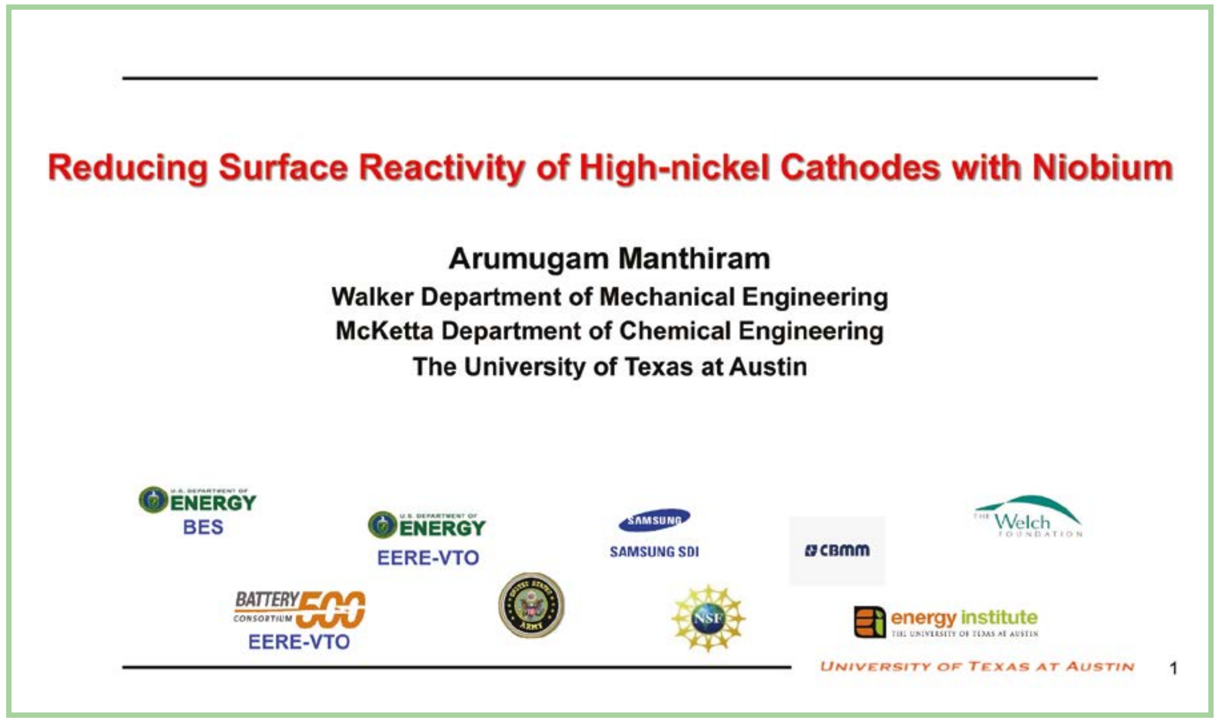
Prof. Arumugam Manthiram

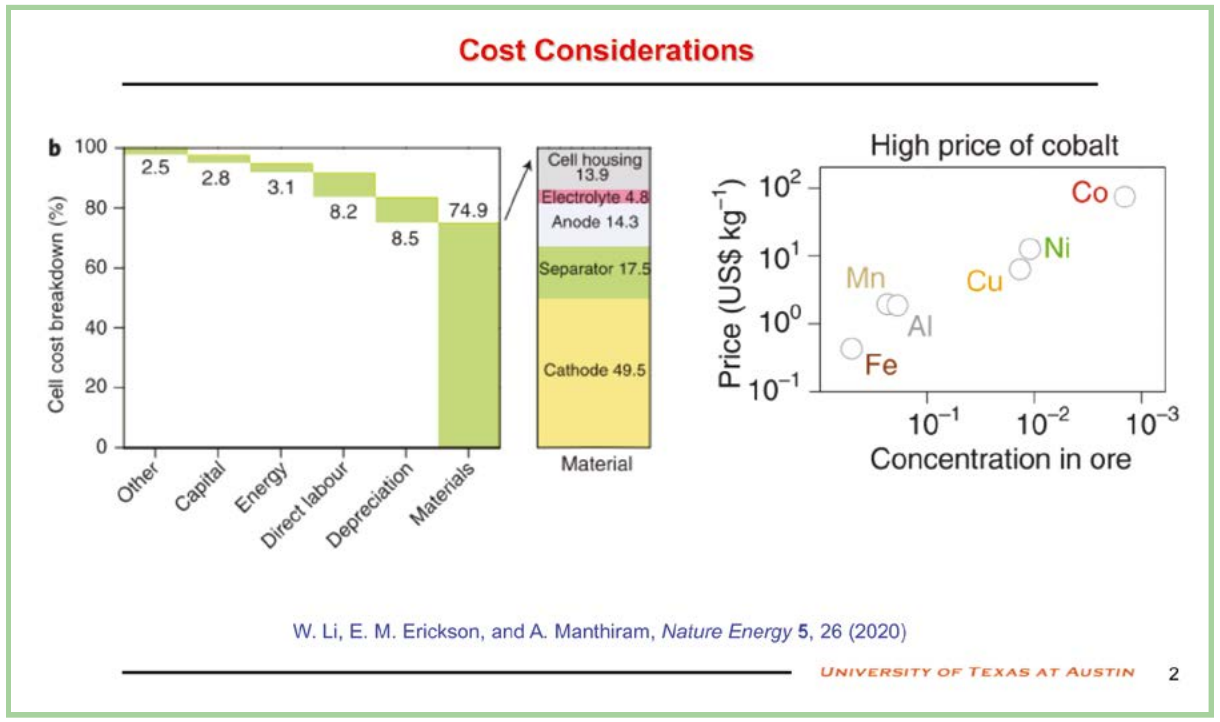
The University of Texas at Austin

ARUMUGAM MANTHIRAM 目前是奥斯汀德克萨斯大学科克雷尔家族董事会工程系主席和德克萨斯材料研究所所长。他撰写了810篇期刊文章，引用次数为6万9千次，h指数为130。他为260名学生和博士后研究员提供了研究培训，包括62名博士生和26名硕士生的毕业。他代表 JOHN GOODENOUGH 教授在斯德哥尔摩发表了2019年诺贝尔化学奖演讲。

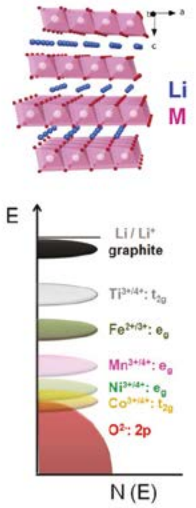
Arumugam Manthiram is currently the Cockrell Family Regents Chair in Engineering and Director of the Texas Materials Institute at the University of Texas at Austin. He has authored 810 journal articles, with 69,000 citations and an H-index of 130. He has provided research training to 260 students and postdoctoral fellows, including the graduation of 62 Ph.D. students and 26 M.S. students. He delivered the 2019 Chemistry Nobel Prize Lecture on behalf of Professor John Goodenough in Stockholm.

2022 International Conference on Niobium Based Batteries
5TH EDITION





Effect of Co, Ni, and Mn in Layered $LiMO_2$ Cathodes



Ion	Octahedral CFSE	Tetrahedral CFSE	Octahedral-site stabilization energy
Mn^{3+}: d^4	$t_2^3e^1$: -0.6 Δ	$e^2t_2^2$: -0.18 Δ	-0.42 Δ
Ni^{3+}: d^7	$t_2^6e^1$: -1.88 Δ	$e^4t_2^3$: -0.53 Δ	-1.35 Δ
Co^{3+}: d^6	$t_2^6e^0$: -2.4 Δ	$e^3t_2^3$: -0.27 Δ	-2.13 Δ

- $M^{3+/4+}$ ion characteristics/behavior are determined by
  - position of metal:3d band relative to that of O^{2-}:2p band
  - stability of metal ions in octahedral vs. tetrahedral sites
- **High-Ni oxides:**
  - high capacity, tap density, volumetric energy, and rate
  - cycle, thermal, air instabilities: involves bulk and surface of both electrodes (cathode and anode) and electrolyte

Chemical stability:
Mn > Ni > Co

Structural Stability:
Co > Ni > Mn

Conductivity:
Co > Ni > Mn

Dissolution Stability:
Co > Ni > Mn

Abundance:
Mn > Ni > Co

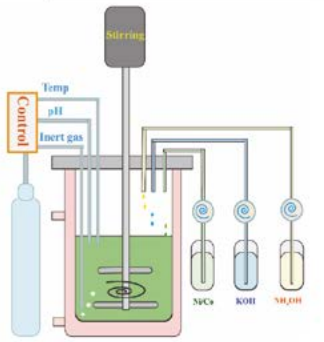
Affordability (low cost)
Mn > Ni > Co

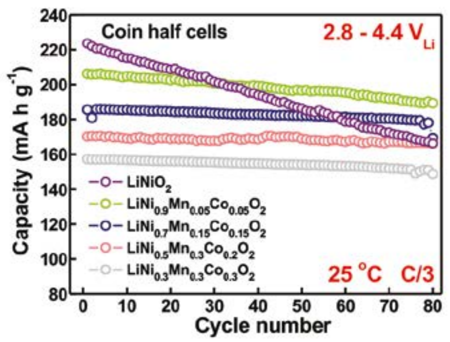
Environmental:
Mn > Ni > Co

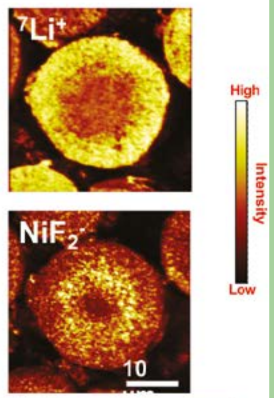
A. Manthiram, *Nature Communications* **11**, 1550 (2020)

UNIVERSITY OF TEXAS AT AUSTIN 3

Challenges with Increasing Ni Content







- 10 kg per batch of hydroxide precursor with any Ni content (0 – 100%)
- Incorporation of hard-to-dope ions like Al, Mg, *etc.* during coprecipitation
- XPS, TOF-SIMS, SEM, TEM, NMR, ….. synchrotron

UNIVERSITY OF TEXAS AT AUSTIN 4

2022 International Conference on Niobium Based Batteries
5TH EDITION

Incorporation of Niobium into High-nickel Layered Oxide Cathodes

- Solution-mediated mixing of high-nickel metal hydroxide precursors with ammonium niobium oxalate (ANO)

  $Ni(OH)_2$, $Ni_{0.90}Mn_{0.05}Co_{0.05}(OH)_2$, $Ni_{0.90}Mn_{0.05}Al_{0.05}(OH)_2$

- Calcination of ANO-coated precursor with LiOH under oxygen atmophere at an optimum temperature to yield niobium-incorporated high-nickel layered oxide cathodes

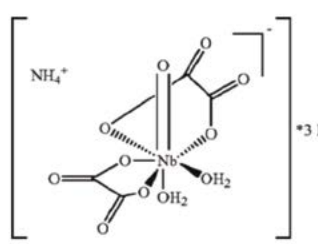
  Nb-$LiNiO_2$, Nb-$LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$, Nb-$LiNi_{0.90}Mn_{0.05}Al_{0.05}O_2$

Nb-$LiNiO_2$	Nb-$LiNi_{0.90}Mn_{0.05}Co_{0.05}O_2$	Nb-$LiNi_{0.90}Mn_{0.05}Al_{0.05}O_2$
700°C	750°C	760°C

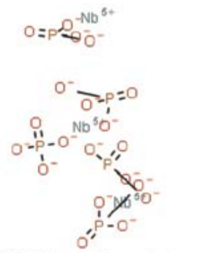
UNIVERSITY OF TEXAS AT AUSTIN 5

Niobium Source Selection

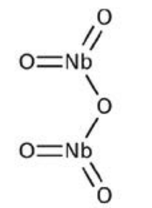
- Various niobium precursors exhibit excellent stability and are low cost



Ammonium niobium oxalate
$NH_4[NbO(C_2O_4)_2(H_2O)_2]*H_2O$



Niobium phosphate
$Nb_3(PO_4)$



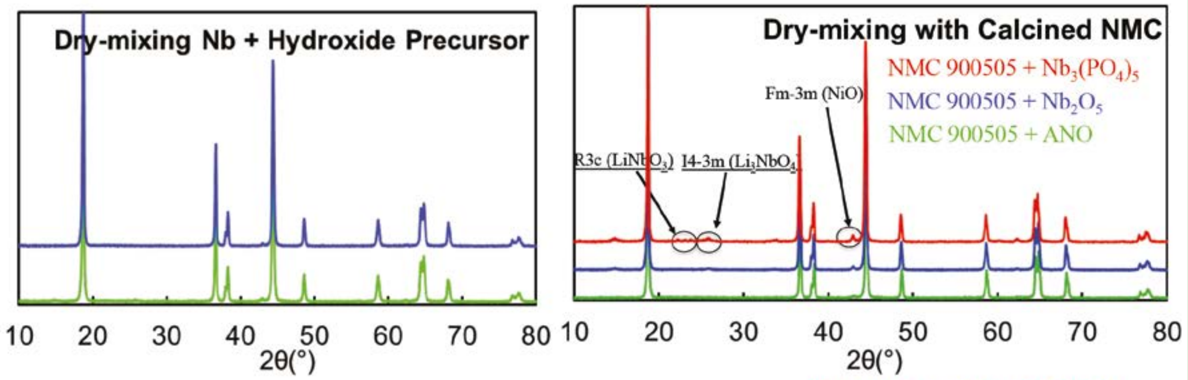
Niobium Oxide
Nb_2O_5

- Nb introduction by dry mixing and solution-mediated coating methods
  - Incorporation in hydroxide precursors vs. layered oxides after lithiation
- Comparative study of niobium sources on NMC 90:05:05

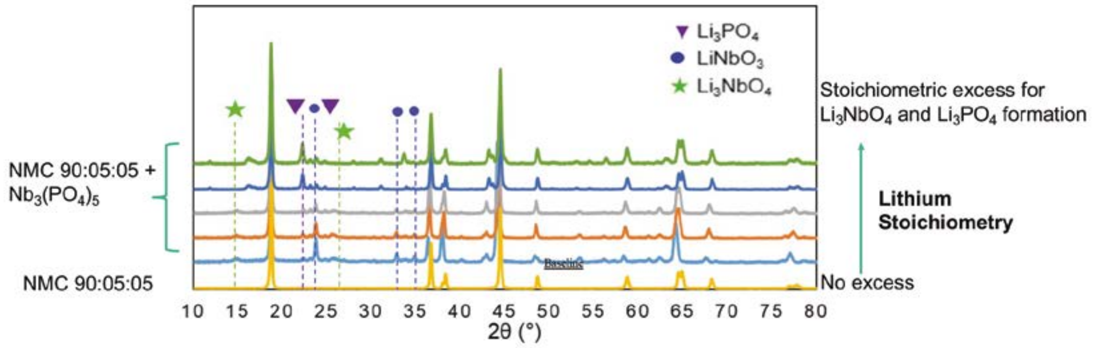
UNIVERSITY OF TEXAS AT AUSTIN 6

XRD of Samples Obtained with 1% Nb Incorporation in NMC 900505

- ANO-NMC and Nb_2O_5-NMC show similar XRD patterns
- $Nb_3(PO_4)_5$ yields heterogeneous phase formation even at a small concentration



XRD of Samples Obtained with 10% Nb with $Nb_3(PO_4)_5$ in NMC 900505

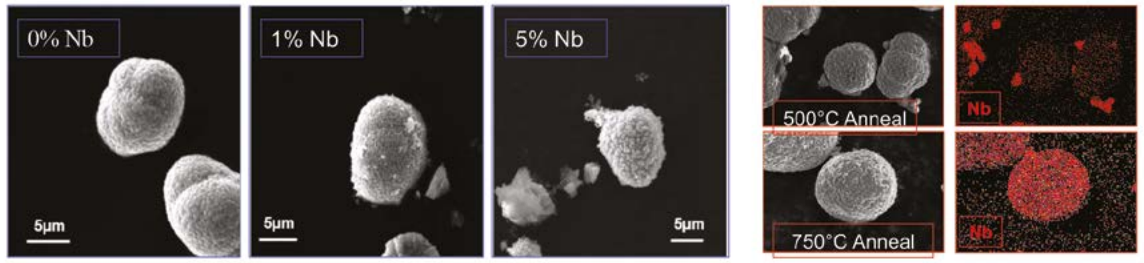


- $Nb_3(PO_4)_5$ precursor yields various heterogeneous phases in NMC 90:05:05
- Type and extent of phase formation depends on lithium stoichiometry
  - Excess Li is required for formation of Li_xNbO_y, Li_xPO_y without delithiation of layered phase

2022 International Conference on Niobium Based Batteries

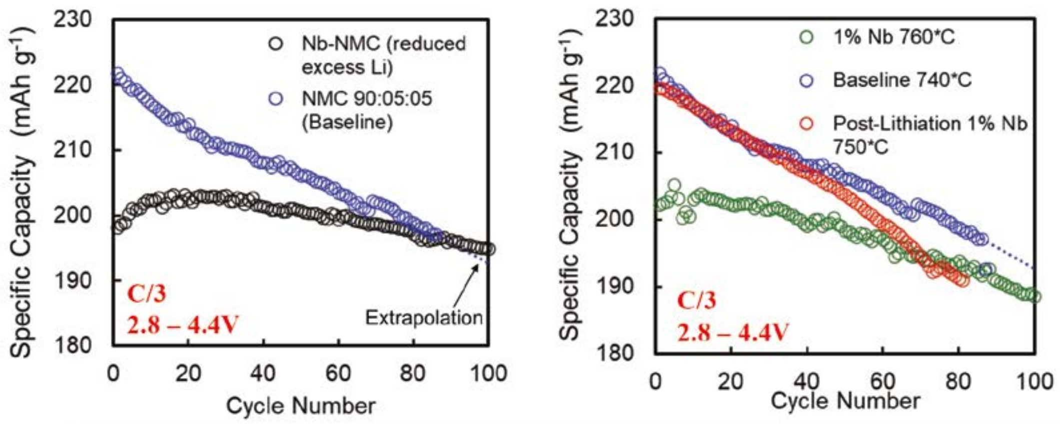
5TH EDITION

Methods of Nb Introduction



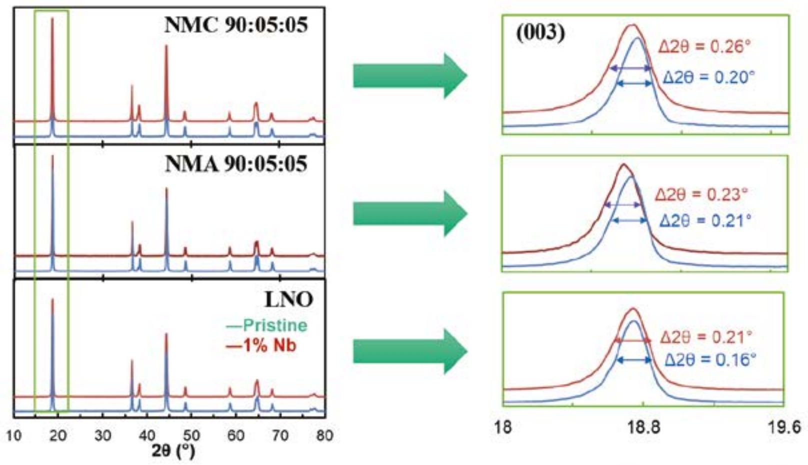
- Solution-mediated coating of hydroxide precursor with ANO
- Addition of ANO after calcination, followed by annealing step
- Dry-mixing ANO with hydroxide precursor

Electrochemical Performance of Nb-NMC 900505



- Nb incorporation into precursor yields optimal electrochemical performance
- Nb incorporation after calcination does not improve stability
- Possibly due to reduced Li inventory caused by Li_3NbO_4 phase formation

XRD of Various 1 % Nb-incorporated Samples



UNIVERSITY OF TEXAS AT AUSTIN 11

Effect of 1 % Nb incorporation on Crystal Chemistry

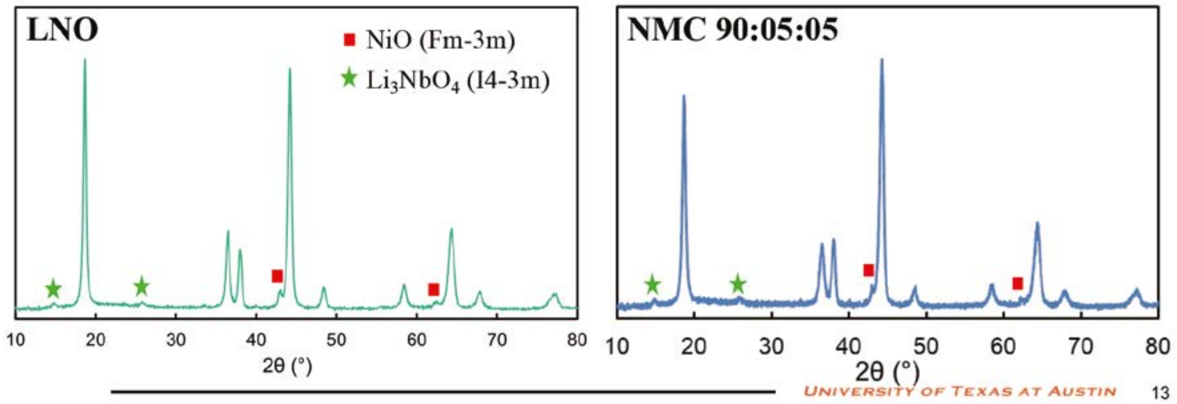
- Slight changes in structural features on 1% Nb incorporation
  - Reduced crystallite size
  - Increased structural disordering
  - Slight lattice expansion in 90% Ni materials
- Nb forms surface phase in intergranular space: Li_xNbO_y
- Slight bulk doping effect at high synthesis temperatures

Composition	*a (Å)*	*c(Å)*	*Li/Ni Mixing*	*Domain Size*
LNO	2.874	14.187	1.89	0.733
Nb-LNO	2.875	14.183	3.50	0.437

UNIVERSITY OF TEXAS AT AUSTIN 12 12

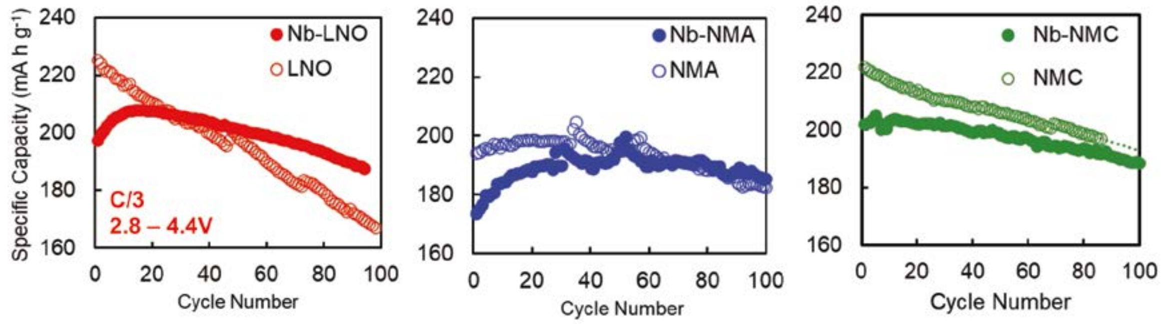
Effect of 10% Nb incorporation on Crystal Chemistry

- Li_xNbO_y phase forms primarily as Li_3NbO_4
- Increasing Nb content forms excessive NiO rock salt-like phase
- Li_3NbO_4 phase formation causes delithiation in $LiNiO_2$ to form rock salt phase



UNIVERSITY OF TEXAS AT AUSTIN 13

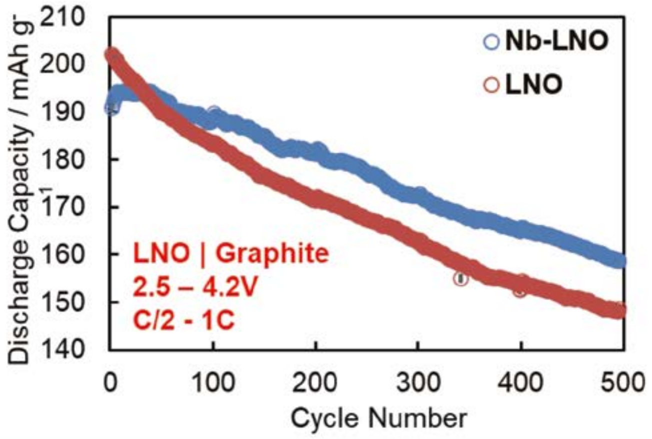
Electrochemical Performance Various High-nickel Cathodes: Half Cells



- Nb incorporation improves the electrochemical stability of various high-nickel cathode materials
- Consistent differences in the 'activation' period suggest different structural impacts during cycling

UNIVERSITY OF TEXAS AT AUSTIN 14

Electrochemical Performance of Nb-LiNiO$_2$: Pouch Full Cells



- Nb incorporation enhances cycling stability
- Voltage curves indicate improved structural stability in Nb-LNO

UNIVERSITY OF TEXAS AT AUSTIN 15

Conclusions

- Nb incorporation improves the electrochemical performance of various High-nickel cathodes
- Nb forms Li_3NbO_4 phase as a coating during heat treatment
  - Reduced primary particle size, intergranular Li_3NbO_4 phase
- Bulk doping effects may also contribute to stability and Li^+ mobility
- Method of Nb introduction significantly impacts Nb distribution and performance characteristics

UNIVERSITY OF TEXAS AT AUSTIN 16

2022 International Conference on Niobium Based Batteries

5TH EDITION

Acknowledgements

ENERGY BES

BATTERY 500 CONSORTIUM EERE-VTO

ENERGY EERE-VTO

NSF

SAMSUNG SDI

TESLA

Welch FOUNDATION

UNIVERSITY OF TEXAS AT AUSTIN 17

Notes

2022 International Conference on Niobium Based Batteries

Notes

5TH EDITION

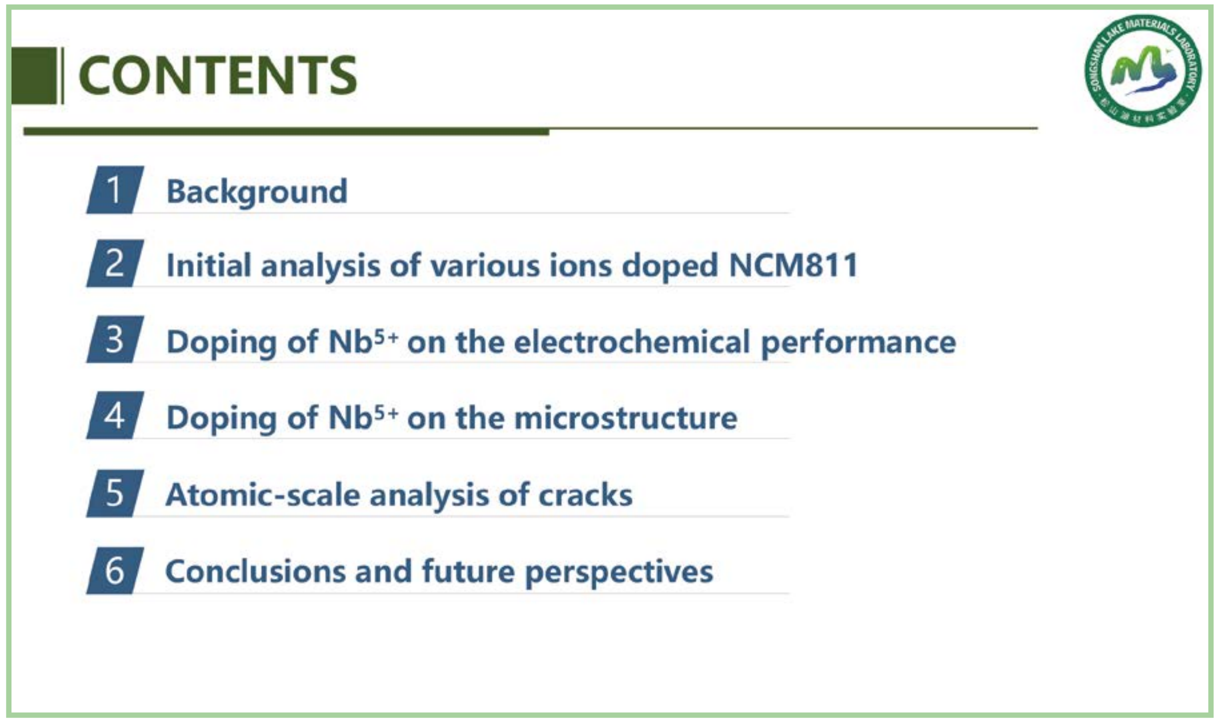
Prof. Dr. Xuejie Huang

Songshan Lake Materials Lab

黄学杰博士，现任中国科学院物理所研究员，博士生导师，兼任松山湖材料实验室副主任，广州中科院工业技术研究院锂离子动力电池工艺技术装备基础服务平台主任、中国电池工业协会副理事长。从1996起主持中科院物理所锂离子电池及其关键材料的研究、开发和产业化工作。主要从事于锂二次电池及其相关材料、工艺和装备技术的研究，推动锂离子动力和储能电池的产业发展。

Dr. Xuejie Huang, a Professor at the Institute of Physics, Chinese Academy of Sciences (IOP/CAS), Deputy Director of Songshan Lake Laboratory for Materials, Director of Research/Development/Service Platform of Manufacturing Arts and Machining Technology, Guangzhou-CAS Institute of Industry, and Vice President of China Battery Industrial Association. Since 1996, he chairs the group of Solid-State Ionics at IOP/CAS and works on secondary lithium batteries and related materials. He has published over 200 peer-reviewed journal papers, and has more than 30 patents granted. He has developed technologies for materials, batteries and machines for the Li-ion battery industry in China. He prospected several companies to develop and produce large size Li-ion batteries for electrical vehicle and energy storage applications.

2022 International Conference on Niobium Based Batteries
5TH EDITION

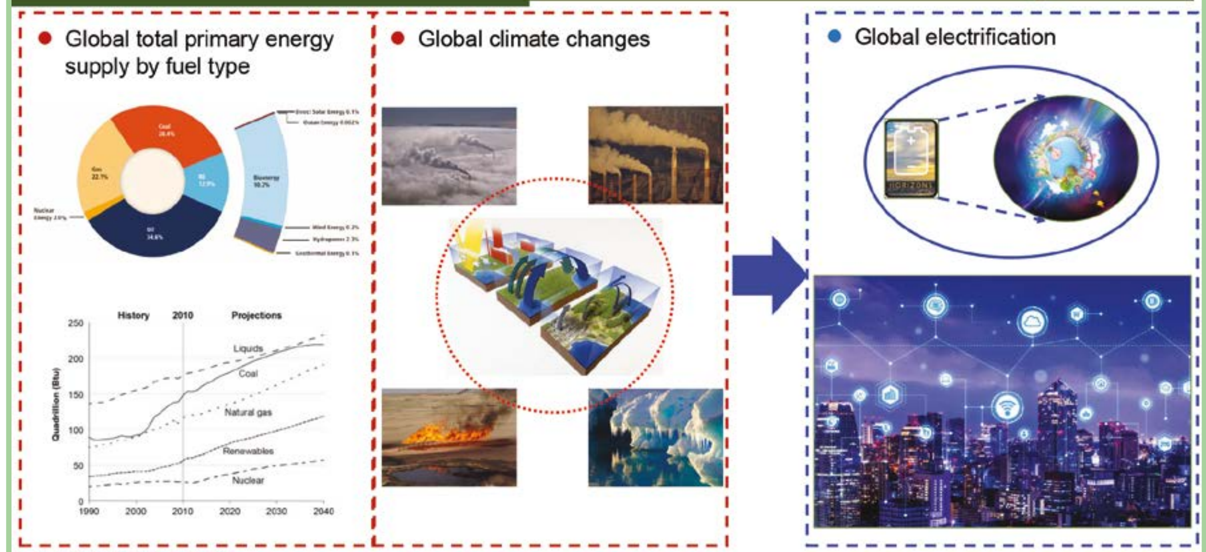


5TH EDITION

CONTENTS

1.1 Energy Security and Environmental Issues Drive Global Electrification

SONGSHAN LAKE 松山湖材料实验室

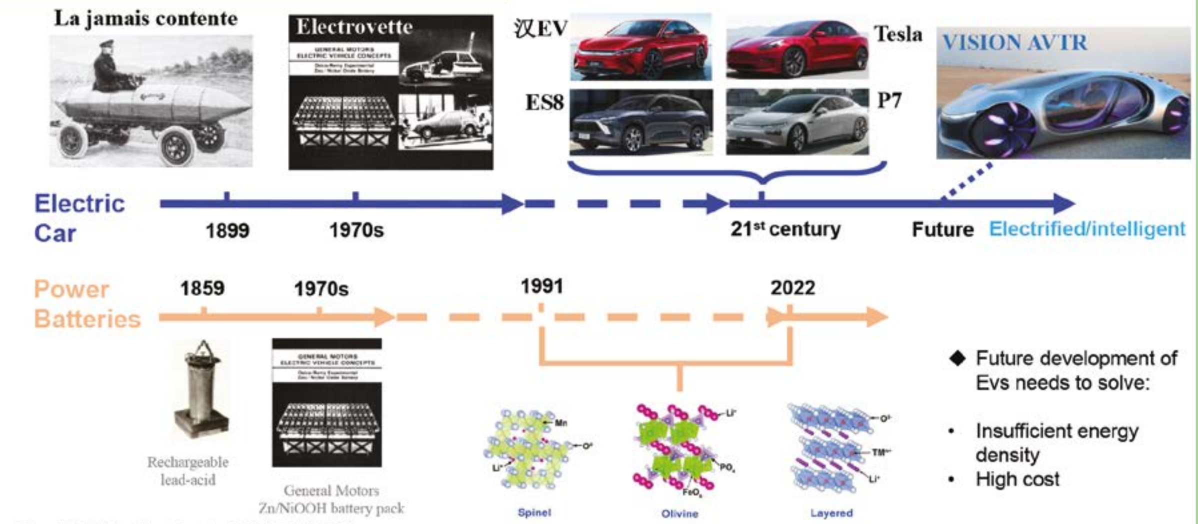


- https://www.nationalgeographic.org/
- IEA. Renewable Energy Sources and Climate Change Mitigation
- Clean Coal Engineering Technology (Second Edition): Butterworth-Heinemann, 2017: 757-774.

4

1.2 Development History of Electric Vehicles and Power Batteries

SONGSHAN LAKE 松山湖材料实验室



- Future development of Evs needs to solve:
  - Insufficient energy density
  - High cost

- Journal of Solid State Electrochemistry, 2011,15(7-8):1623-30.
- Nature, 2008, 451(7179): 652-657.
- Annu Rev Chem Biomol Eng, 2010, 1: 299-320.
- Journal of Materials Chemistry A, 2019, 7(7): 2942-2964.
- 各类电动汽车图片来自官网

5

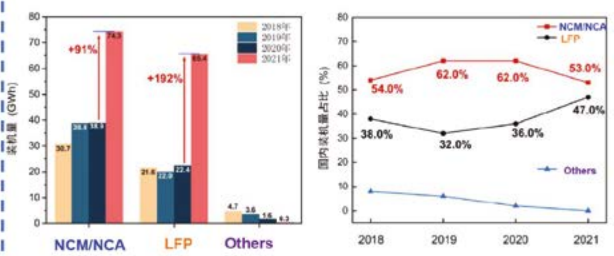
1.3 Main Cathode Materials for Power Batteries

SONGSHAN LAKE 松山湖材料实验室

➢ Main NEVs and power batteries

车型	类型	电池容量(kWh)	纯电续航里程(km)	动力锂电池类型
特斯拉 Model 3	纯电动	60.0	556	磷酸铁锂电池 LFP
		78.4	675	三元锂离子电池NCANCM
特斯拉 Model Y	纯电动	60.0	545	磷酸铁锂电池 LFP
		78.4	640	三元锂离子电池NCA/NCM
蔚来 ES8	纯电动	100	500	三元锂离子电池NCM
蔚来 ES6	纯电动	100	610	三元锂离子电池 NCM
小鹏 P7	纯电动	83.1	670	镍钴锰三元锂离子动力蓄电池 NCM
广汽埃安 Aion.S	纯电动	58.93	510	三元锂离子电池NCM
五菱宏光 mini	纯电动	26.5	300(CLTC)	磷酸铁锂蓄电池 LFP
比亚迪 汉 EV	纯电动	85.44	715	磷酸铁锂蓄电池LFP
比亚迪 汉 DM-i	插电式混合	37.555	206(WLTC)	磷酸铁锂电池 LFP
理想 ONE	插电式混合	38.5	130(WLTC)	三元锂离子电池NCM

➢ Domestic power battery installed capacity in 2018-2021



- The current mainstream power batteries are LFP and NCM/NCA, the market share of LFP battery increased obviously in the past two years.

- 工信部. 免征车辆购置税的新能源汽车车型目录和相应《新能源汽车推广应用推荐车型目录》
- 未来智库. 新能源汽车动力电池行业专题报告：2021年国内动力电池市场回顾

6

1.4 Comparison of Cathode Materials

	项目	三元镍钴锰	磷酸铁锂	锰酸锂
	化学式	$Li(Ni_xCo_yMn_{1-x-y})O_2$	$LiFePO_4$	$LiMn_2O_4$
	理论比容量 /($mAh\cdot g^{-1}$)	273~285	170	148
	实际比容量 /($mAh\cdot g^{-1}$)	<220	130~140	100~120
	电芯比能量 /($Wh\cdot kg^{-1}$)	180~240	130~160	130~180
	平均电压/V	3.6	3.4	3.8
Cycling	循环性/次	800~2000	2000~6000	500~2000
	环保性	镍、钴有毒	无毒	无毒
	安全性能	尚好	好	良好
	使用温度/°C	-20~55	-20~75	>50
Price	价格（万元/吨）2021 年 9 月 30 日上海有色网价格	20~25	6.5~7.5	5.5~6.5

◆ Considering the development of high energy density EV battery in the future

- Longer range (1000 km per charge)
- Higher driving enjoyment (auxiliary driving and intelligent car, etc.)

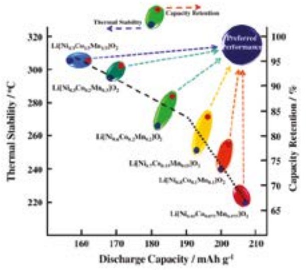
✓ High Ni NCM/NCA with higher theoretical energy density have more application prospects in the future

- 王伟东。锂离子电池三元材料:工艺技术及生产应用

7

1.5 High-Ni NCA/NCM Issues and Solutions

➢ Problems：



Surface instability | Bulk instability | Cracks

Lattice oxygen stability | Mechanical stability

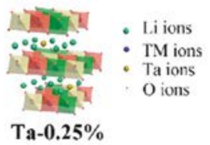
- Chemistry of Materials, 2019,31(18):7574-83.

➢ Modifications：

- Coating

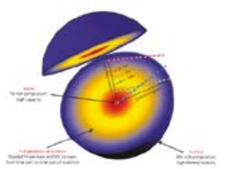
- Nature Energy, 2021, 6(4): 362-371.

- Doping



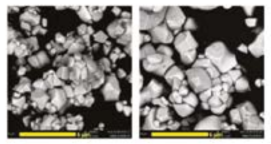
- ACS Sustainable Chemistry & Engineering, 2020, 8(8): 3082-3090.

- Concentration gradient



- Nature Materials, 2012,11(11):942-7.

- Single-crystallization

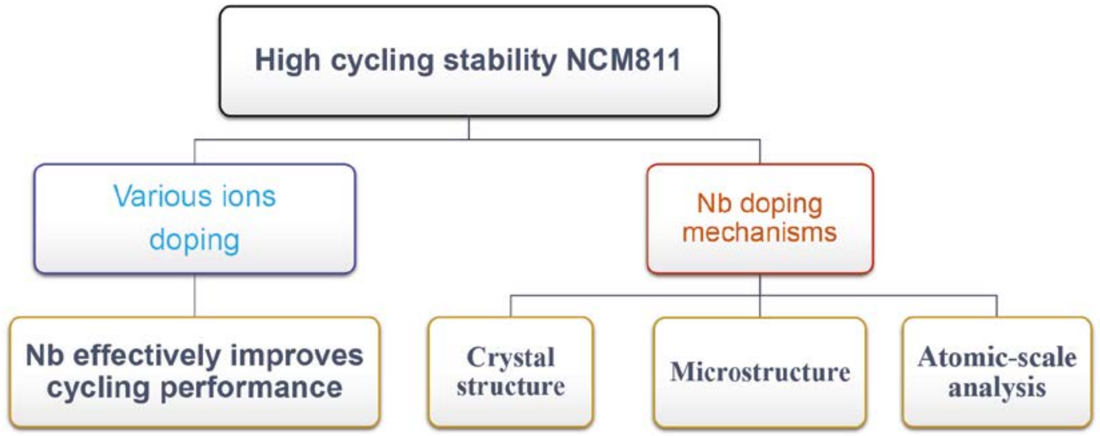


- Journal of The Electrochemical Society, 2021, 168(4): 040531.

8

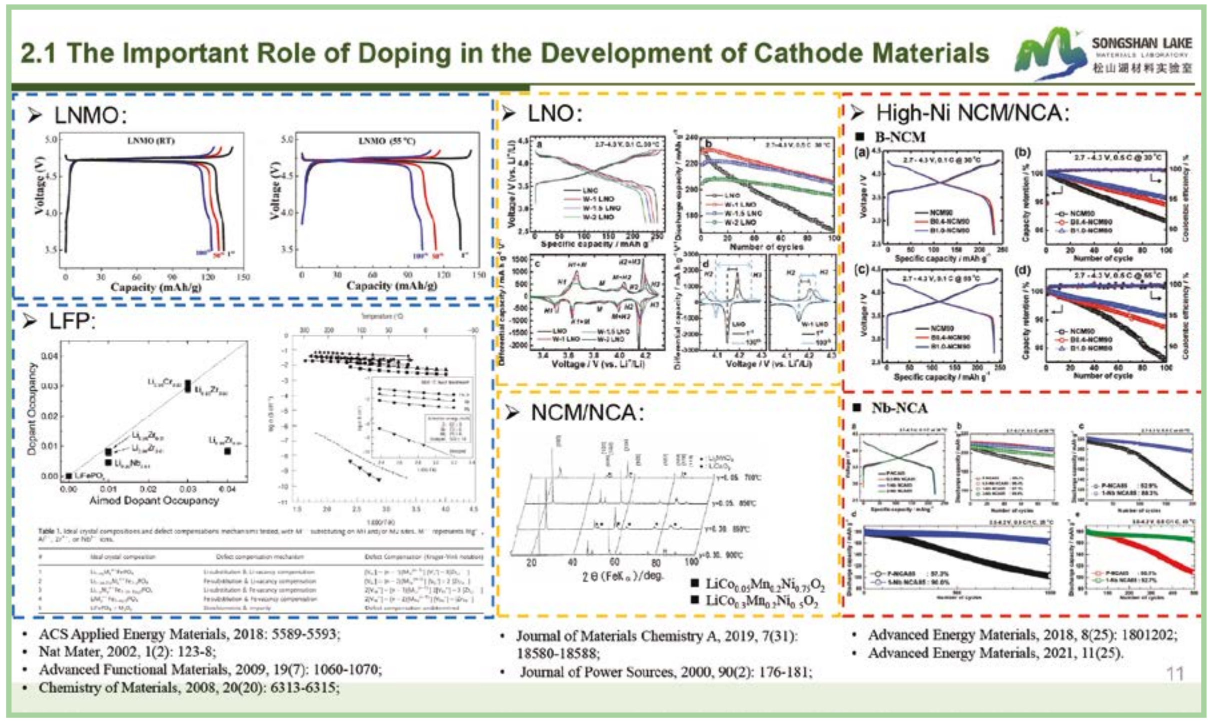
2022 International Conference on Niobium Based Batteries

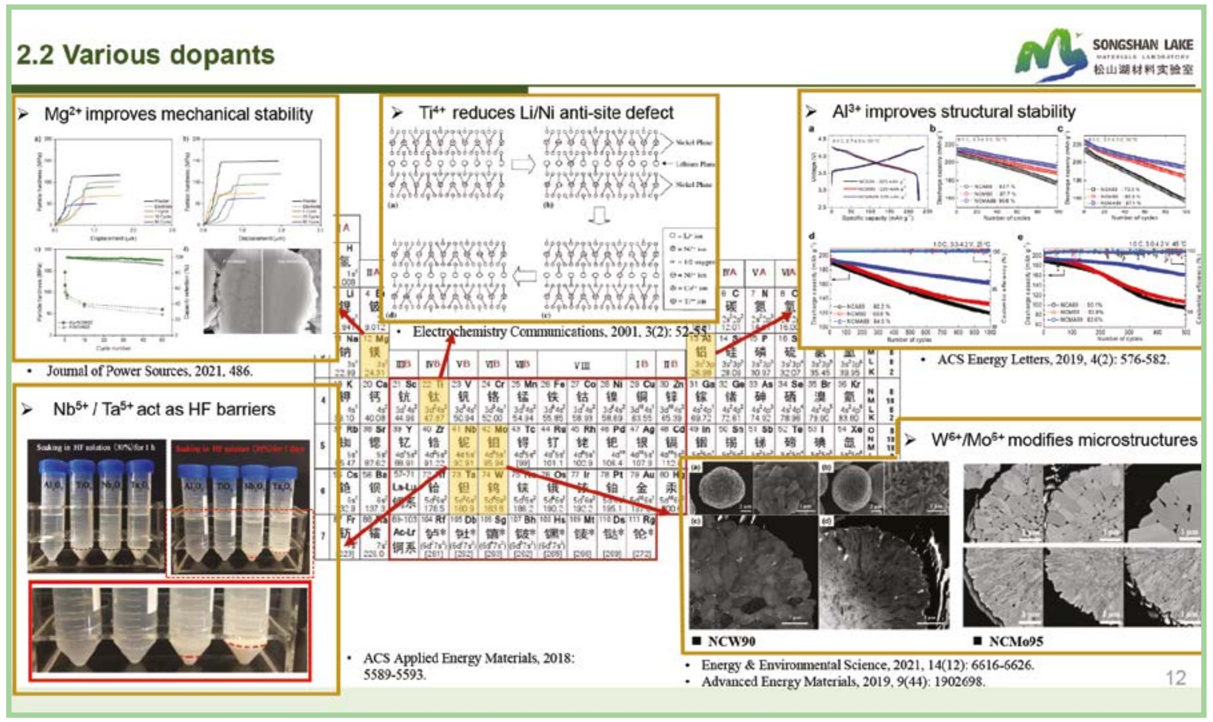
1.6 Research Strategies



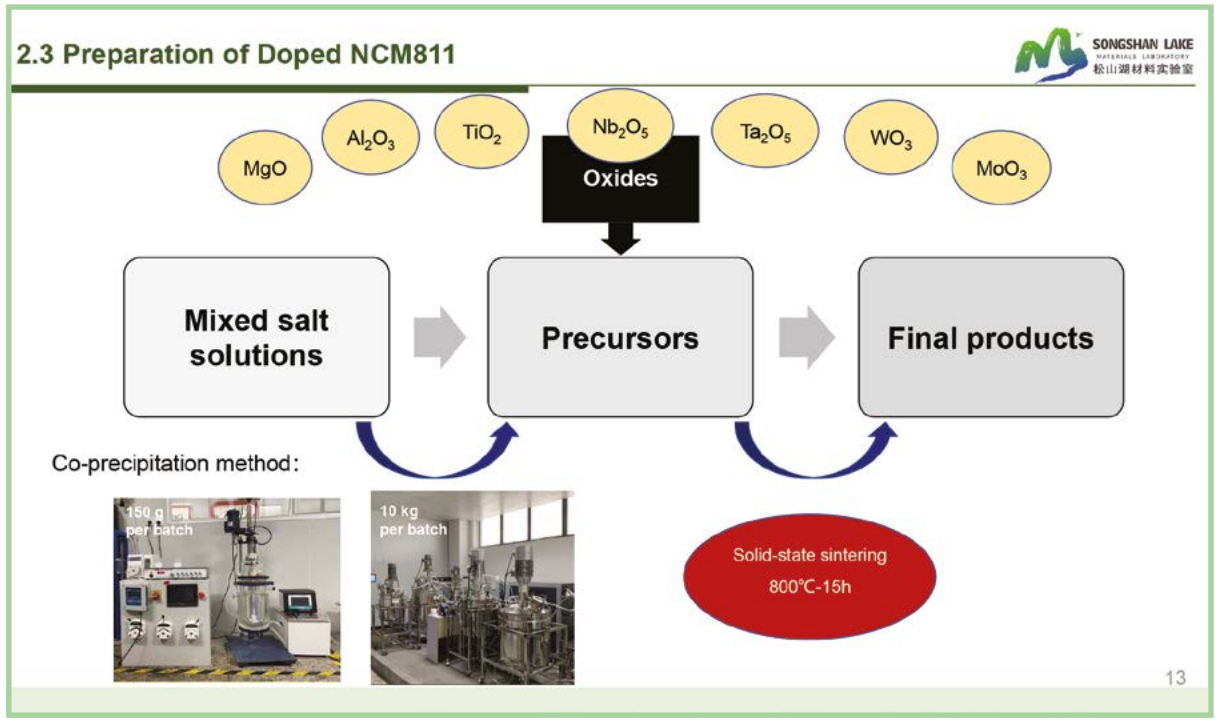
9

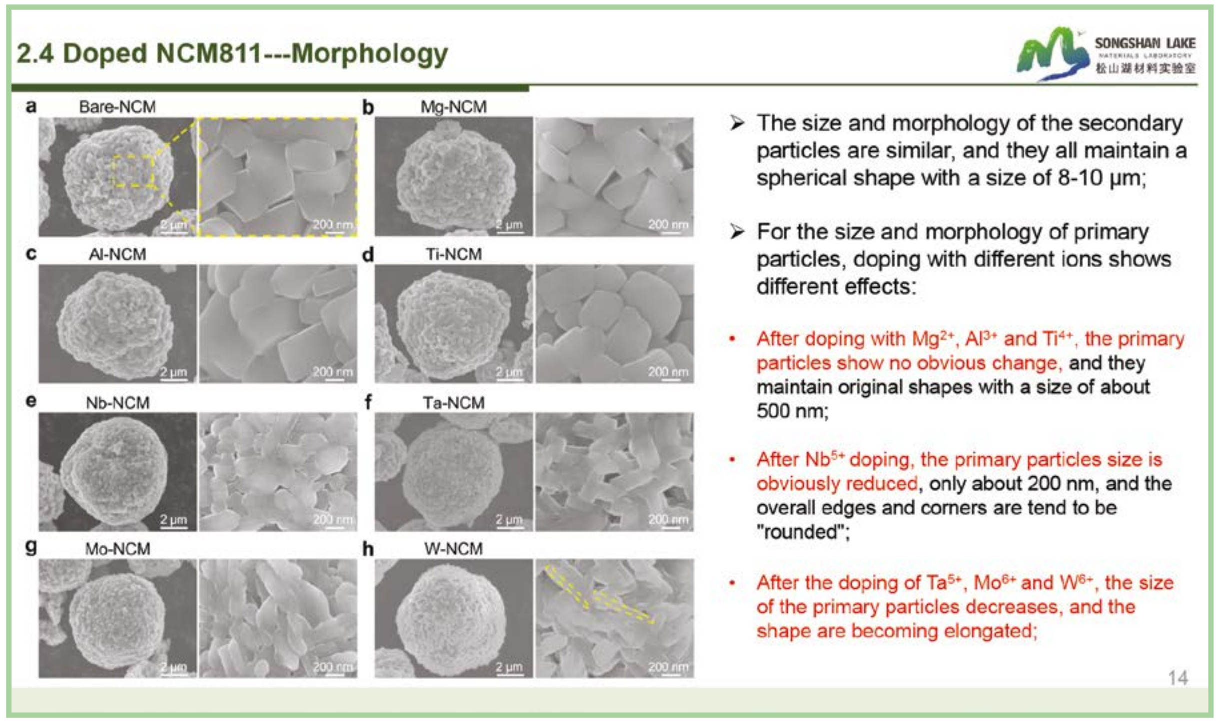
CONTENTS



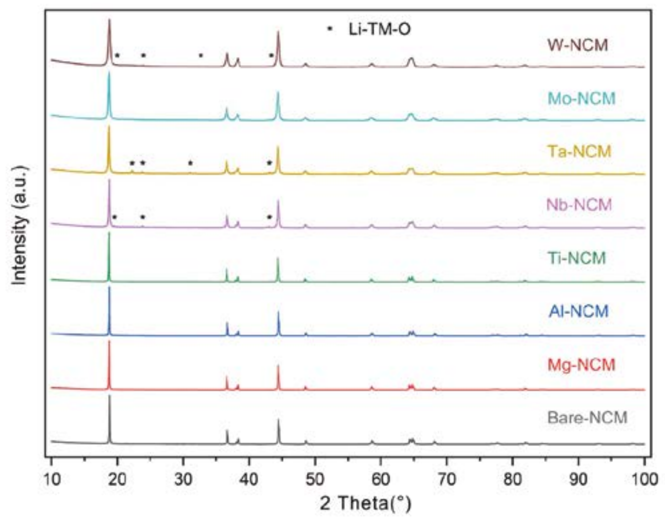


2022 International Conference on Niobium Based Batteries





2.4 Doped NCM811---Crystal Structure

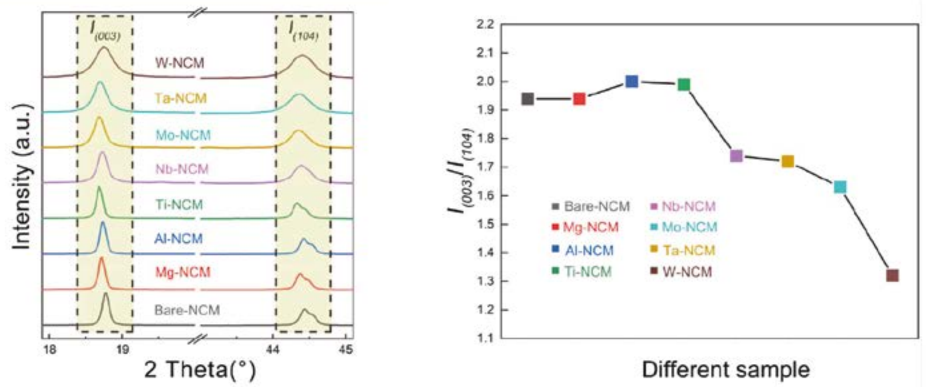


3 mol% dopant ions:

- All samples maintained the standard layered α-$NaFeO_2$ crystal structure, and no change of the original crystal structure can be observed;
- Doping with high valent ions will cause the weakening of the (006)/(012) and (108)/(110) peak splitting, which may relate to the broadening of the peaks after the grain size decreases;
- In addition, high-valent ions doping will cause the formation of the second phase of Li-TM-O, which is related to the fact that doping reach the solid solution limit.

15

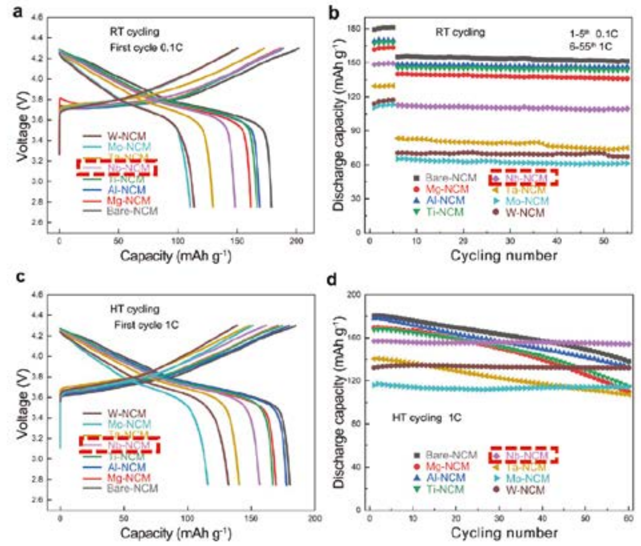
2.4 Doped NCM811---Li/Ni Anti-site Defect



- With 3 mol% dopants, the I(003)/I(104) value decreases significantly with doping with high-valent ions, indicating an increase in the degree of Li/Ni anti-site defect.
- In addition, the enlarged XRD patterns can clearly show the broadening of XRD lines with the doping of high-valent elements, indicating that grain size changes in these samples;

16

2.4 Doped NCM811---RT and ET Cycling



Capacity:

- With 3 mol% dopants, the discharge capacity of the NCM cathode decreases regardless of RT or ET cycling, and the capacity decrease caused by the doping of high-valent ions is more serious.

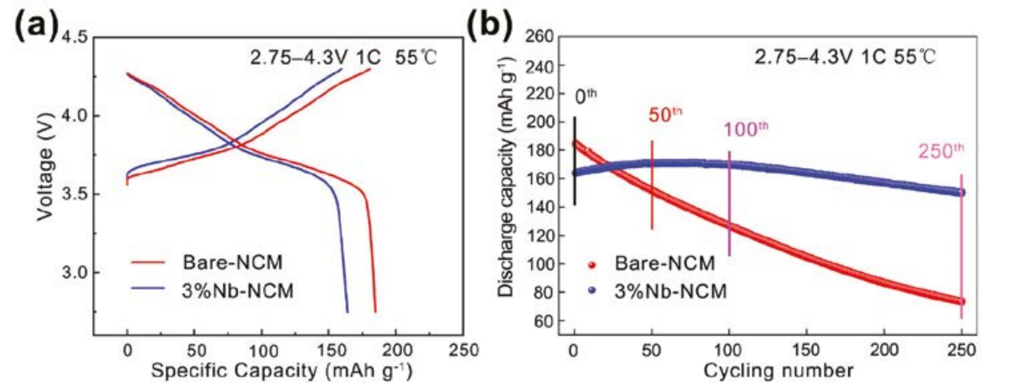
Retention:

- All cathodes have relatively good cycling stability at room temperature; At elavated temperature, the performance of the pristine NCM cathode decays rapidly; while Nb^{5+}, Mo^{6+} and W^{6+} doping helps significantly to improve the cycle performance.

■ Nb-NCM has the best comprehensive electrochemical performance.

17

2.5 Cycling Performances of Bare and Nb^{5+} Doped NCM811 at 55℃



- The pristine NCM811 material decays rapidly at 55 °C, while the addition of Nb^{5+} greatly improves the cycling performance at 55℃ .

18

2022 International Conference on Niobium Based Batteries

5TH EDITION

2.6 Conclusions for the Doping into NCM811

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室

Conclusions of Part 2:

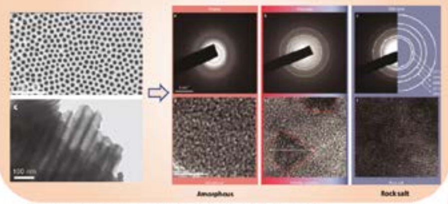
- Doping with high-valent ions will significantly change the morphology of the primary particles, significantly reduce the size of the primary particles (Nb^{5+}), and significantly affect the particle morphology (Ta^{5+} , Mo^{6+} and W^{6+});
- Under 3 mol% doping, low-valent ions have no obvious effect on the layered crystal structure, while doping with high-valent ions will lead to an increase in cation mixing and the generation of Li-TM-O second phase, which will play a role in the cycling capacity. cause varying degrees of impact;
- All cathode materials show good electrochemical stability at room temperature, but at high temperature cycling, the electrochemical performance of high-nickel cathode materials decays rapidly, and high-valent Nb^{5+}, Mo^{6+} and W^{6+} ions doping can significantly improve the material's cycling stability.
- Comprehensive consideration of the electrochemical performance, it is clear that the NCM material doped with Nb^{5+} can significantly improve the material stability, especially the high temperature cycling stability, with a small loss of reversible capacity.

19

3.1 Wide Application of Nb Element in Battery Materials

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室

- 非晶态纳米通道Nb_2O_5在电化学驱动下结晶而获得一种岩盐结构Nb_2O_5 Anode Materials



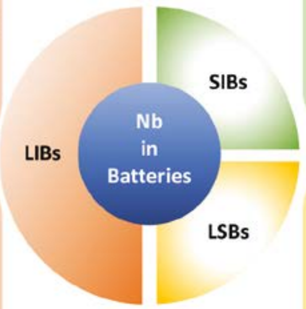
- Nat. Mater. (2022): doi.org/10.1038/s41563-022-01242-0

- 石榴石型 Solid Electrolyte$Li_5La_3M_2O_{12}$ (M = Nb, Ta) {$Li_5La_3Nb_2O_{12}$ 块体传导率 10^{-6} S/cm (25°C)，离子传导激活能(<300°C) 为0.43 eV}

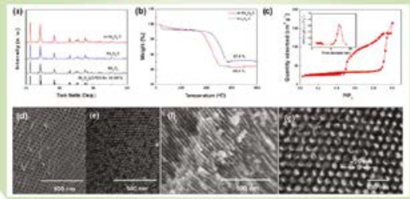
Table II. Synthesis Conditions and Comparison of Lattice Parameters of Garnet-Type $Li_5La_3M_2O_{12}$ (M = Nb, Ta)

Compound	Synthesis conditions	Lattice parameter (Å)
$Li_5La_3Nb_2O_{12}$	700°C/24 h, 800°C/24 h, 850°C/12 h, and 950°C/24 h	12.762(3)
$Li_5La_3Ta_2O_{12}$	700°C/24 h, 800°C/24 h, 850°C/12 h, and 950°C/24 h	12.766(3)
$Li_5La_3Nb_2O_{12}$	500°C–850°C/6 h	12.797
$Li_5La_3Nb_2O_{12}$	700°C–900°C/24 h	12.889(3)
$Li_5La_3Ta_2O_{12}$	500°C–850°C/6 h	12.804
$Li_5La_3Nb_2O_{12}$	700°C–900°C/24 h	12.823(2)

- J. Am. Ceram. Soc., 86 [3] 437–40 (2003)

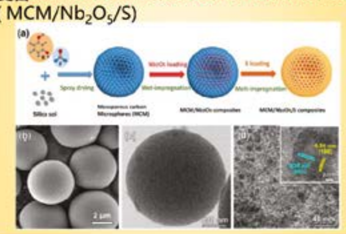


- 介孔Nb_2O_5/碳 复合材料作为 Na Insertion Materials



- Nano Energy (2015) 16, 62–70

- 超细Nb_2O_5纳米晶，合成介孔碳微球/Nb_2O_5/硫复合Cathode Materials for Li-S Batteries (MCM/Nb_2O_5/S)



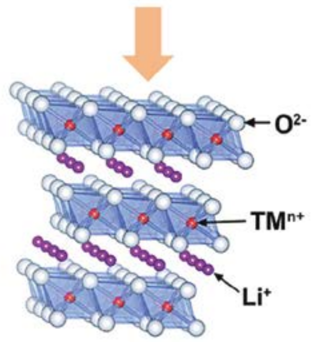
- Energy Environ. Sci.,2016, 9, 3230

21

CONTENTS

3.2 Modification of NCM811 with Nb^{5+}

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



Crystal Structure

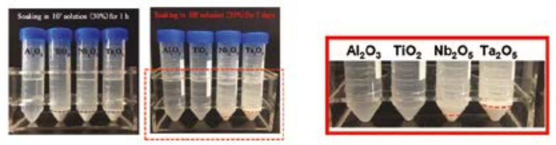
- High Nb-O bonding energy

	Nb-O	Ni-O	Co-O	Mn-O
键离解能 (KJ mol^{-1})	753	391.6	368	402

- Solid State Ionics, 2021, 359: 9;
- Electrochimica Acta, 2016, 188: 48-56.

- High resistance to HF

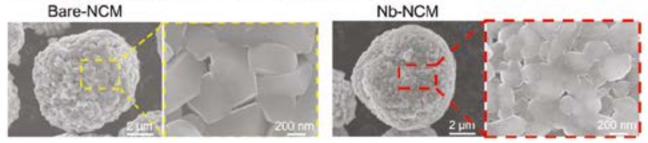
Surface stability



- ACS Applied Energy Materials, 2018: 5589-5593.

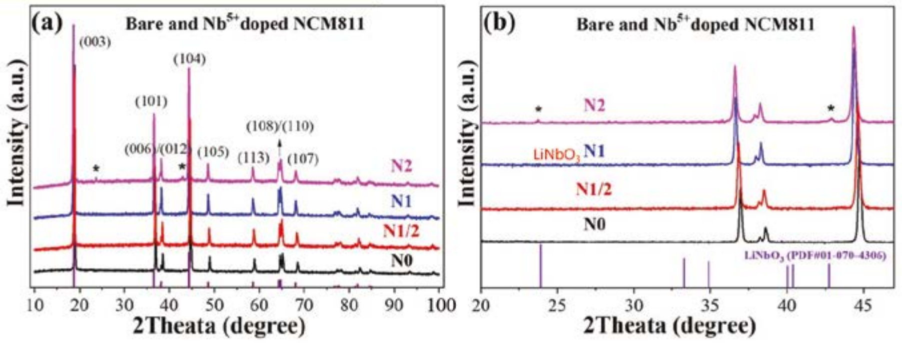
- Effectively modifies particle morphology

Particle mechanical stability



22

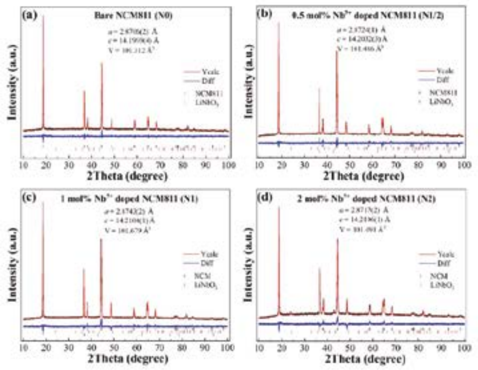
3.3 Nb^{5+} doped NCM811---Crystal Structure



- All cathodes have a standard layered $LiNiO_2$ structure with clear (006)/(012) and (108)/(110) peak splits;
- With the gradual addition of Nb^{5+}, a slight shift of the peak position to a low angle can be seen, indicating that Nb^{5+} enters the layered lattice;
- When the doping content is 2 mol%, the second phase of $LiNbO_3$ begins to appear, which means that the solid solution limit is reached at this time, and the residual Nb^{5+} does not enter the lattice and reacts with the Li source to form the $LiNbO_3$ phase;

23

3.3 Nb^{5+} doped NCM811---Structure Refinement



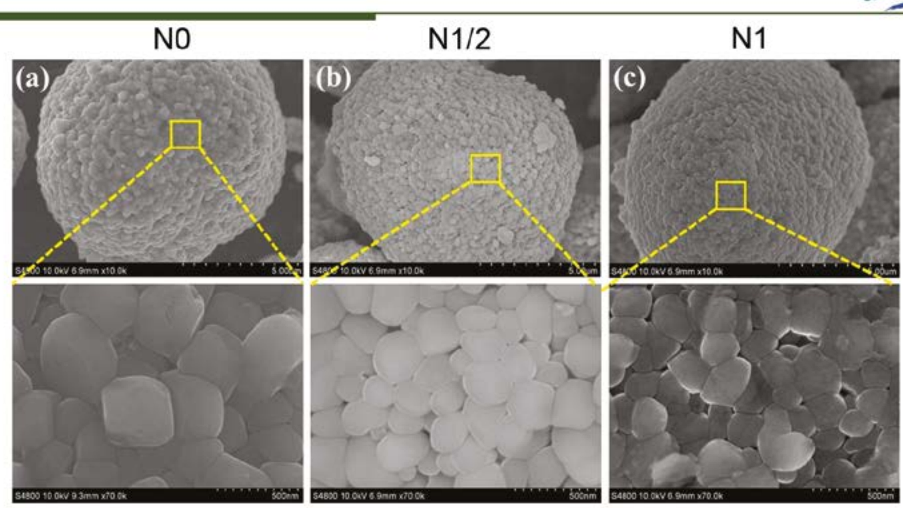
	Phase%		Lattice Parameter (Å)		Cell Volume	Ni/Li
	NCM811	$LiNbO_3$	*a*	*c*	(Å³)	Mixing%
N0	100%	0%	2.8706(2)	14.1969(4)	101.312	4.26
N1/2	100%	0%	2.8724(1)	14.2032(3)	101.486	1.92
N1	99.94%	0.06%	2.8743(2)	14.2104(1)	101.679	2.31
N2	99.31%	0.69%	2.8717(2)	14.2106(1)	101.491	4.43

- Rwp and Rp: N0 (4.59%, 3.64%) N1/2 (4.73%, 3.81%) N1 (4.43%, 3.41%) N2 (3.56%, 3.71%)

- The refinement results show that the N1/2 and N1 samples hardly contain the second phase of $LiNbO_3$, while the second phase of $LiNbO_3$ appears obviously in the N2 sample (~0.69 wt%), indicating that the solid solution limit is reached at this time;
- The degree of Li/Ni mixing decreased from 4.26% of N0 to 1.92% of N1/2 and 2.31% of N1, but increased to 4.43% in N2 cathode, indicating the increase of mixing caused by excessive doping.

24

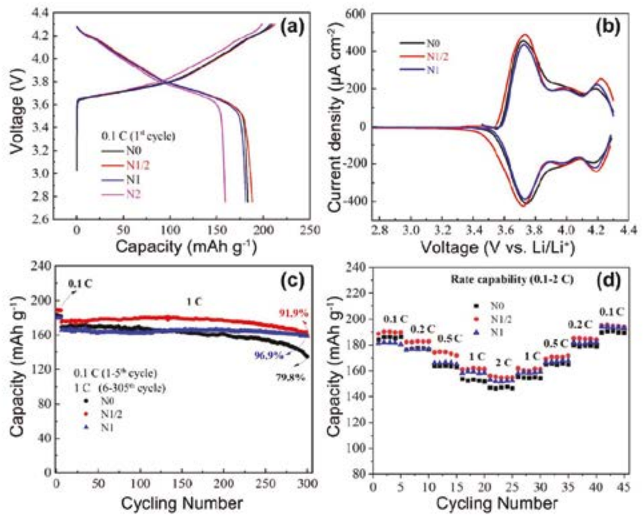
3.3 Nb^{5+} doped NCM811---Morphology



- The primary particle size in the pristine NCM811 cathode is 300-500 nm, while the primary particle size is reduced to about 200 nm under Nb doping.

25

3.3 Nb^{5+} doped NCM811---Cycling Performances

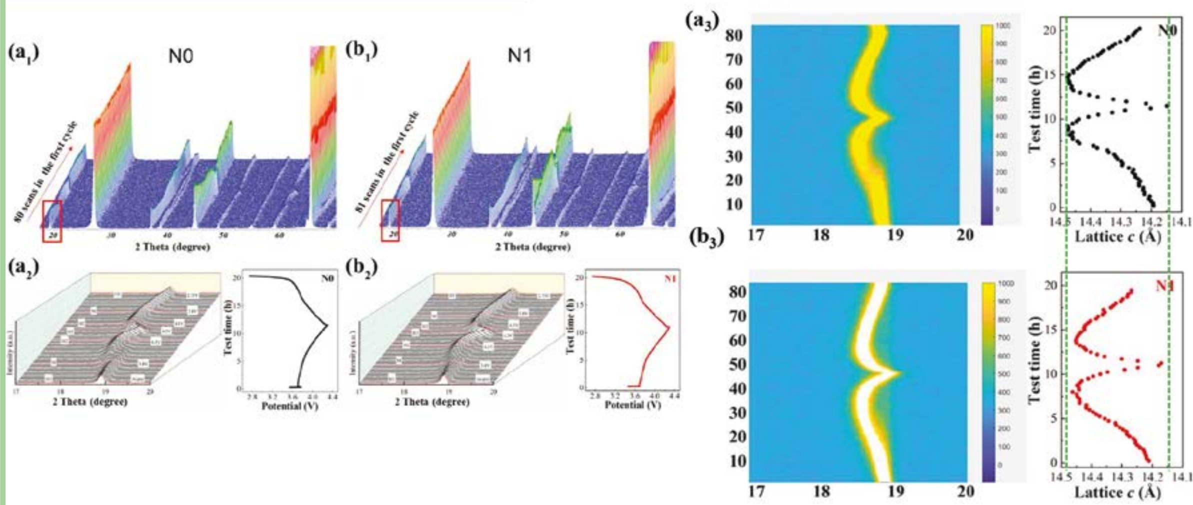


- Excessive Nb^{5+} doping will lead to a large capacity degradation;
- The lower content of Nb^{5+} doping can significantly improve the cycle stability of the material under the premise of less impact on the capacity;
- N1 has the best electrochemical performance, with a capacity retention rate of 96.9% after 300 cycles at 1 C at room temperature;
- The addition of Nb^{5+} also improves the rate performance of the material.

26

2022 International Conference on Niobium Based Batteries

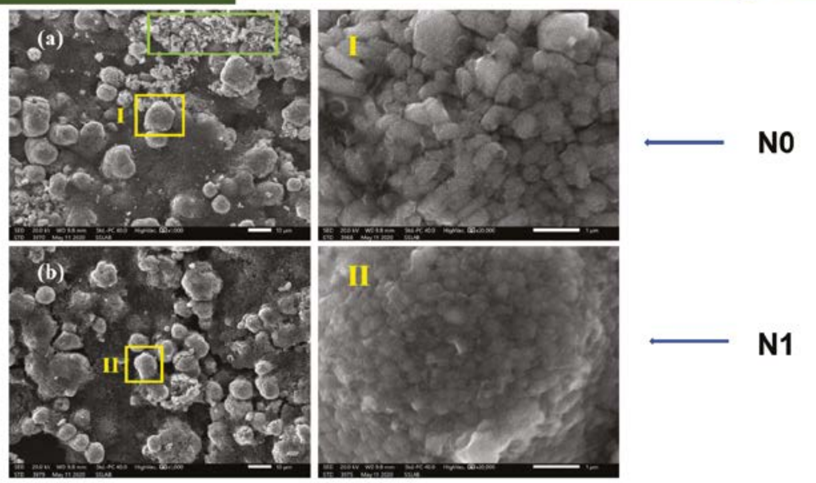
3.3 Nb^{5+} doped NCM811---Structure Evolution



- In situ XRD analysis shows that Nb^{5+} doping can alleviate the change of the unit cell parameter *c* during cycling, which is helpful to improve the stability of the crystal structure.

27

3.3 Nb^{5+} doped NCM811---Morphology after cycling



- After 300 cycles at room temperature, the N0 material exhibited severe particle cracking and pulverization;
- However, thank to the doping with Nb element, the cracking situation in N1 material is obviously alleviated;

28

3.4 Conclusions of Nb^{5+} Doping on the Structure and Cycling performances

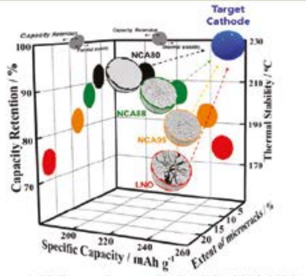
Conclusions of Part 3:

- Through the study of Nb doping with different contents, it is determined that 1 mol% Nb^{5+} doping is the optimal doping content, which can significantly improve the cycle stability under the premise of effectively minimizing the sacrificed capacity;
- An appropriate amount of Nb^{5+} doping can effectively reduce the cation mixing and alleviate the change of unit cell parameters during the cycle, thereby helping to improve the stability of the crystal structure of high-nickel materials;
- In addition, the cycle cracking problem of high-nickel cathode particles is solved after Nb element doping.

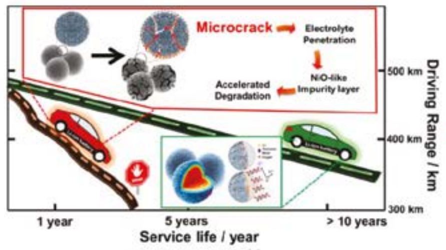
29

CONTENTS

4.1 High-Ni NCA/NCM

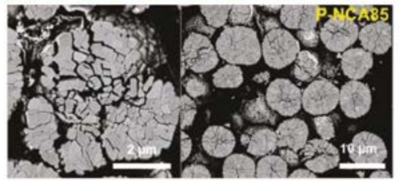


• ACS Energy Letters, 2019, 4(12): 2995-3001.

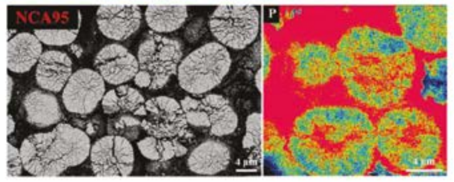


• ACS Energy Letters, 2019, 4(5): 1042-1044.

- The instability of the crystal structure and the atomic structure of the surface interface brings about the attenuation of material properties;
- The problem of cracking and pulverization is a more critical factor to cause the performance degradation of high-nickel cathodes



• Advanced Energy Materials, 2021, 11(25).



• Energy & Environmental Science, 2021, 14(12): 6616-6626.

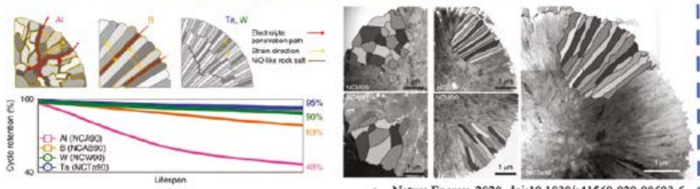
- A large number of cracks were observed in the electrode after cycling, resulting in severe performance degradation.

31

4.2 Particle Structure Engineering works

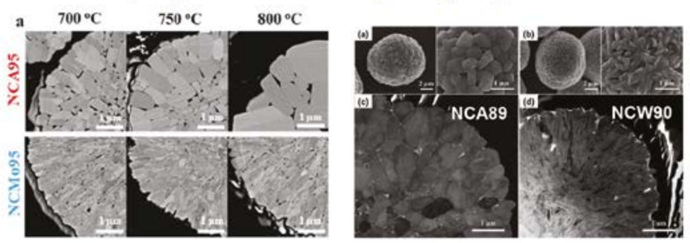
➢ Doping ions to build a special secondary particle microstructure, improve the mechanical strength of the secondary particle, and inhibit the growth of cracks;

- Build acicular primary particle radial arrangement;



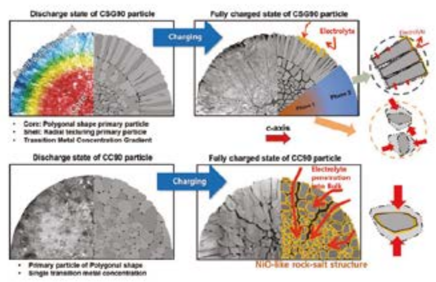
• Nature Energy, 2020. doi:10.1038/s41560-020-00693-6

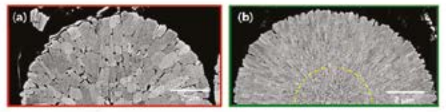
- Reduce primary particle size to achieve "fine grain strengthening"



• Energy & Environmental Science, 2021, 14(12): 6616-6626. • Advanced Energy Materials, 2019, 9(44): 1902698.

➢ Design concentration gradient cathode, build external needle-like radial arrangement microstructure, inhibit crack propagation;



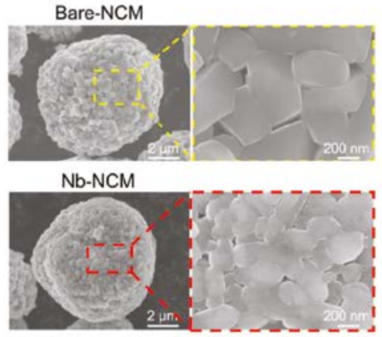


• Advanced Energy Materials, 2019, 9(15).
• ACS Energy Letters, 2021, 6(1): 216-223.

32

4.3 Nb^{5+} doping on the Microstructure of NCM811---Nano-CT Analysis

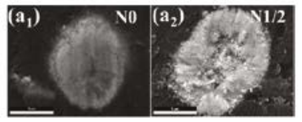
➢ Considering the effect of Nb element doping on particle morphology



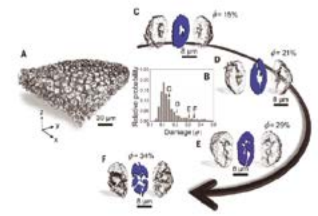
Particle mechanical structure stabilization

➢ Limitations of traditional 2D topography characterization;

- Particle damage caused by mechanical polishing;
- Incomplete topographic information brought by 2D slicing;

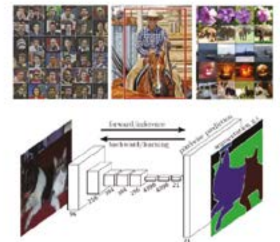


➢ Wide application of X-ray CT Technology.



• Science, 2022, 376(6592): 517-521.

➢ The continuous development of deep learning methods in the field of computer vision.



• 内容摘自，向世明．"深度学习新模型及其应用"报告，2020，中科院自动化所．

33

4.4 Nano-CT image and Quantification Analysis

➢ A non-destructive and efficient three-dimensional visualization and quantitative analyses scheme were proposed for the study of the microstructure of high Ni cathode particles;

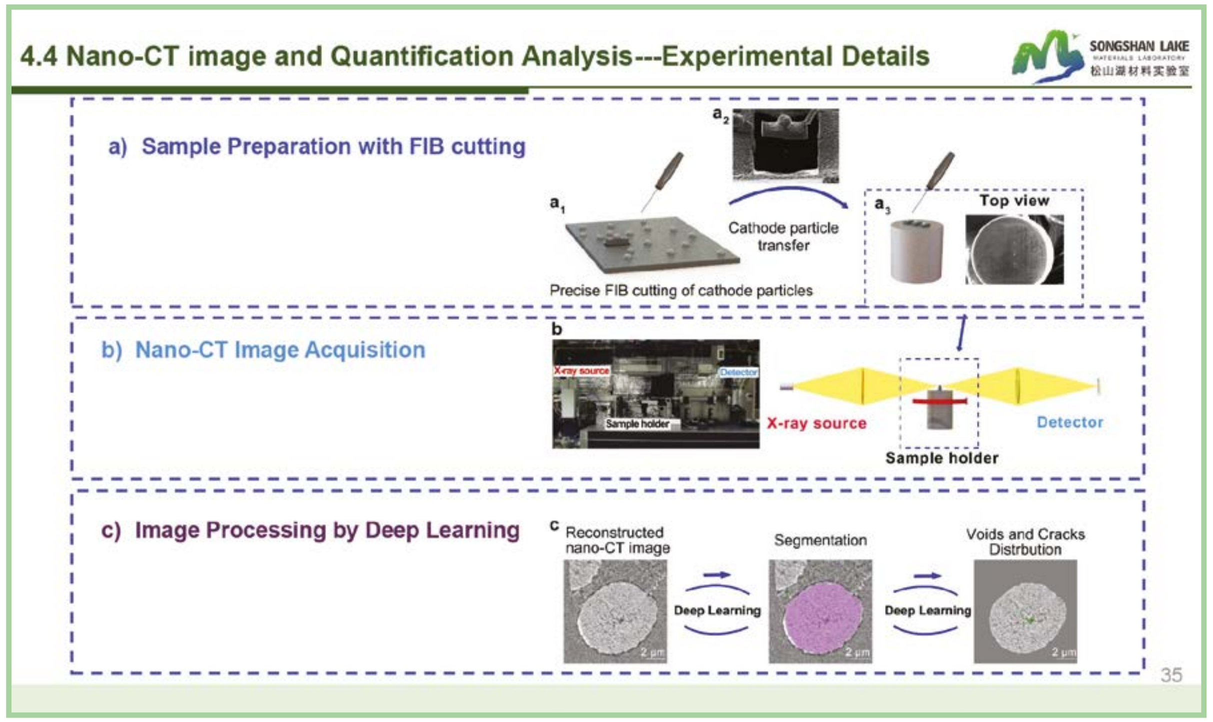
Sample preparation + **Image reconstruction** + **Image segmentation and quantification**

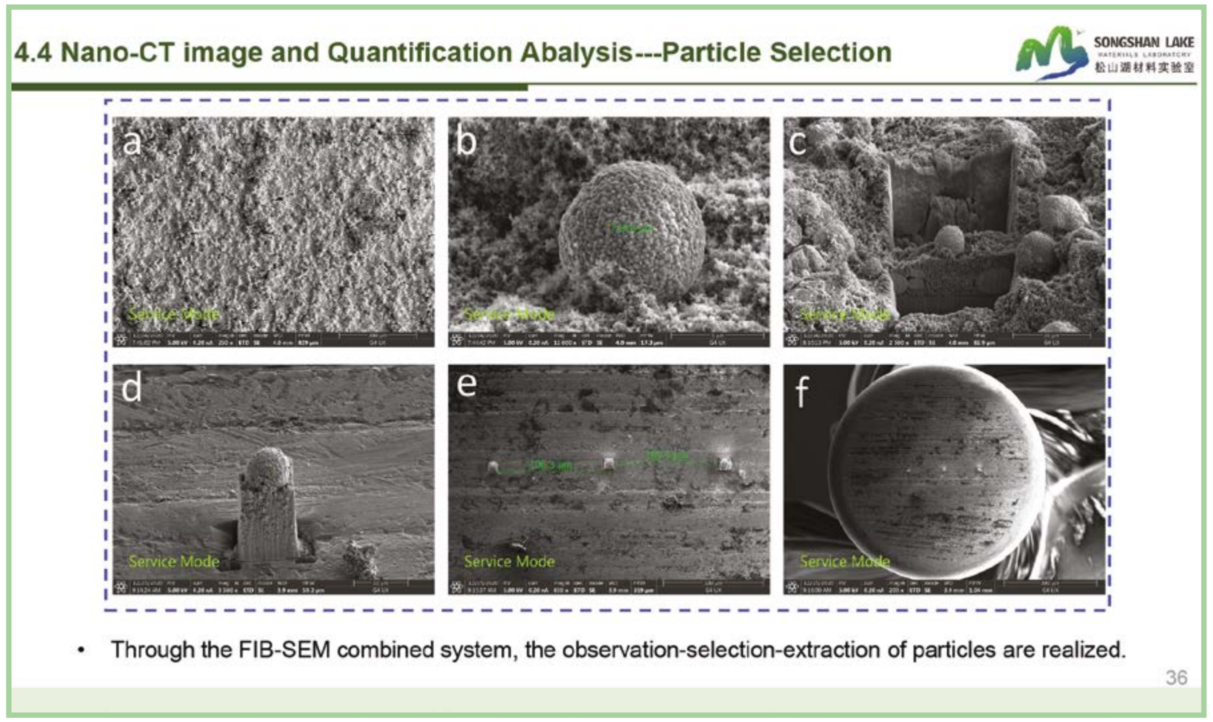
Ethos-NX5000 focused ion beam | Xradia-800 Ultra Nano-CT | Deep learning U-NET

3D Cracks and Voids Distribution

➢ The three-dimensional visualization and quantitative analyses of the internal pores and cracks of the quasi-in-situ secondary particles under different electrochemical states are realized.

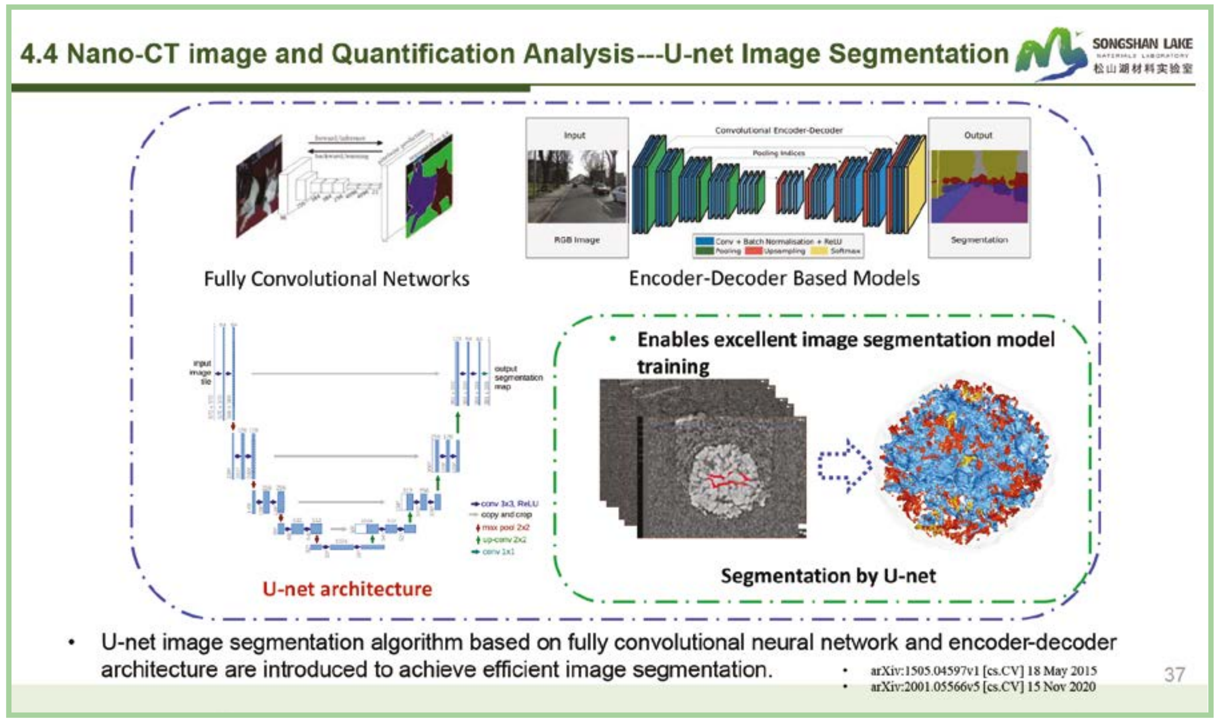
34

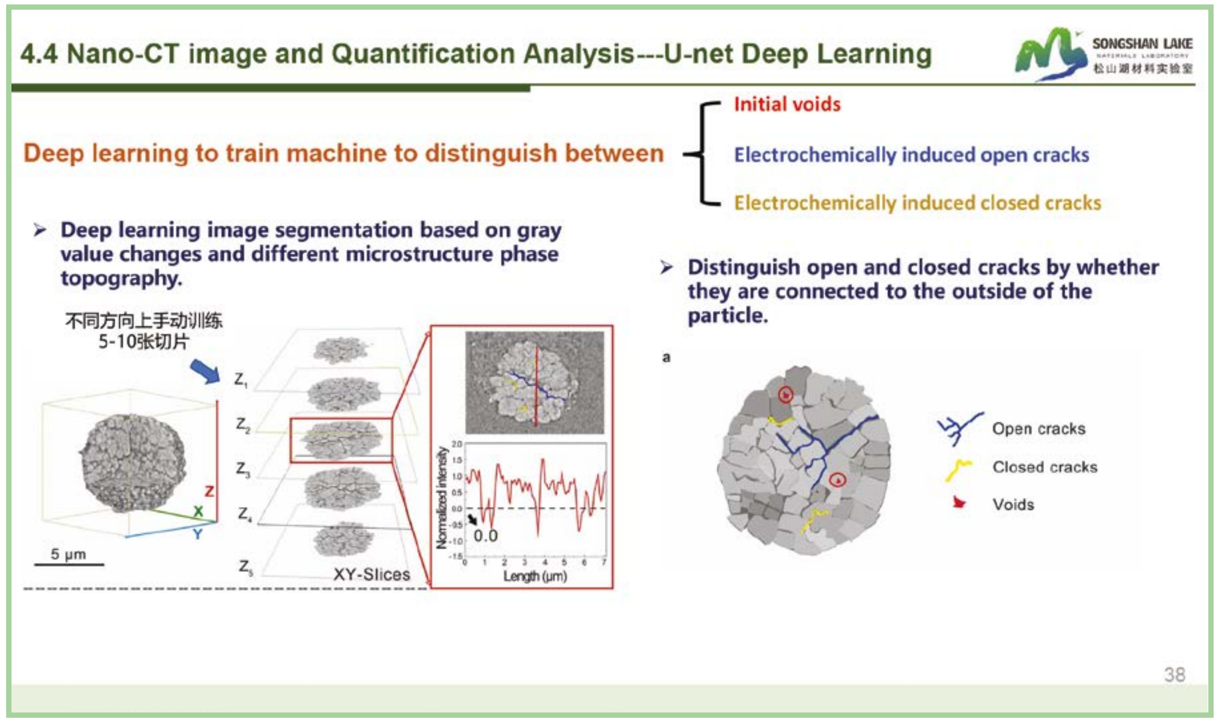




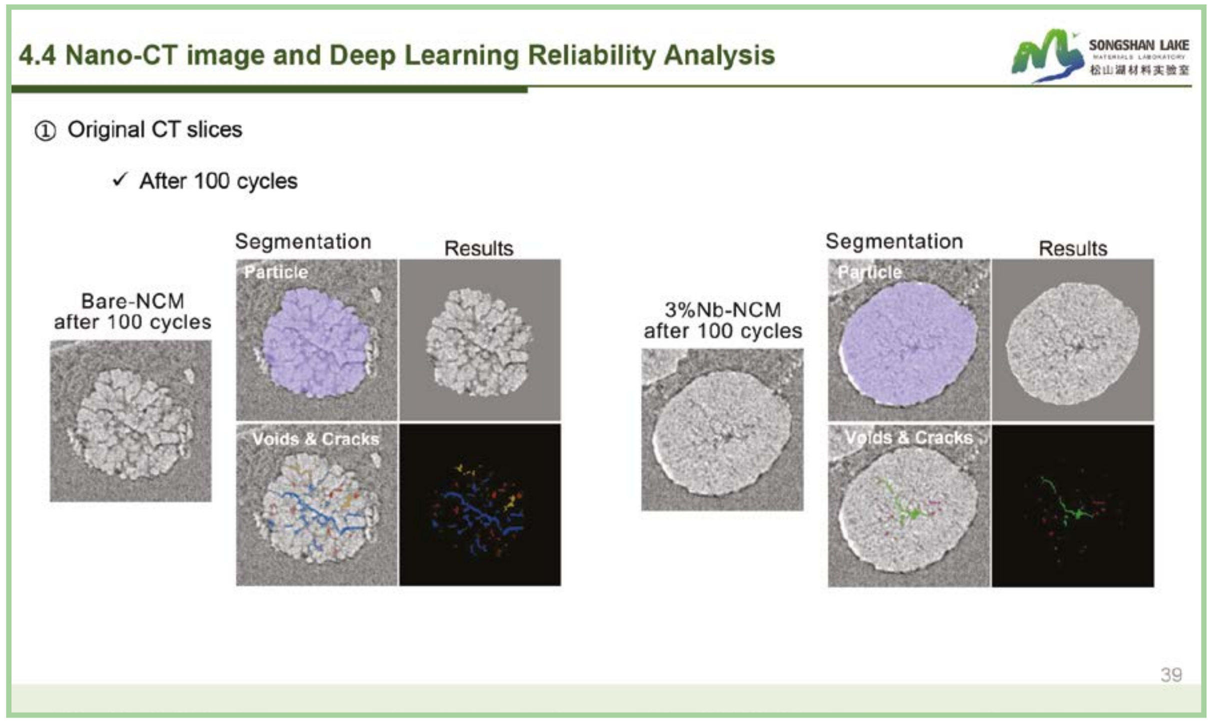
2022 International Conference on Niobium Based Batteries

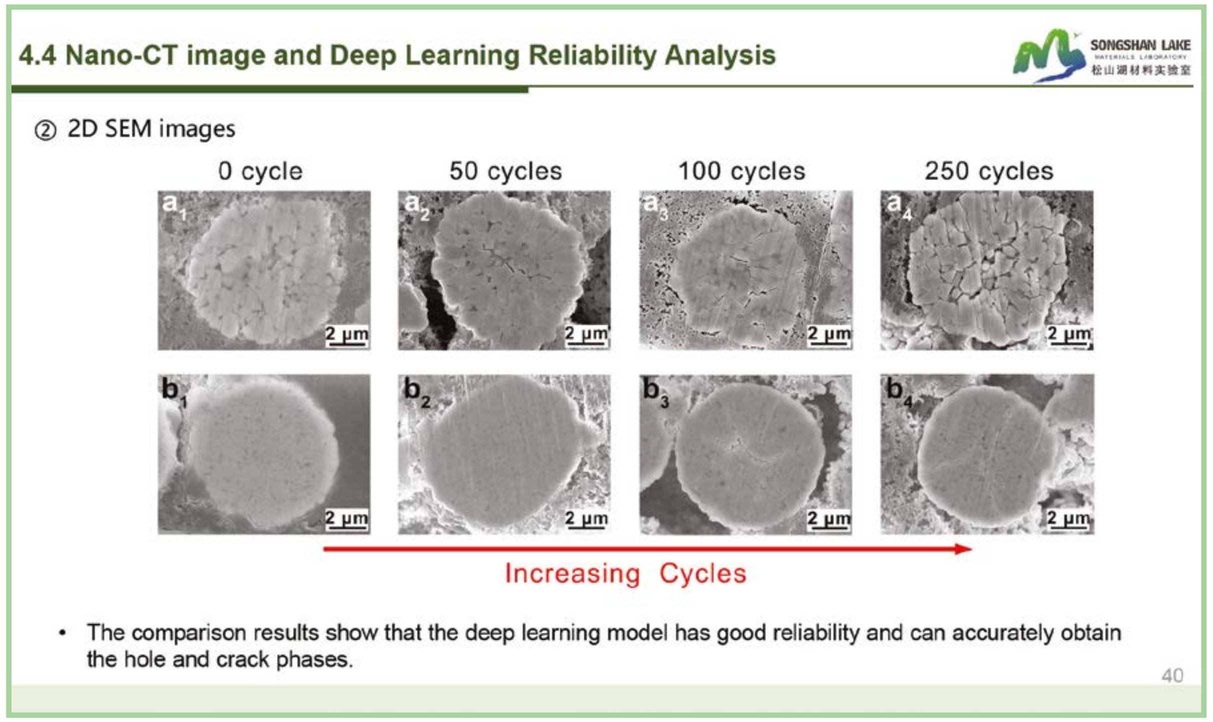
5TH EDITION

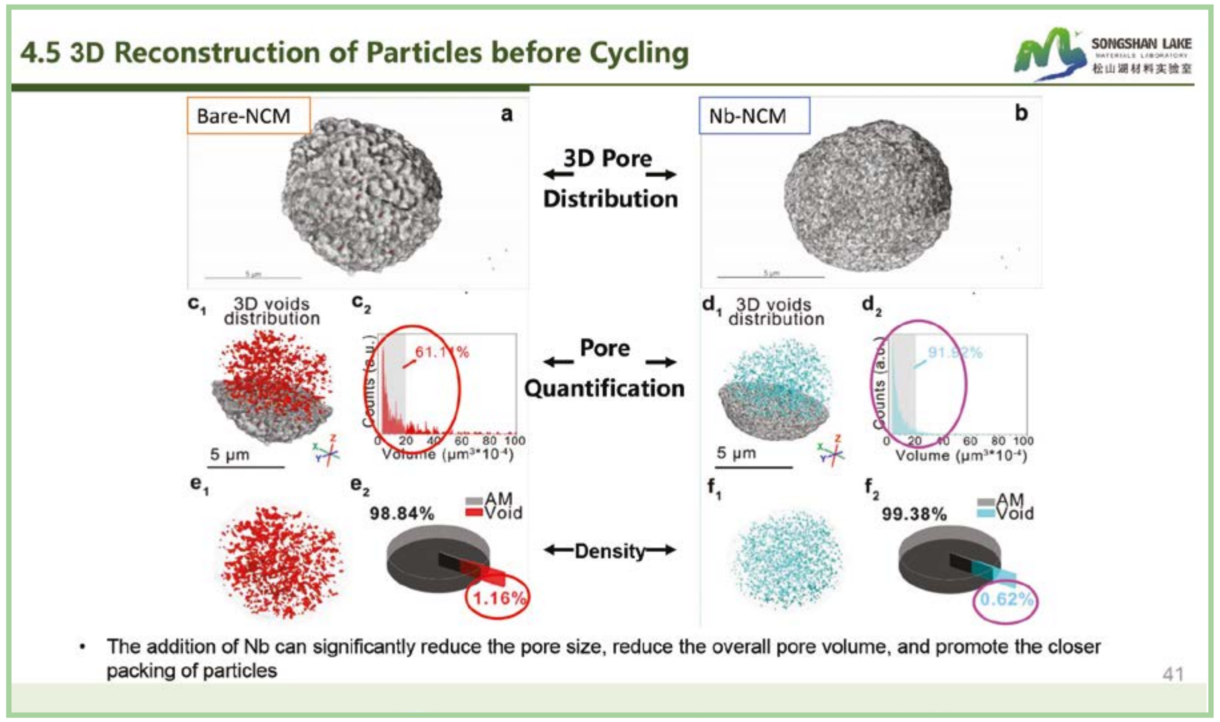


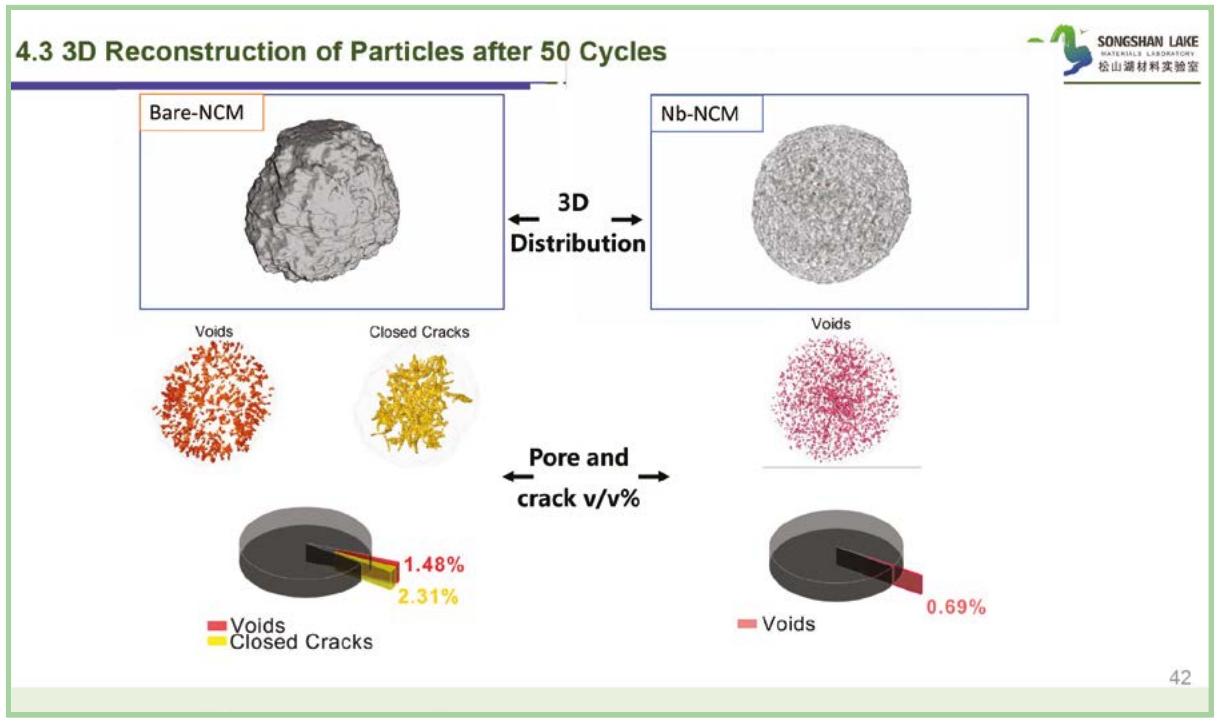


2022 International Conference on Niobium Based Batteries

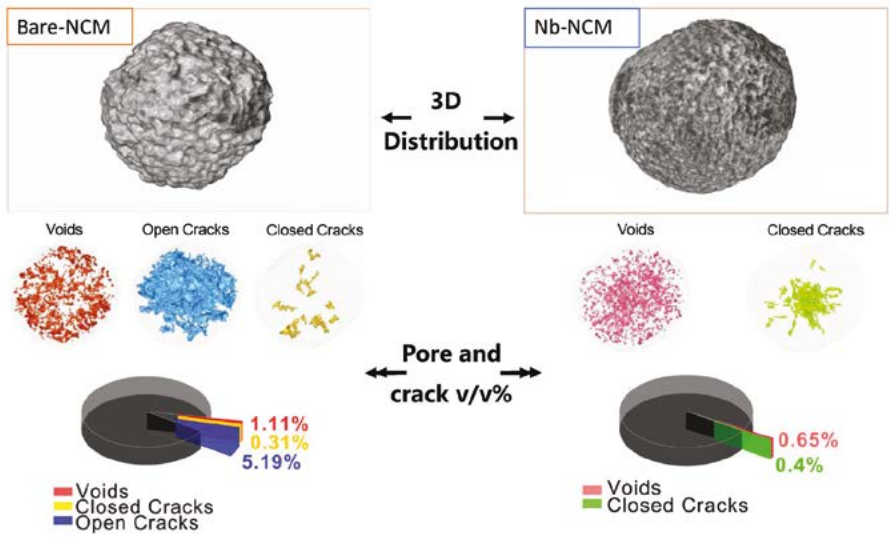






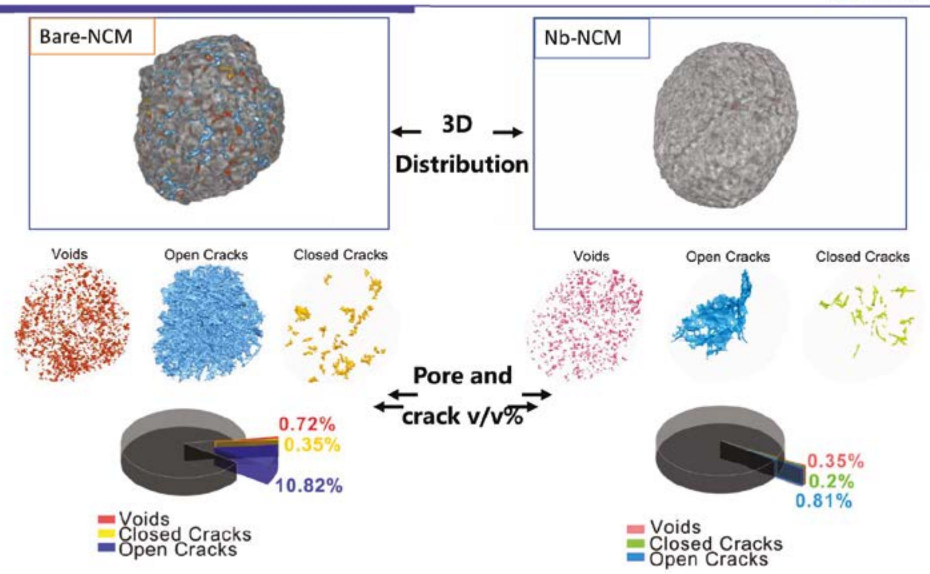


4.5 3D Reconstruction of Particles after 100 Cycles



43

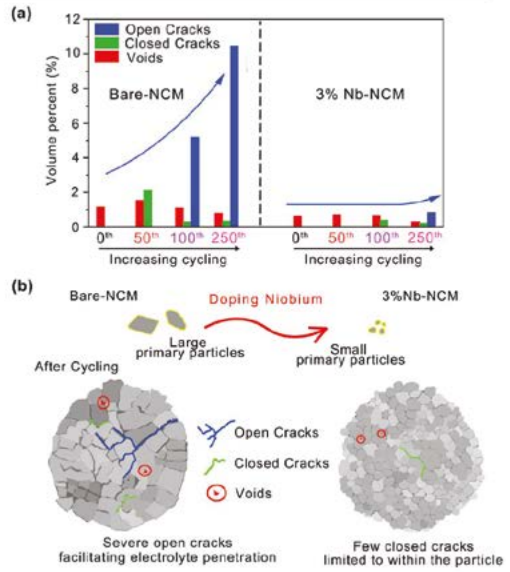
4.5 3D Reconstruction of Particles after 250 Cycles



44

2022 International Conference on Niobium Based Batteries
5TH EDITION

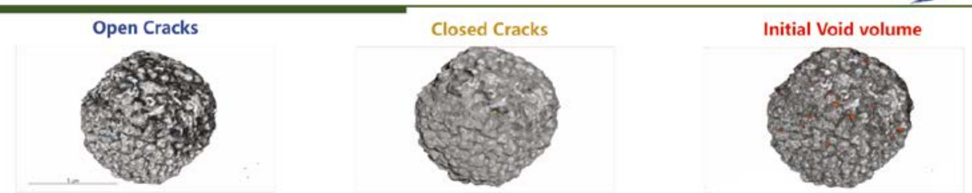
4.6 Results of Nb^{5+} doping on the Secondary Particles



- ◆ The results of quantification of the circulation microstructure show that
  - ➢ The generation of a large number of open cracks is the key factor that causes the performance degradation of NCM811 material at high temperature;
  - ➢ The addition of Nb greatly inhibits the generation of open cracks, thereby significantly improving the cycling stability.
- ◆ Effect of Nb Element on Microstructure
  - ➢ By reducing the size of the primary particles, it promotes closer packing between the primary particles, thereby improving the inherent mechanical strength of the positive electrode particles;
  - ➢ In addition, the accumulation of small-sized primary particles forms a large number of grain boundaries, which can effectively release the strain energy and hinder the propagation of cracks, thereby greatly inhibiting the formation of open cracks.

45

4.7 Conclusions of Nb^{5+} doping on the Secondary Particles



Conclusions of Part 4:

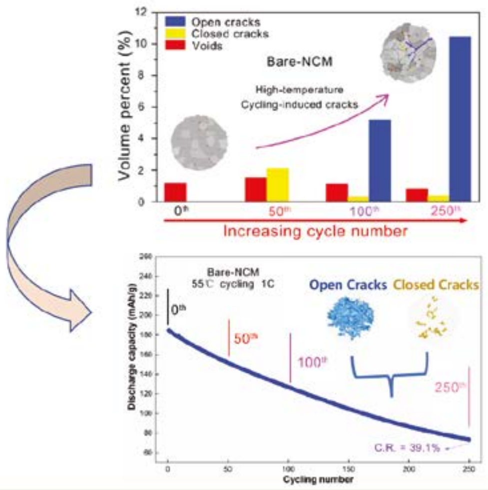
- Through the combination of X-ray Nano-CT and deep learning method, the non-destructive 3D visualization and quantitative analysis of the internal microstructure (holes, open cracks and closed cracks) of secondary particles under different cycle states were successfully achieved;
- The quantitative results show that the growth of open cracks more mainly contributes to the degradation of cycle performance;
- After doping with Nb^{5+} ions, by reducing the size of the primary particles, a more stable secondary particle microstructure is constructed, which improves the mechanical stability of the cathode particles, effectively inhibits the growth of open cracks, and thus significantly improves the cycle performance of high-nickel materials.

46

CONTENTS

5.1 Further Analyses of Cracks on Performance

➢ Through 3D visualization and quantitative analysis, it is found that high temperature cycling will induce a large number of cracks, and the rapid growth of open cracks is the key factor causing high temperature performance degradation.



➢ Further combining STEM and EELS, direct evidence of the effects of open cracks and closed cracks on material properties is given from the perspectives of atomic structure, elemental composition distribution and transition metal ion oxidation state;

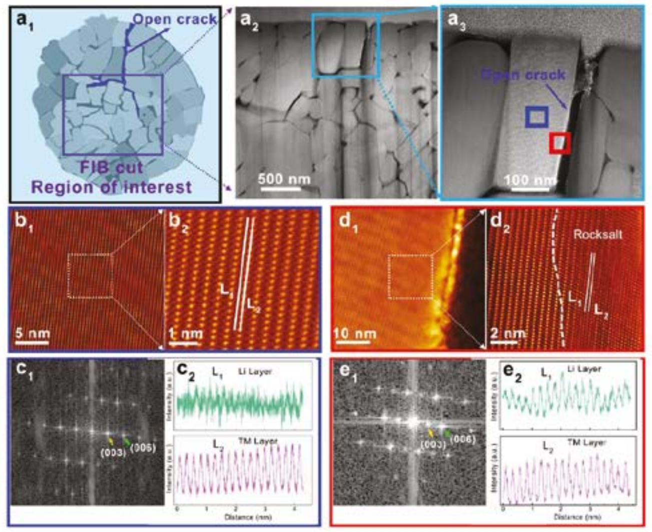
- Extraction-cut-thinning of the particles of Bare-NCM cathode material after 100 cycles of high temperature for subsequent analysis.

- Ethos-NX5000 focused ion beam for sample preparation

- JEOL ARM200 Scanning transmission electron microscopy

48

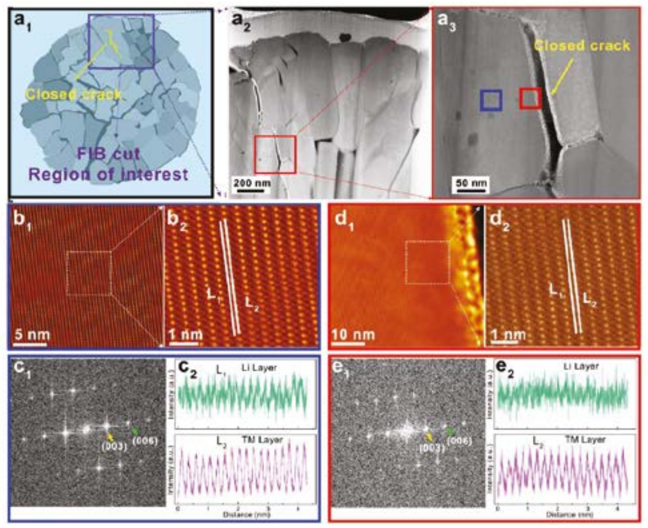
5.2 STEM Analysis---Atomic-Structure in Open Crack Region



- The inner region of the primary particle has a standard layered transition metal arrangement, and there is no structural distortion caused by the migration of the transition metal to the Li layer;
- In the surface area of the primary particle near the open crack, there is obvious severe structural distortion caused by the migration of transition metal to the Li layer, and this area is about 5 nm.

49

5.2 STEM Analysis---Atomic-Structure in Open Crack Region



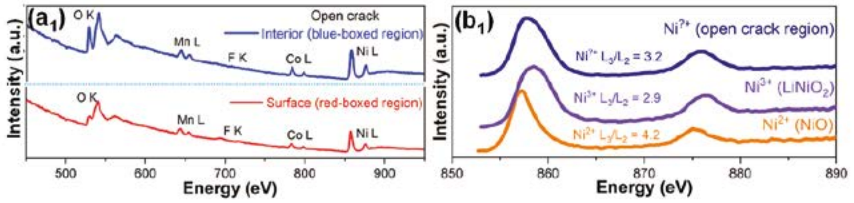
- Both the interior and surface area of primary particles have standard layered transition metal arrangement, and no structural distortion caused by the migration of transition metal to Li layer is observed.

50

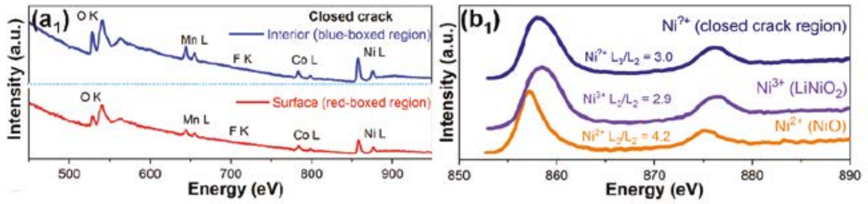
5.3 EELS Analysis---Element Concentration and Oxidation Distribution

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室

➢ Open crack region

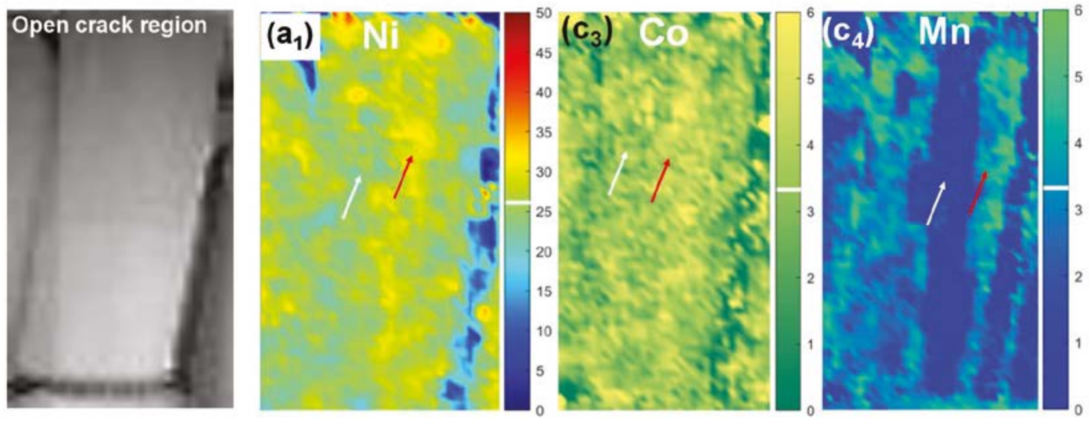


➢ Closed crack region



5.4 Element Distribution in Open Crack Region

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



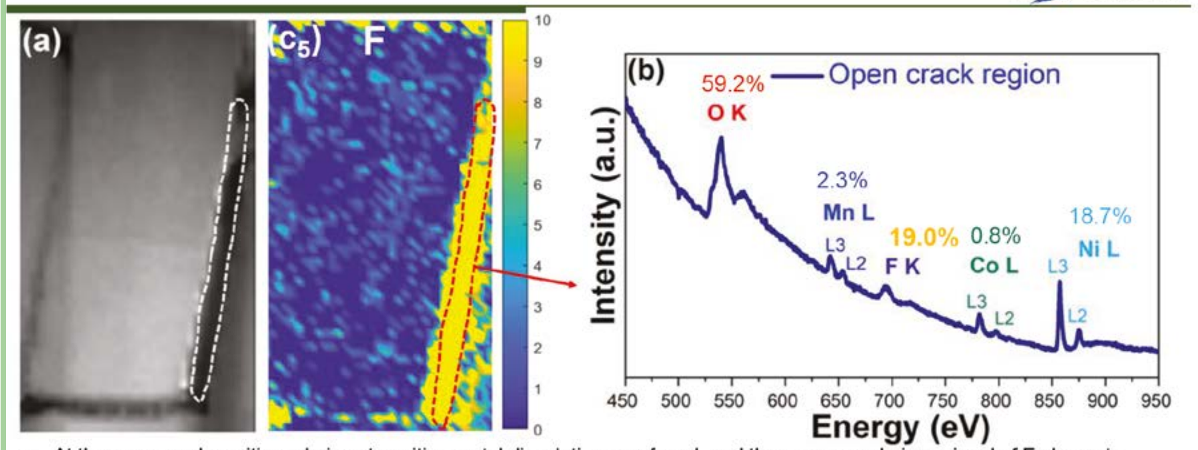
- The distribution of Ni, Co and Mn elements is uneven in the open crack area, and the transition metal elements are missing in the primary particles, especially the Mn element.

2022 International Conference on Niobium Based Batteries

5TH EDITION

5.4 Element Distribution in Open Crack Region

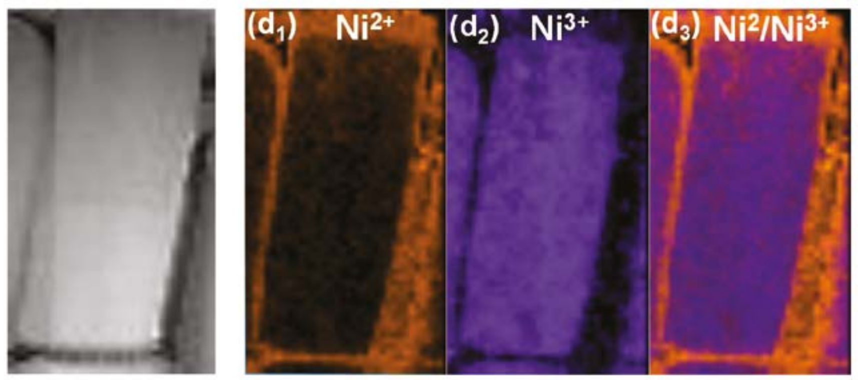
SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



- At the open crack position, obvious transition metal dissolution was found, and there was an obvious signal of F element;
- This shows that the electrolyte will indeed enter the interior of the secondary particles through the open crack channel, resulting in the migration and dissolution of transition metals;
- The dissolved transition metal ions react with the electrolyte, resulting in the accumulation of insulating fluoride $(Ni_xCo_yMn_z)F_2$ and rock-salt phase $(Ni_xCo_yMn_z)O$ at open crack sites, and resulting in uneven distribution of elements within the lattice.

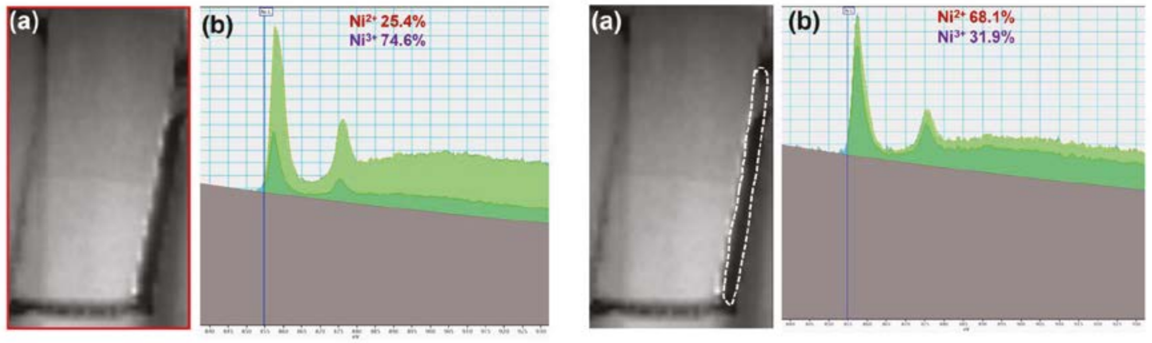
5.4 Ni^{2+}/Ni^{3+} Oxidation Distribution in Open Crack Region

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



- Ni^{2+} has a higher concentration at the edge of the primary particle, especially near the edge of the open crack, which is consistent with the results observed in the atomic structure analysis, indicating that severe interfacial side reactions occur at the open crack;
- In contrast, the content of Ni^{3+} is relatively uniform in the whole primary particle.

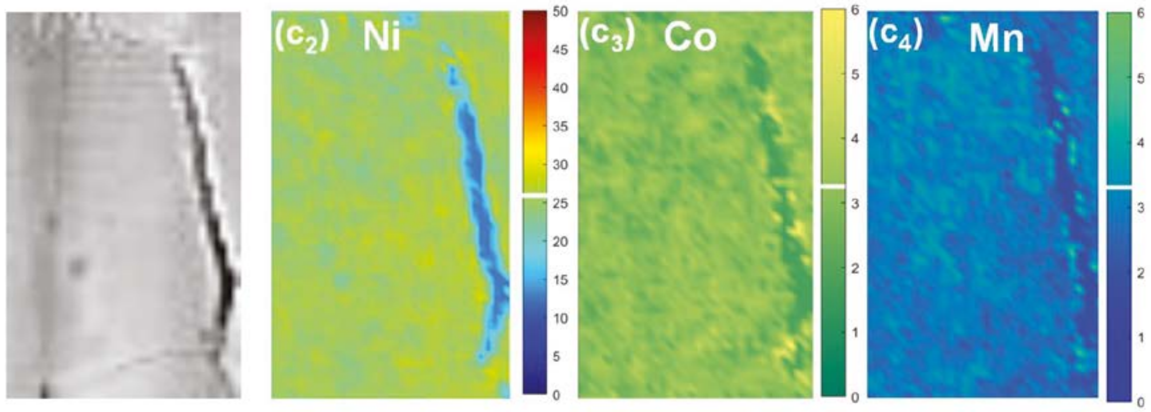
5.4 Ni^{2+}/Ni^{3+} Oxidation Distribution in Open Crack Region



- Near the open crack, both the overall area (marked by the red box) and the specific crack position (marked by the white dotted line) show high Ni^{2+} content;

55

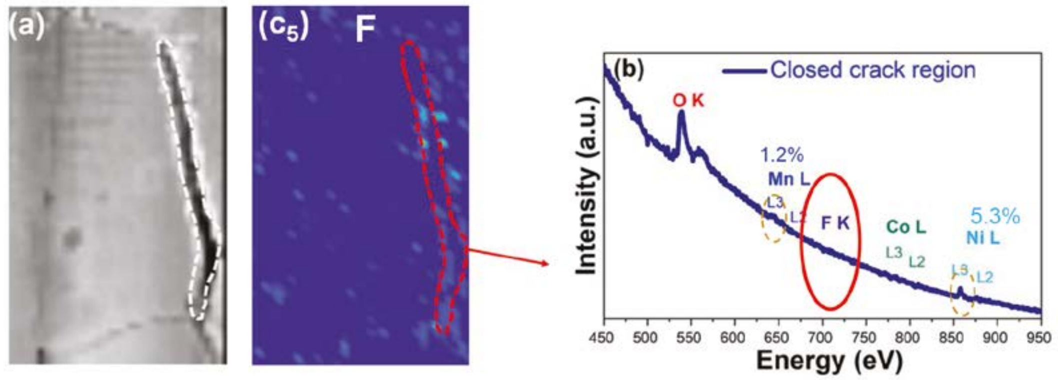
5.5 Element Distribution in Closed Crack Region



- All transition metal elements have uniform distribution throughout the primary particles.

56

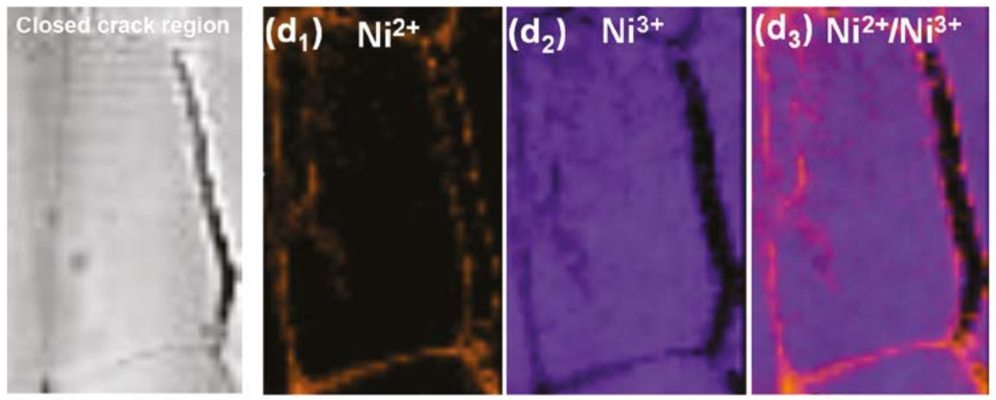
5.5 Element Distribution in Closed Crack Region



- At the closed crack position, there is no obvious F element signal, only a small amount of Ni and Mn elements are distributed, and there is no serious transition metal dissolution phenomenon.
- It shows that although the closed crack is close to the outer surface of the particle (about 500 nm), the infiltration of electrolyte into the closed crack will not occur, and it will not cause serious interfacial side reactions inside the particle, which is consistent with the results of atomic structure analysis.

57

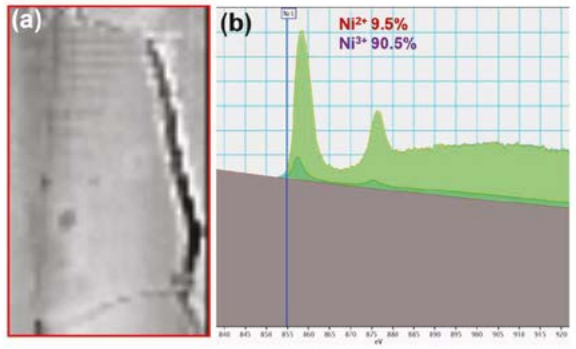
5.5 Ni^{2+}/Ni^{3+} Oxidation State Distribution in Closed Crack Region



- The Ni^{2+} content at the closed crack is obviously reduced, and only a small amount is observed at the edge of the primary particle;;
- And Ni^{3+} is relatively uniformly distributed in the whole primary particle.

58

5.5 Ni^{2+}/Ni^{3+} Oxidation State Distribution in Open Crack Region

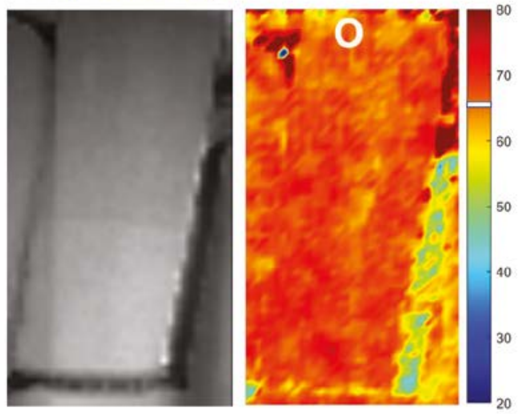


- Near the closed crack, the proportion of Ni^{2+} in the whole area is only 9.5%, which is much lower than the Ni^{2+} content in the open crack.

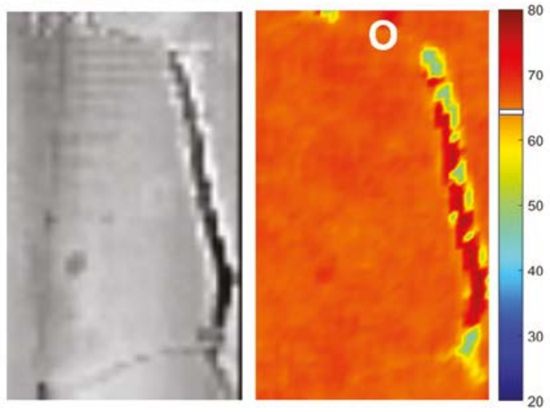
59

5.6 O Element Distribution in Open and Closed Crack Regions

Open crack region



Closed crack region



- Compared with the oxygen content distribution at the open crack, the closed crack has a smaller lattice oxygen loss.

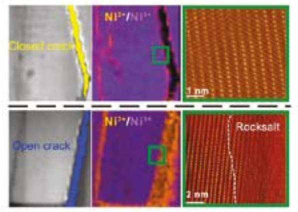
60

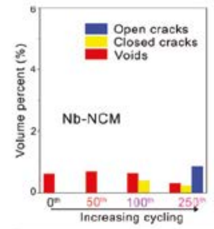
2022 International Conference on Niobium Based Batteries
5TH EDITION

5.7 Conclusions of Atomic-Scale Structure Analysis

Conclusions of Part 5:

- At the open crack, serious interfacial side reactions occur inside the particles due to the immersion of the electrolyte, resulting in the loss of lattice oxygen, the distortion of the lattice structure, the dissolution of transition metal ions and the generation of a large number of Ni^{2+} ions, resulting in the destruction of the lattice structure and the large reversible capacity.
- At the closed crack, although there is a small amount of oxygen loss and Ni^{2+} generation, there is no obvious lattice distortion and element dissolution, and the internal crystal structure can be better maintained, thus making no significant contribution to the performance degradation.
- Combined with the three-dimensional analysis results of the particle microstructure and further considering the doping of Nb^{5+}, the addition of Nb^{5+} greatly reduces the generation of cycle-induced open cracks, thereby avoiding more serious internal particle side reactions caused by electrolyte immersion, effectively maintaining the positive electrode. The integrity of the particle crystal structure and elemental composition results in excellent material stability.





61

CONTENTS

Conclusions

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室

1. By systematically synthesizing high-nickel materials doped with different elements, it is determined that Nb element doping can improve the cycling stability of high-nickel ternary cathode materials, especially the improvement of high-temperature cycling stability.

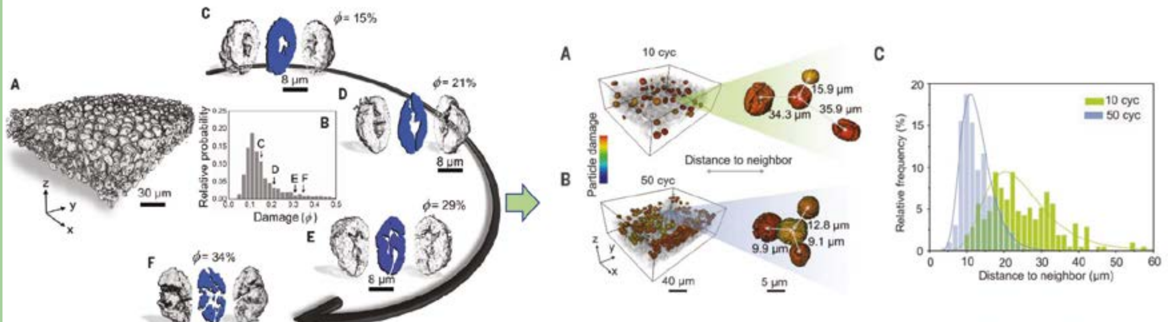
2. Through experiments with different doping contents, 1 mol% Nb^{5+} doping was determined as the best doping scheme;

3. Using different advanced characterization methods, including in-situ XRD, Nano-CT/DL, and STEM/EELS, it was determined that Nb element doping, on the one hand, has an effect on the stability of crystal structure by reducing cation mixing and alleviating cyclic lattice distortion to a certain extent. On the other hand, by adjusting the morphology of the primary particles, a more stable secondary particle microstructure is constructed, which effectively inhibits the generation of open cracks, and finally realizes the synthesis of high-stability and high-nickel ternary materials at high temperatures.

63

Future perspectives

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



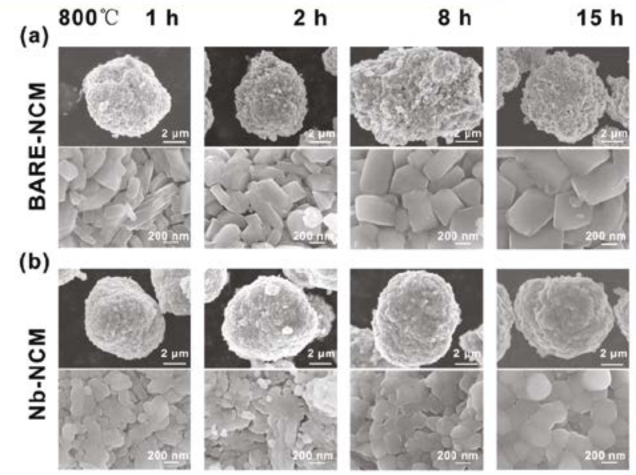
• Science, 2022, 376(6592): 517-521.

(1) In the future, it is hoped to further optimize the experimental acquisition and analysis methods, to achieve simultaneous acquisition and efficient analysis of a sufficient number of particles through a single experiment, and to give experimental conclusions from a statistical point of view, which can better promote the development of materials research and have more Strong generalizability。

64

Future perspectives

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室



• Under the doping of Nb element, the crystal growth and morphology were observed during sintering at 800 °C.

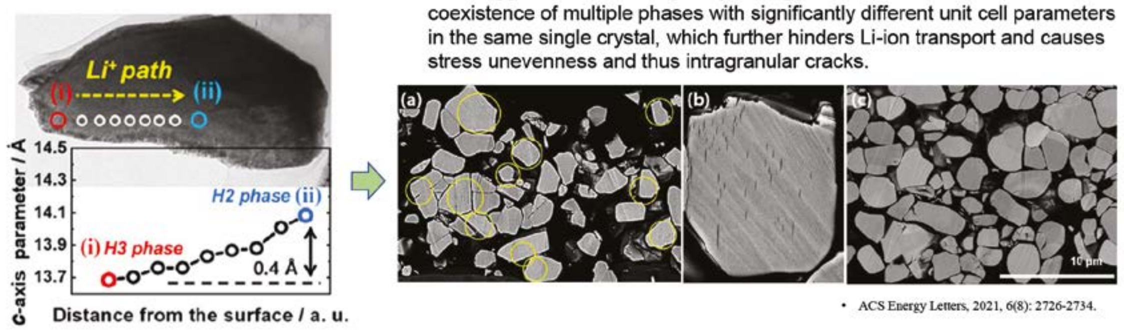
(2) The modification of the particle microstructure by Nb element doping is essentially the regulation of the primary particle size by Nb element doping. How does Nb affect the crystal growth of the high nickel layered cathode and how to reduce the primary particle size? Further studies are needed to better understand the regulation mechanism of elemental doping on morphology and microstructure.

65

Future perspectives

SONGSHAN LAKE MATERIALS LABORATORY 松山湖材料实验室

• The sluggish kinetics in single-crystal high-nickel cathodes lead to the coexistence of multiple phases with significantly different unit cell parameters in the same single crystal, which further hinders Li-ion transport and causes stress unevenness and thus intragranular cracks.



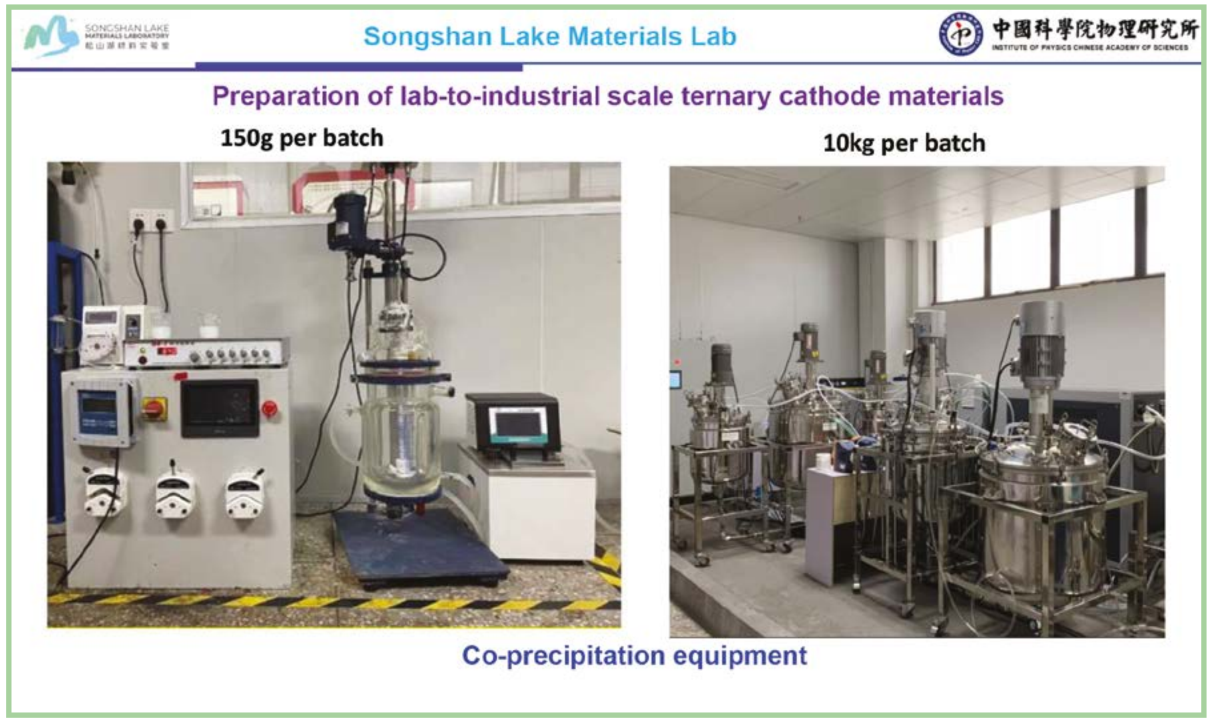
• ACS Energy Letters, 2021, 6(8): 2726-2734.

(3) Large-size single-crystal high-nickel materials have always been considered to be a better choice for next-generation cathode materials, especially favored by the industry, and single-crystal materials for high voltage can make up for the lack of energy density, but the kinetic performance is not good. The high synthesis cost still limits the further promotion of single-crystal high-nickel materials. Considering the excellent modification effect of Nb^{5+} on polycrystalline high-nickel cathodes, this opens up new possibilities for the future development of polycrystalline materials.

66


Songshan Lake Materials Lab
SONGSHAN LAKE
松山湖材料实验室
Customer
Innovation Drives the Progress of New Energy World
https://en.sunwoda.com/
Sunwoda
CATL
http://www.catl.com/
Strong strategic industrial collaborations
https://www.huawei.com
Huawei
SVOLT
http://www. en.svolt.cn/
Who is Huawei?


Songshan Lake Materials Lab
SONGSHAN LAKE
松山湖材料实验室
Preparation and characterization of lab-to-to-industrial scale batteries
10 kg
100 kg
Synthesis
Test
Characterization


Songshan Lake Materials Lab
中國科學院物理研究所
INSTITUTE OF PHYSICS CHINESE ACADEMY OF SCIENCES
Preparation of lab-to-industrial scale ternary cathode materials
150g per batch
10kg per batch
Co-precipitation equipment


SONGSHAN LAKE MATERIALS LABORATORY
松山湖材料实验室
松山湖材料实验室
SONGSHAN LAKE MATERIALS LABORATORY
This work has been supported by CBMM and CITIC Metal Co., Ltd.

Notes

2022 International Conference on Niobium Based Batteries
5TH EDITION

Notes

Prof. Yang-Kook Sun

FRS Chemistry Department - Hanyang University

韩国首尔汉阳大学的 YANG-KOOK SUN 教授是材料化学和化学工程领先科学家。他成功地设计、合成和用于电化学装置结构分析、锂离子电池、锂硫电池、锂空气电池和钠离子电池的先进储能和转换材料。在相关成就中，他设计的浓度梯度锂镍钴锰氧化物正极已获得电池公司的许可，并用于电动汽车电池的生产，最近受到了持续的工业关注。

Professor Yang-Kook Sun of Hanyang University, Seoul, South Korea, is a leading materials chemistry and chemical engineering scientist. He succeeded in design, synthesis and structural analysis of advanced energy storage and conversion materials for application in electrochemical devices, lithium-ion, lithium-sulfur, lithium-air, and sodium-ion batteries. Among the relevant achievements, the concentration-gradient lithium-nickel-cobalt-manganese oxide cathode designed by himself has been licensed by battery companies, undergone production for use in EV batteries and recently received continuous industrial attention.

2022 International Conference on Niobium Based Batteries

High-Energy Nb-doped Ni-rich NCA, NCM Cathodes Materials

Yang-Kook Sun
Department of Energy Engineering, Hanyang University

Abstract

Lithium-ion batteries (LIBs) have become the main power sources for electric vehicles (EVs) because of their high energy density and long service life. However, currently available state-of-the-art LIBs are still inadequate for EVs that will appeal to a wider consumer base, mainly because of the short drive range per charge. Hence, improvements in the energy density and cycling stability of LIBs, as well as cost reduction, are prerequisites for envisioned general electromobility. The overall performance and cost of LIBs are largely determined by the cathode material because of its relatively low capacity and poor cycling stability compared to those of graphite. Hence, recent research on LIBs has concentrated mainly on identifying and optimizing high-capacity cathodes; the primary candidate materials are Ni-rich layered $LiMO_2$ (M = Ni, Co, Mn, called NCM or Al called NCA). To increase the capacity of current NCM and NCA cathodes, the fraction of Ni in the cathodes has been progressively increased. However, this approach is limited by the deterioration of capacity retention and thermal stability resulting from excessive Ni enrichment due to the anisotropic volume change caused by the phase transition (H2-H3) at approximately 4.2 V. This volume variation generates internal microcracks that propagate to the particle surface, facilitating electrolyte penetration along the grain boundary into the particle interior. This accelerates the surface degradation of internal primary particles by reacting the exposed, reactive, and unstable Ni^{4+} with a deleterious electrolyte to form a NiO-like impurity layer.

In this presentation, to overcome the tradeoff relationship between reversible capacity and cycling stability, one approach is introduced. The concept of radially aligned primary particles with crystallographic texture was successfully confirmed by Nb-doped Ni-rich layered cathodes. Nb plays a vital role in producing highly oriented and elongated primary particles, which can effectively dissipate the internal strain resulting from H2-H3 phase transitions, realizing a significant improvement in cycling stability. As such, 1-Nb-doped NCA85 cathode demonstrated 90% of its initial capacity after 1000 cycles while an undoped cathode retains 57.3%.

Notes

2022 International Conference on Niobium Based Batteries

Notes

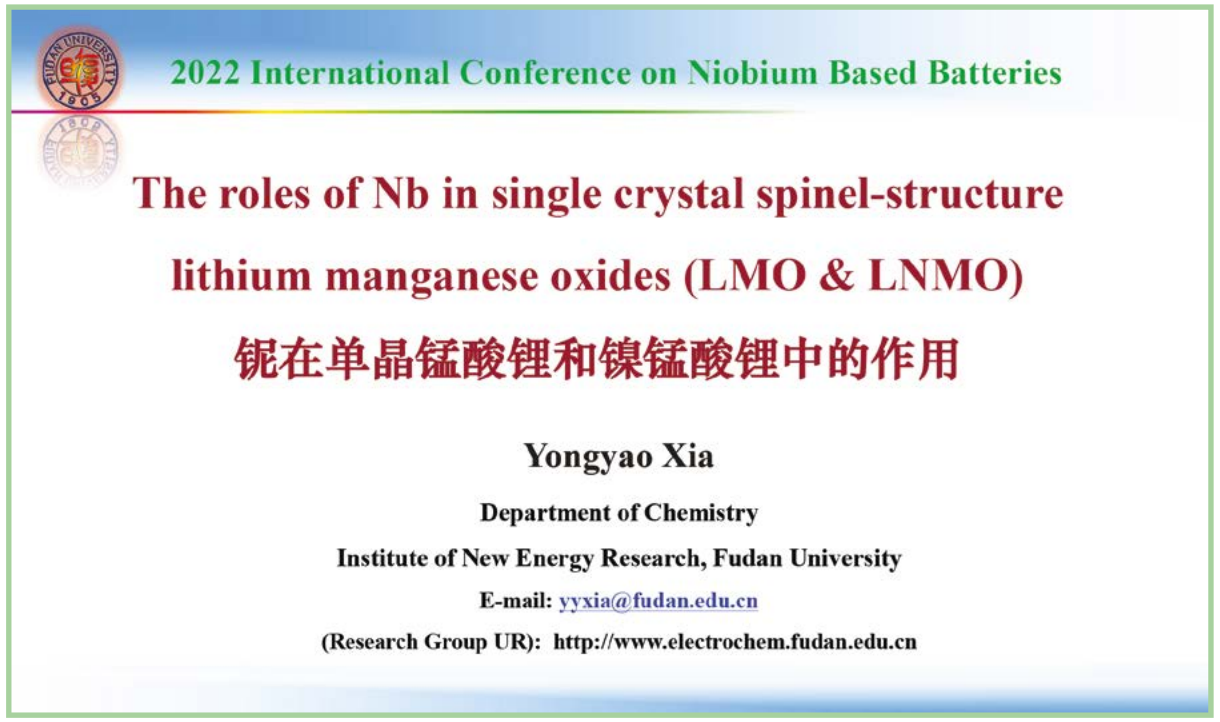
2022 International Conference on Niobium Based Batteries

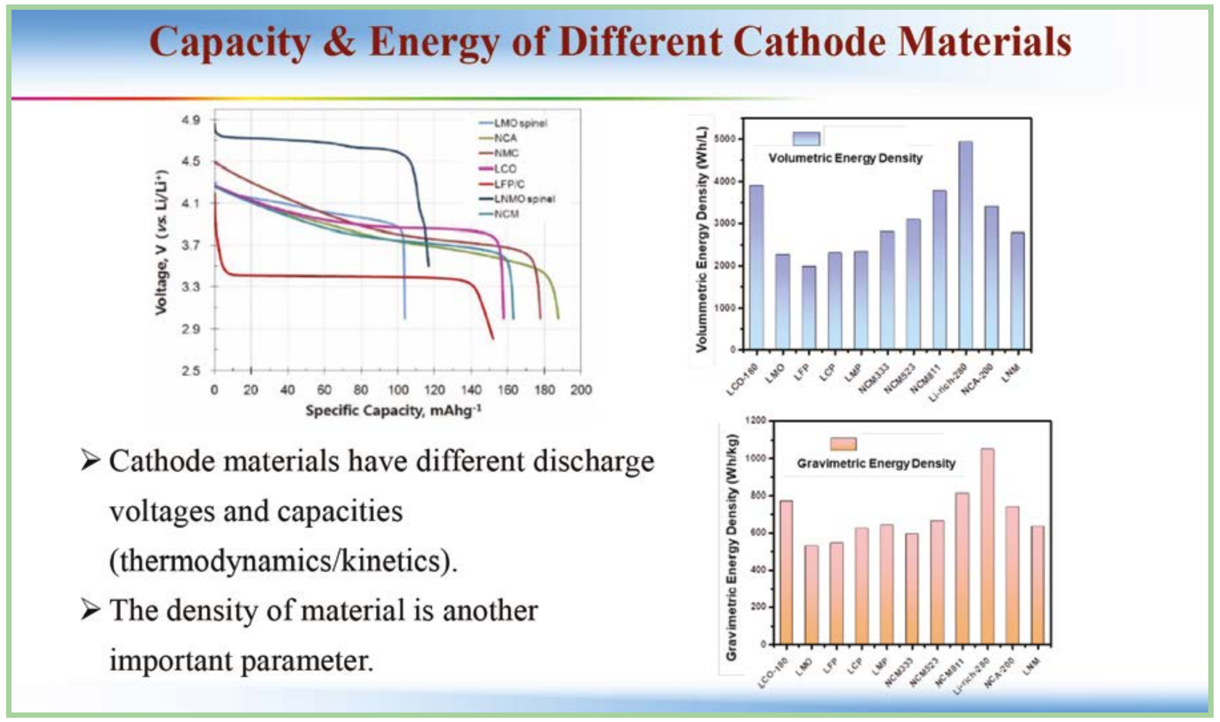
Prof. Dr. Yongyao Xia

Fudan University

夏永姚，工学博士，博士生导师，复旦大学特聘教授。国际电化学会（ISE）FELLOW，J. POWER SOURCES 杂志编辑，中国电化学会主任。
1987年毕业于浙江师范大学化学系，1990年获吉林大学化学系电化学专业理学硕士学位，1990-1994在长春应用化学研究所工作，1997年获日本佐贺大学能源-材料科学专业工学博士学位，同年留校任日本文部省教官讲师。1998年赴美国南卡罗来纳州化学工程系做博士后研究员。1999-2001年在大阪工业技术研究所做博士后研究员。2001-2002年进入日立Maxell公司电池开发中心工作。2003年回复旦大学化学系工作。从1990起一直从事新型储能材料和技术的研究，包括锂（钠）离子电池、电化学电容器和新型电池体系等。共发表SCI论文399篇，他引30000余次， H-INDEX 91，入选2017-2021年CLARIVATE ANALYTICS 高引作者，授权专利30余项。

Dr. Yongyao Xia, Distinguished Professor of Fudan University. Fellow of International Electrochemical Society (ISE), editor of J. Power Sources magazine, Director of China Electrochemical Society.
He graduated from the Department of Chemistry of Zhejiang Normal University in 1987 and received a Master of Science degree in electrochemistry from the Department of Chemistry of Jilin University in 1990. He worked at Changchun Institute of Applied Chemistry from 1990 to 1994. He received a doctorate engineering degree in energy and material Science from Saga University, Japan, in 1997. In 1998, he went to the Department of Chemical Engineering, South Carolina, USA, as a postdoctoral researcher. From 1999 to 2001, he was a postdoctoral researcher at the Osaka Institute of Industrial Technology. From 2001 to 2002, he worked in the Battery Development Center of Hitachi Maxell. He returned to work in the Chemistry Department of Fudan University in 2003. Since 1990, he has been researching new energy storage materials and technologies, including lithium (sodium) ion batteries, electrochemical capacitors, and new battery systems. He has published 399 SCI papers, has more than 30,000 citations, H-index 91, and was selected as the highly cited author of Clarivate Analytics from 2017 to 2021, and has more than 30 authorized patents.

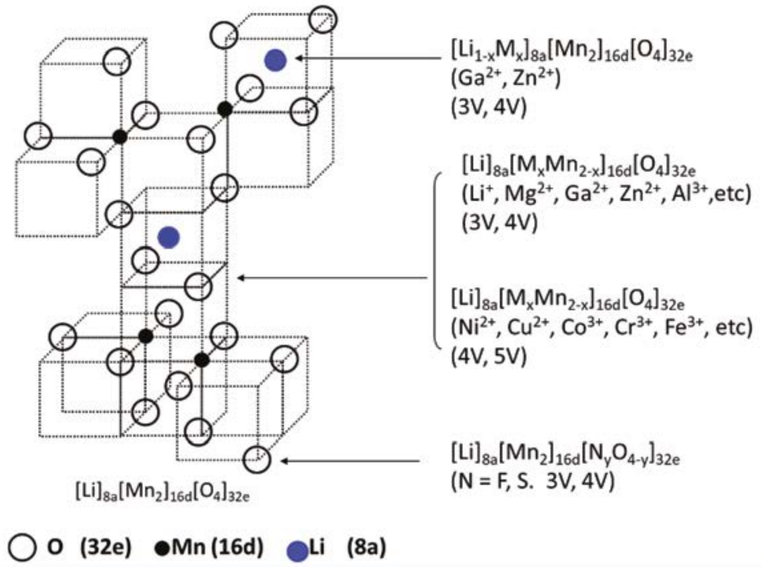


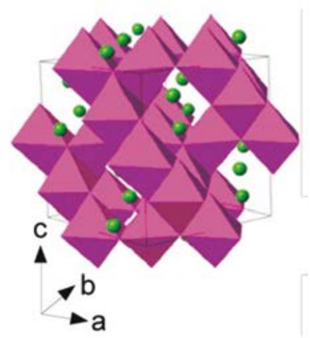


Summary of Various Cathode Materials

	LCO	NCA	NMC	LMO	LFP
Capacity (CHG cut off)	-160mAh/g (@4.4V)	-190mAh/g (@4.3V)	-180mAh/g (@4.5V)	-105mAh/g (@4.3V)	-160mAh/g (@4.0V)
Cost	High	High	Moderate	Low	Very Low
Process Difficulty	-1,000°C，air Easy	-800°C,O_2 Difficult	-1,000°C，air Less difficult	-900°C，air Less difficult	-700°C，N_2 Difficult
Environment	Poor	Slightly poor	Slightly poor	Good	Good
Thermal Stability	Slightly poor	Poor	Good	Very good	Excellent
Remark	Small-Mid size High Energy Mobile devices	Small-Mid size High Energy EV	Small-Mid size High Energy EV，ESS	Small-Large size High power Power tools，EB, EV	Small-Large size Long cycles/safety EB, EV, ESS

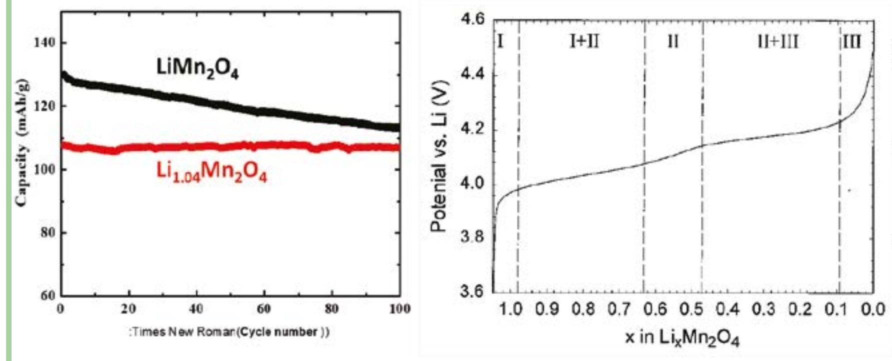
Crystal Structure of Spinel





High rate capability due to the three –demission structure for Li-ion diffusion.

Phase Transition Model for $Li_xMn_2O_4$

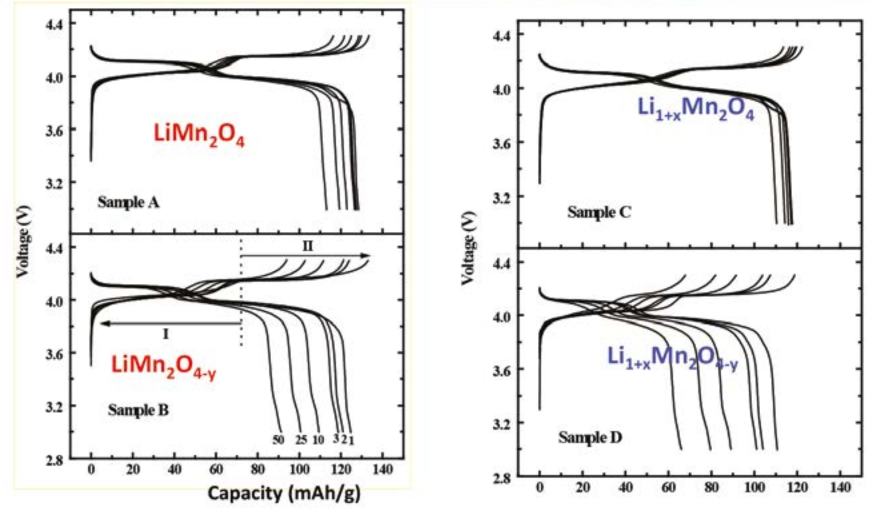


- Y. Xia et al., One-Phase Model
- T. Ohzuku et al., Two-Phase Model (*JES., 137, 769 ,1990).*
- W.Liu, et al., Three-Phase Model. *(JES, 145, 459,(1998).*

Lithium-rich spinel exhibits better cycling stability with one-phase transition

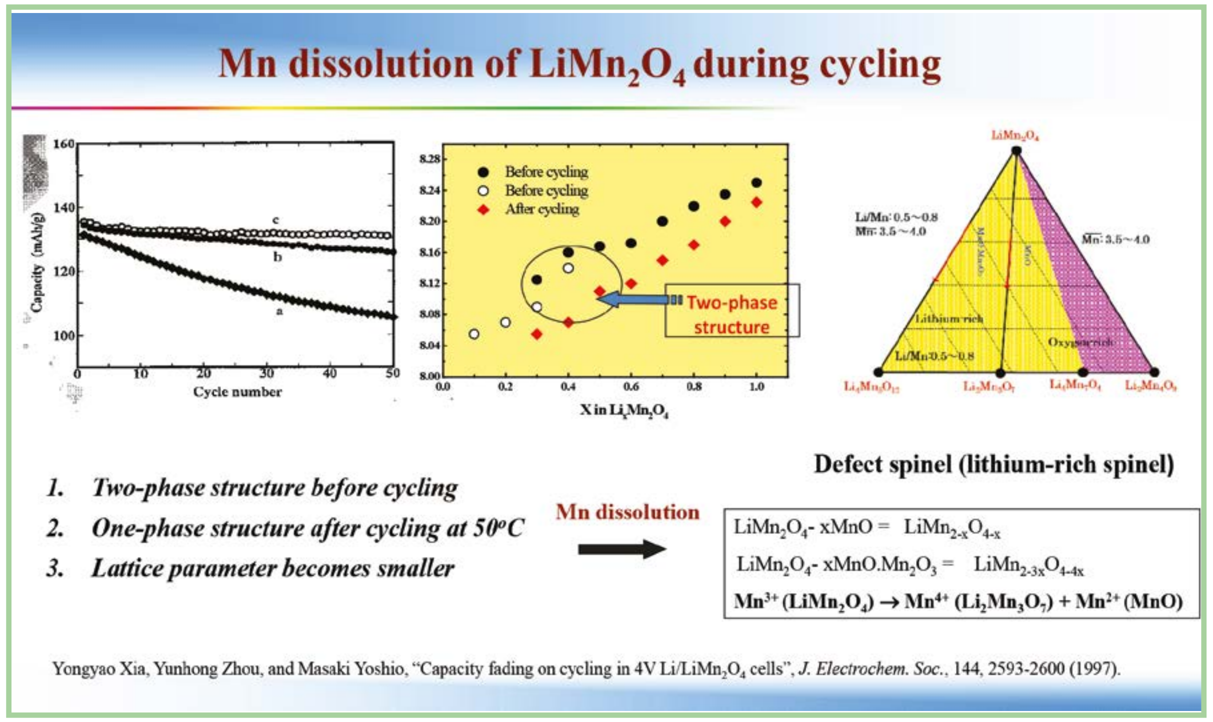
Yongyao Xia and Masaki Yoshio, "An investigation on the lithium ions insertion into the spinel structure Li-Mn-O compounds". *J. Electrochem. Soc.*, 143, 825-833 (1996).

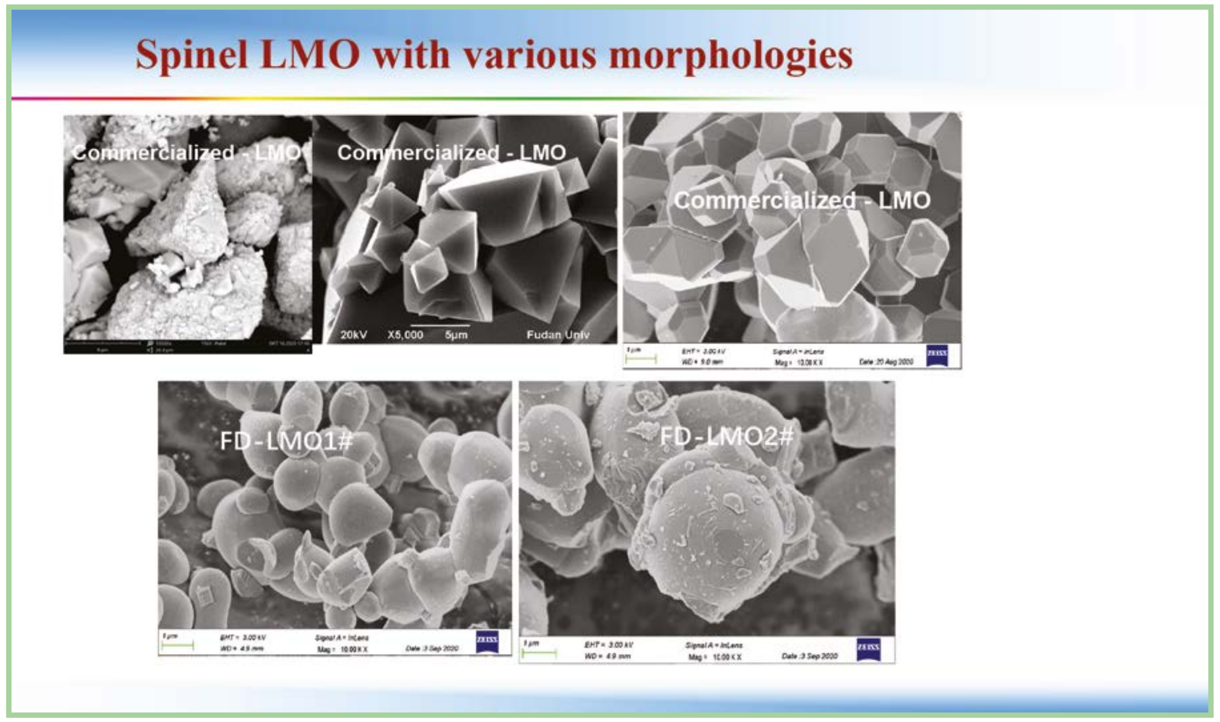
Oxgen-stoichiometric & Oxygen-defect spinel

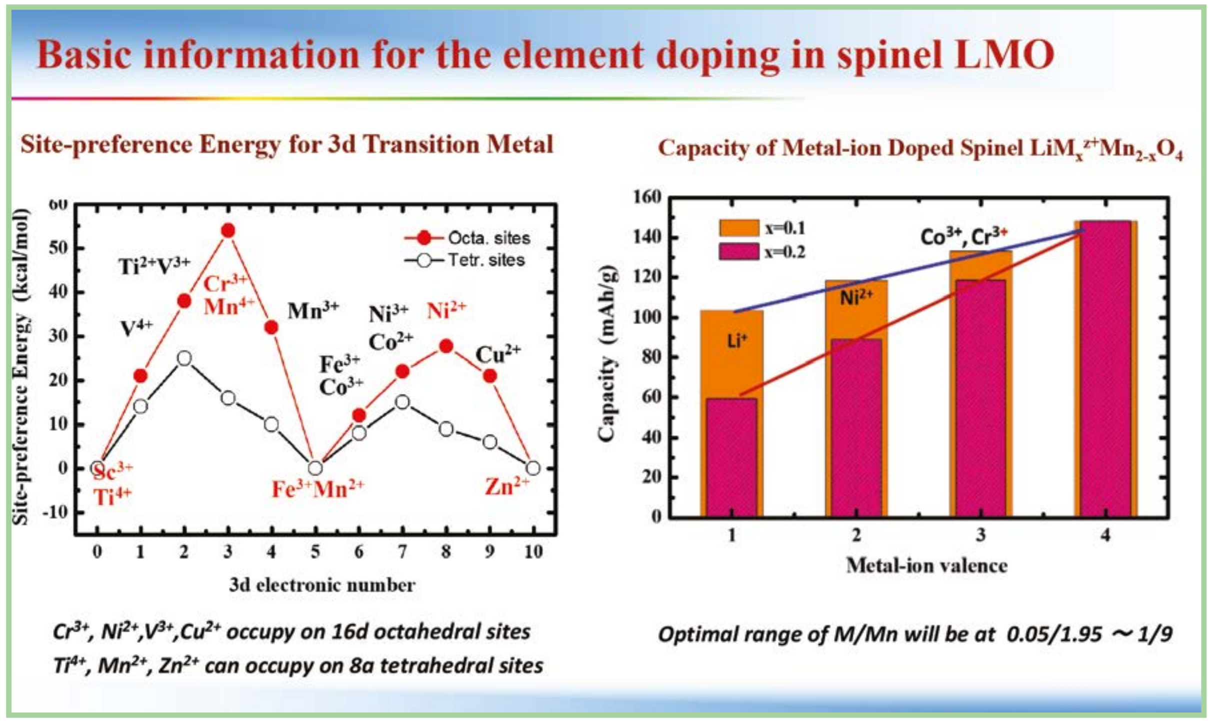


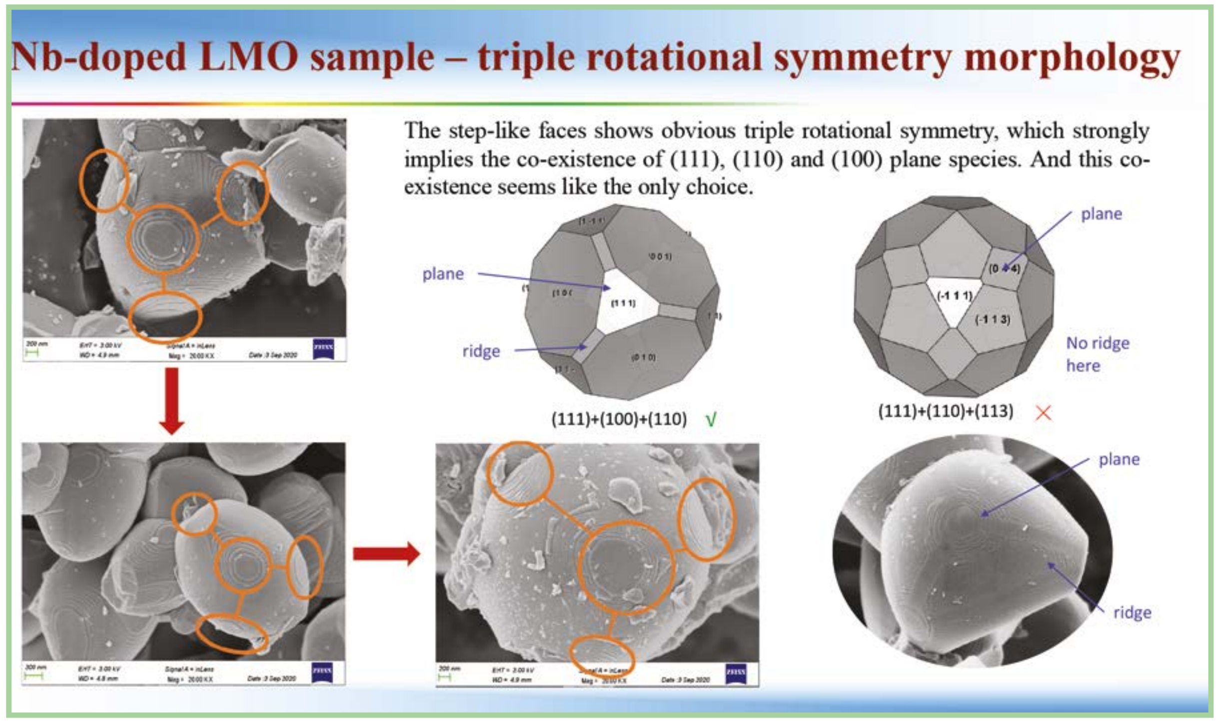
0.4 mA/cm² between 3.0 and 4.5 V at room temperature

Xia et al., "Correlating capacity fading and structural changes in $Li_{1+y}Mn_{2-y}O_{4-\delta}$ spinel cathode materials - A systematic study on the effects of Li/Mn ratio and oxygen deficiency", *J. Electrochem. Soc.*, 148(7), A723-A729 (2001).


Mn dissolution of $LiMn_2O_4$ during cycling
Capacity (mAh/g)
Cycle number
Before cycling
Before cycling
After cycling
Two-phase structure
X in $Li_xMn_2O_4$
Defect spinel (lithium-rich spinel)
1. Two-phase structure before cycling
2. One-phase structure after cycling at 50°C
3. Lattice parameter becomes smaller
Mn dissolution
$LiMn_2O_4$- xMnO = $LiMn_{2-x}O_{4-x}$
$LiMn_2O_4$- $xMnO.Mn_2O_3$ = $LiMn_{2-3x}O_{4-4x}$
Mn^{3+} ($LiMn_2O_4$) → Mn^{4+} ($Li_2Mn_3O_7$) + Mn^{2+} (MnO)
Yongyao Xia, Yunhong Zhou, and Masaki Yoshio, "Capacity fading on cycling in 4V Li/$LiMn_2O_4$ cells", J. Electrochem. Soc., 144, 2593-2600 (1997).

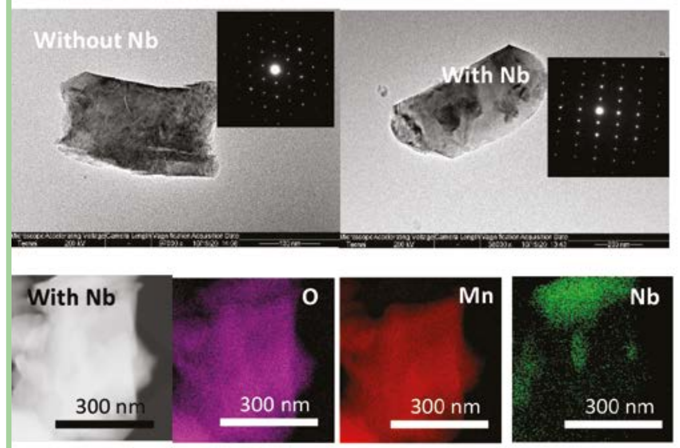

Spinel LMO with various morphologies
Commercialized - LMO
Commercialized - LMO
Commercialized - LMO
FD-LMO1#
FD-LMO2#

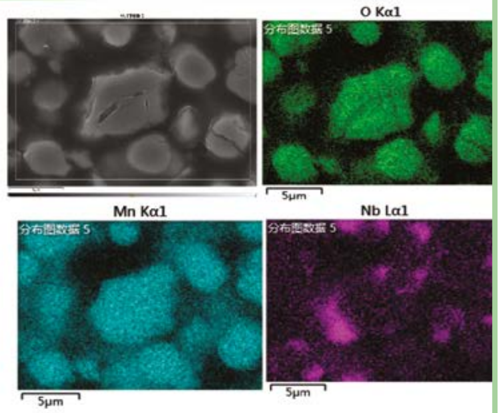

Basic information for the element doping in spinel LMO
Site-preference Energy for 3d Transition Metal
Site-preference Energy (kcal/mol)
3d electronic number
Octa. sites
Tetr. sites
Capacity of Metal-ion Doped Spinel $LiM_x^{z+}Mn_{2-x}O_4$
x=0.1
x=0.2
Capacity (mAh/g)
Metal-ion valence
Cr^{3+}, Ni^{2+},V^{3+},Cu^{2+} occupy on 16d octahedral sites
Ti^{4+}, Mn^{2+}, Zn^{2+} can occupy on 8a tetrahedral sites
Optimal range of M/Mn will be at 0.05/1.95 ～1/9


Nb-doped LMO sample – triple rotational symmetry morphology
The step-like faces shows obvious triple rotational symmetry, which strongly implies the co-existence of (111), (110) and (100) plane species. And this co-existence seems like the only choice.
plane
ridge
(111)+(100)+(110) √
plane
No ridge here
(111)+(110)+(113) ×
plane
ridge

2022 International Conference on Niobium Based Batteries

Niobium Distribution

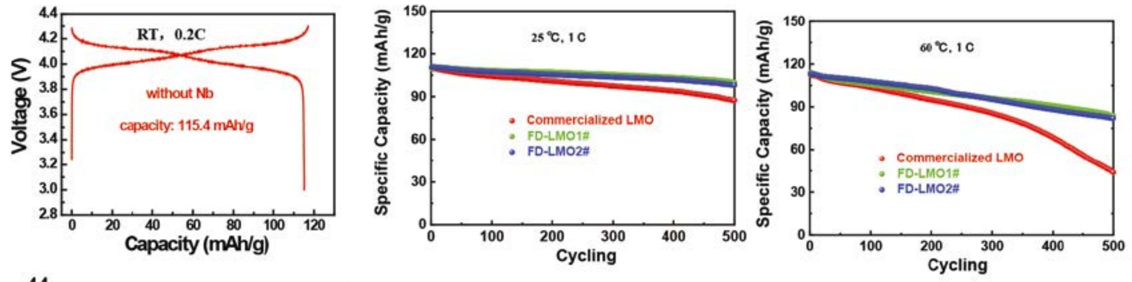


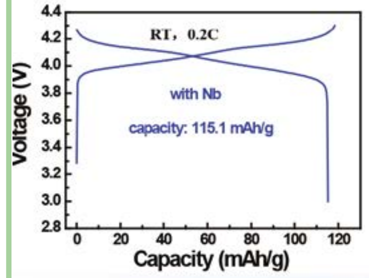


Cross section of Nb doped LMO primary particle

Niobium mainly distributes on the surface of LMO in form of $LiNbO_3$

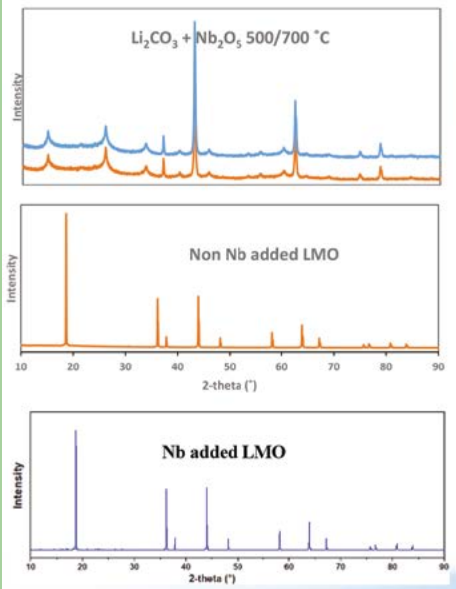
Electrochemical properties （Half-cell）

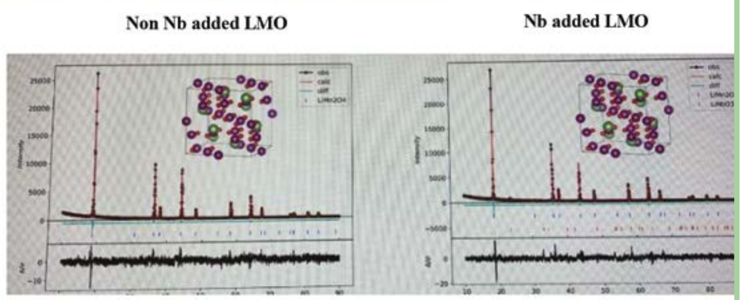




---	25℃首圈比容量 (mAh/g)	25℃ 500 圈容量保持率 (%)	60℃首圈比容量 (mAh/g)	60℃ 500 圈容量保持率 (%)
商业化LMO	109.1	78.1	112.9	44.6
FD-LMO1#	110.3	90.3	113.5	73.3
FD-LMO2#	110.5	89.6	113.4	72.1

XRD Data analysis





Non Nb added LMO

$LiMn_2O_4$
Space group: Fd-3m (original choice 2)
$a=b=c=8.2234$ Å, $\alpha=\beta=\gamma=90°$, Vol=556.1 Å^3

a	b	c	Frac.
0.875	0.875	0.875	1.000
0.000	0.000	0.500	0.950
0.988	0.262	0.988	0.994

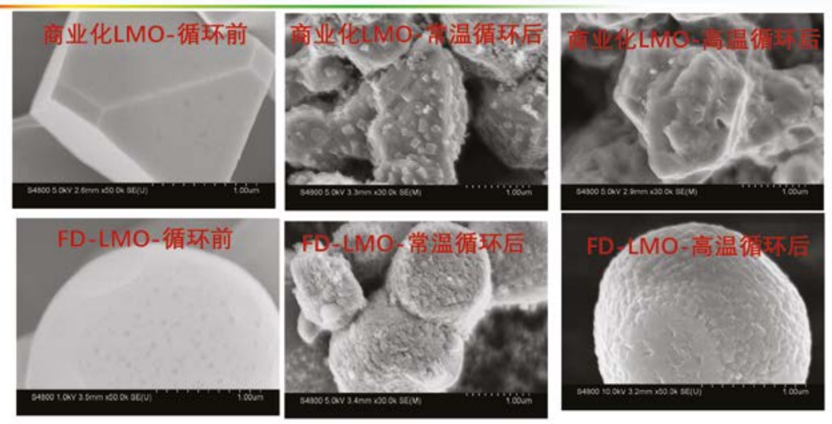
Nb added LMO

$LiMn_2O_4$
Space group: Fd-3m (original choice 2)
$a=b=c=8.2255$ Å, $\alpha=\beta=\gamma=90°$, Vol=556.5 Å^3

	a	b	c	Frac.
Li	0.875	0.875	0.875	1.00
Mn	0.000	0.000	0.500	0.95
O	0.989	0.260	0.989	0.99

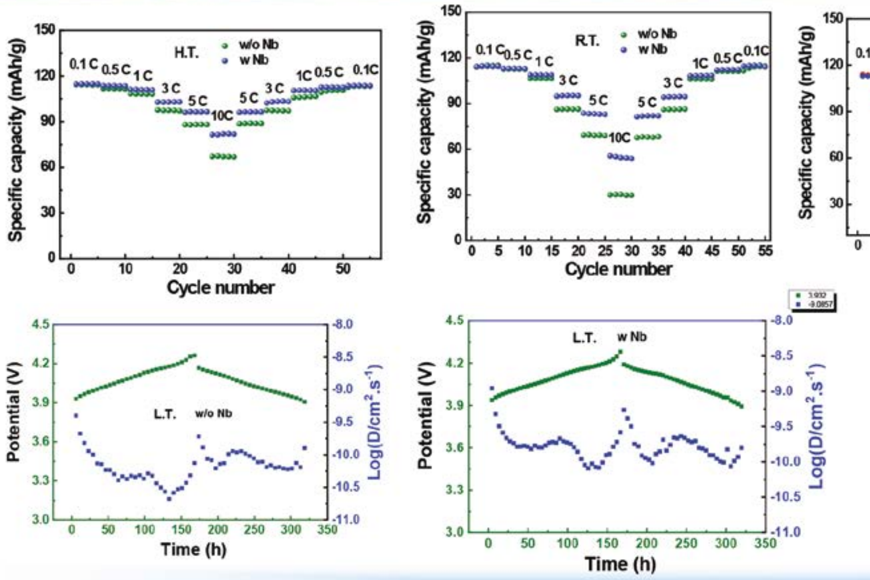
Nb added LMO was identified as LiNbO3 in the surface of LMO

Manganese dissolution



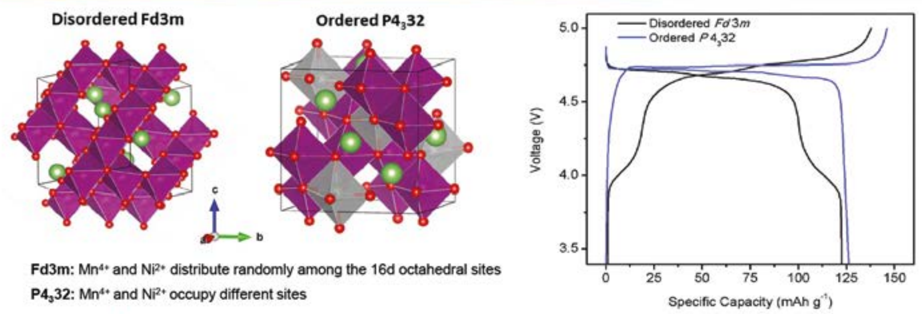
产品编号	25℃-500圈锰溶解率 (%)	60℃-500圈锰溶解率 (%)
商业化LMO	22.6	49.2
FD-LMO1#	7.2	18.5
FD-LMO2#	7.8	19.7

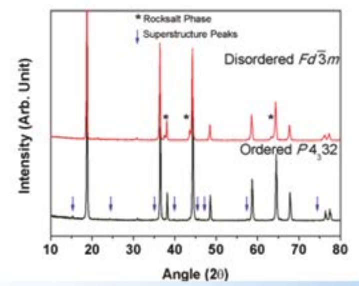
Rate capability at various temperature



- Nb modified LMO shows an improved rate, especially in low temperature, showing its potential usage on high power cells working in cold climate.

High voltage $LiMn_{1.5}Ni_{0.5}O_4$

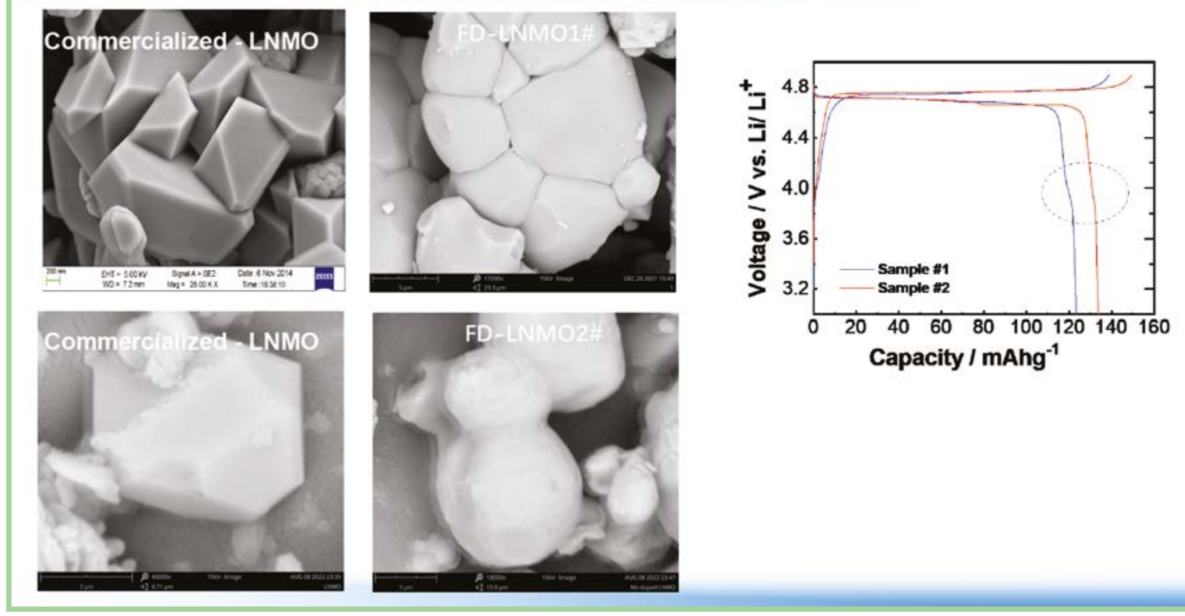




- ✓ The working voltage of $LiMn_{1.5}Ni_{0.5}O_4$ is ~4.7 V.
- ✓ The large differences in the charges and ionic radii of Mn^{4+} and Ni^{2+} lead to the cation ordering.
- ✓ The cation ordering affects the voltage profiles

16

Spinel LNMO with various morphologies



Conclusion

- Nb can be used as additives to stabilize the crystal structure, and as well as coating buffer layer to improve/stabilize electrode/electrolyte interface.
- The existence of little amount of Nb in LMO & LNMO can change crystal shape. The round shape of LMO was observed under various calcinating temperature and time, indicates that the forming process of round shape under these synthesis conditions doesn't face up any kinetical bottleneck.
- Nb added LMO was identified as $LiNbO_3$ in the surface of LMO. The Nb added LMO & LNMO show better cycling stability, especially at the elevated temperatures.

Nb is NB

Acknowledgments

CITIC Metal Co., Ltd and Companhia Brasileira de Metalurgia e Mineracao (CBMM) for the <u>financial support</u> and Nb_2O_5 sample offering

Thank you for your attention !

Home page: http://www.electrochem.edu.cn

2022 International Conference on Niobium Based Batteries

5TH EDITION

Notes

Notes

Notes

Prof. Dr. Yufeng Zhao

Shanghai University

赵玉峰，上海大学理学院/可持续能源研究院教授、博士生导师，可持续能源研究院副院长，英国皇家化学会会士(FRSC)。1996-2003年在天津大学学习分别获得学士/硕士学位，2006年获新加坡南洋理工大学博士学位。随后分别在澳大利亚迪肯大学、德国马尔堡大学从事科研工作。2010年回到燕山大学工作，2019年正式入职上海大学。研究领域：新能源材料与器件，包括钠离子电池、氢能的制备及应用、金属空气电池等。迄今为止在Nature COMM、ADV MATER、ANGEW CHEM、ENERGY ENVIRON SCI、ADV FUNCT MATER等国际期刊发表SCI收录论文150余篇，他引8000余次，申请国家发明专利30余项。

Dr. Yufeng ZHAO, Professor, and Doctoral Supervisor of School of Science/Institute of Sustainable Energy of Shanghai University, Vice President of Institute of Sustainable Energy, and member of the Royal Society of Chemistry (FRSC). From 1996 to 2003, she studied at Tianjin University and obtained a bachelor's degree and a master's degree, respectively. In 2006, she received a doctor's degree from Nanyang Technological University in Singapore. Subsequently, she engaged in scientific research at Deakin University in Australia and Marburg University in Germany. She returned to Yanshan University in 2010 and joined Shanghai University in 2019. Her research fields cover new energy materials and devices, including sodium-ion batteries, preparation and application of hydrogen energy, metal-air batteries, etc. She has published more than 150 papers included in SCI in international journals such as Nature Comm, ADV Mater, Angel Chem, Energy Environment SCI, ADV Function Mater, etc., has been cited more than 8000 times, and applied for more than 30 national invention patents.

Niobium-doped Layered Cathode Material for High-power and Low-temperature Sodium-ion Batteries

Yufeng Zhao
Institute for Sustainable Energy, College of Sciences, Shanghai University, Shanghai 200444, P. R. China

Abstract

Application of sodium ion batteries in grid-scale energy storage demands electrode materials that facilitate fast and stable charge storage from room-temperature to sub-zero temperature range. The key issues that hinder P2-type layered oxides from achieving such goals are their unsatisfied charge transfer kinetics and unavoidable surface fading. Herein, we report a P2-type $Na_{0.78}Ni_{0.31}Mn_{0.67}Nb_{0.02}O_2$, whereby the trace Nb substitution simultaneously reduces the electronic band gap and ionic diffusion energy barrier, thus enables fast electron and Na^+ mobility (~10^{-9} cm s^{-1} at -40° C). While the Nb induced atomic-scale surface pre-construction efficiently prevents the electrolyte penetration and surface metal dissolution. The material demonstrates a record high rate capability (50° C), unprecedented low temperature performance and ultrahigh cycling stability (98% capacity retention at -40 °C with 76% capacity remaining after 1800 cycles). Different from literatures, this work shows that complete solid-solution is not always critical for high rate performance.

Notes

5TH EDITION
2022 International Conference on Niobium Based Batteries

Notes

Dr. Kent Griffith

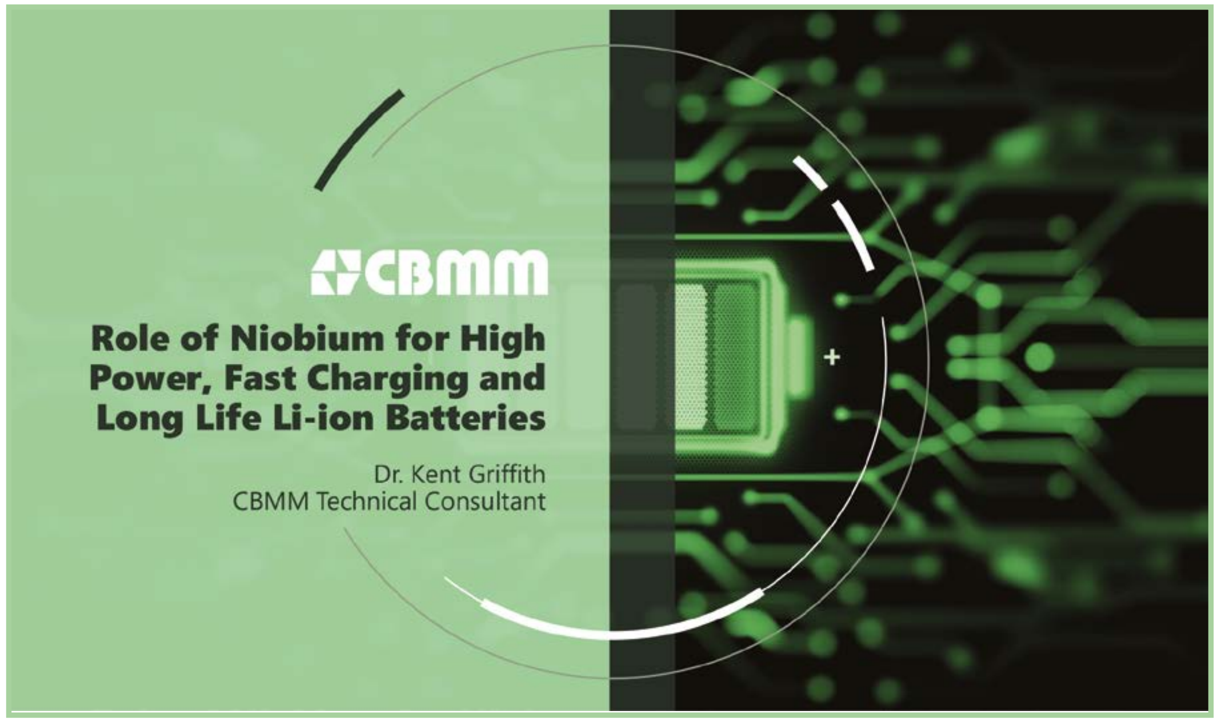
Consultant - CBMM

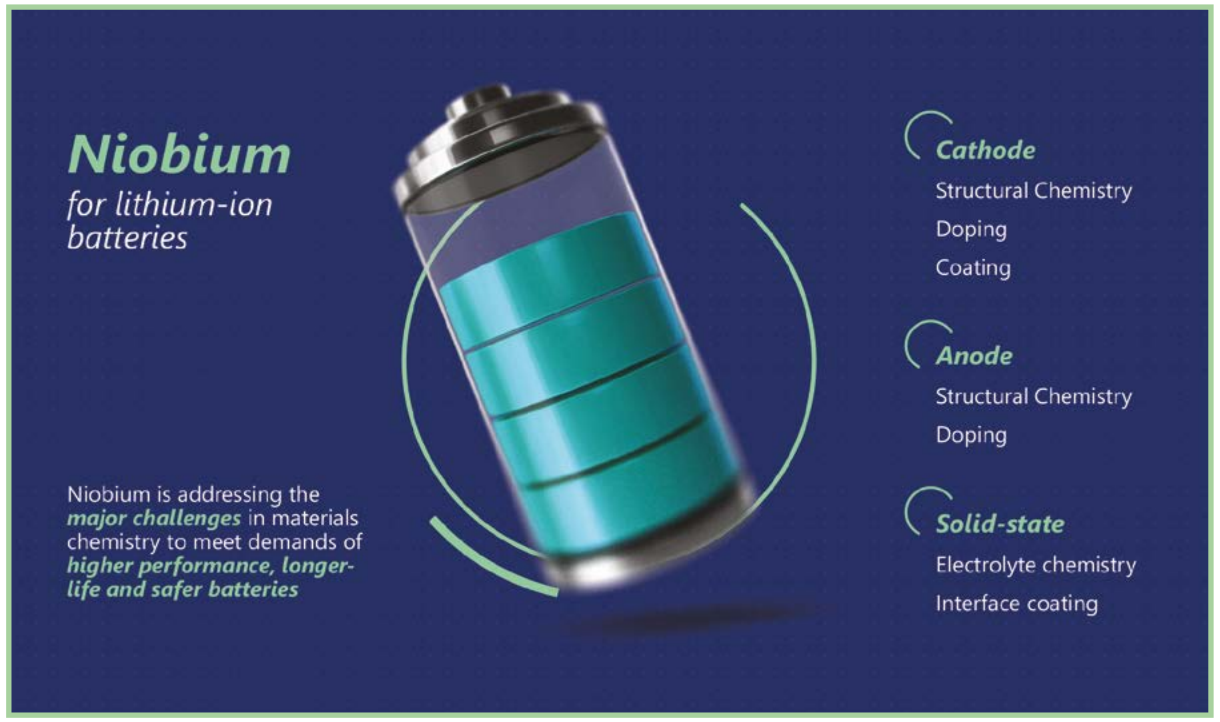
KENT GRIFFITH博士是CBMM的技术顾问和电池材料专家。Kent具有将先进材料转化为商业应用的经验。他获得了剑桥大学的博士学位，并和 CLARE GREY 教授合作在新型快速充电大功率电化学储能电极发现与开发。
Kent 拥有50多份同行评议的科学出版物、专利和关于锂离子电池和未来一代能源技术的书籍章节。他还为业界领先的电池杂志撰写了数十篇文章。他的工作获得了多个国家（美国和英国）和国际奖项的认可，包括丘吉尔奖学金（CHURCHILL SCHOLARSHIP），该奖学金每年颁发给全美最优秀的14名科学、数学和工程大学毕业生；皇家化学学会SHEELAH CAMPBELL电化学奖；材料、矿产和采矿研究所（IOM3）颁发的 CHARLES HATCHETT 奖；英国科技设施委员会颁发的STFC FUTURES EARLY CAREER 奖；以及美国国会设立的 BARRY M. GOLDWATER 奖学金，以表彰自然科学、工程和数学方面的杰出成就 。

Dr. Kent Griffith is a Technical Consultant for CBMM and an expert in battery materials with experience translating advanced materials to commercial applications. He received his PhD from the University of Cambridge for working with Professor Clare Grey on the discovery and development of new fast-charging and high-power electrodes for electrochemical energy storage.
Kent has more than 50 peer-reviewed scientific publications, patents, and book chapters on lithium-ion batteries and future-generation energy technologies. He has also written dozens of articles for industry-leading battery magazines. His work has been recognized with a number of national (US and UK) and international awards including the Churchill Scholarship - awarded to the top 14 science, math, and engineering university graduates from across the US each year; the Sheelagh Campbell Electrochemistry Award from the Royal Society of Chemistry; the Charles Hatchett Award from the Institute of Materials, Minerals, and Mining (IOM3); the STFC Futures Early Career Award from the UK Science and Technology Facilities Council; and the Barry M. Goldwater Scholarship established by the United States Congress to recognize merit in the natural sciences, engineering and mathematics.

2022 International Conference on Niobium Based Batteries

5TH EDITION





2022 International Conference on Niobium Based Batteries

Modern battery technology

Materials chemistry

Chemical energy into electricity

Carbon graphite

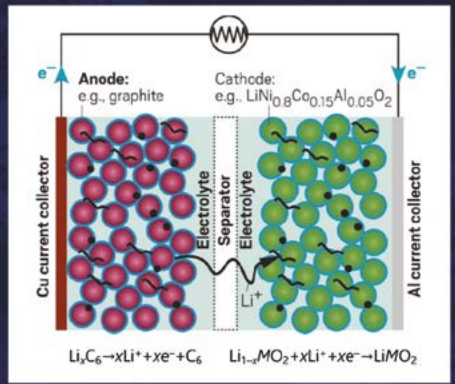
Lithium Titanium Oxide ($Li_4Ti_5O_{12}$ – LTO)

Niobium Titanium Oxide (Nb_2TiO_7 – NTO)

Silicon

Silicon-Graphite Composites

Li metal



Lithium Cobalt Oxide ($LiCoO_2$ – LCO)

Lithium Manganese Oxide ($LiMn_2O_4$ – LMO)

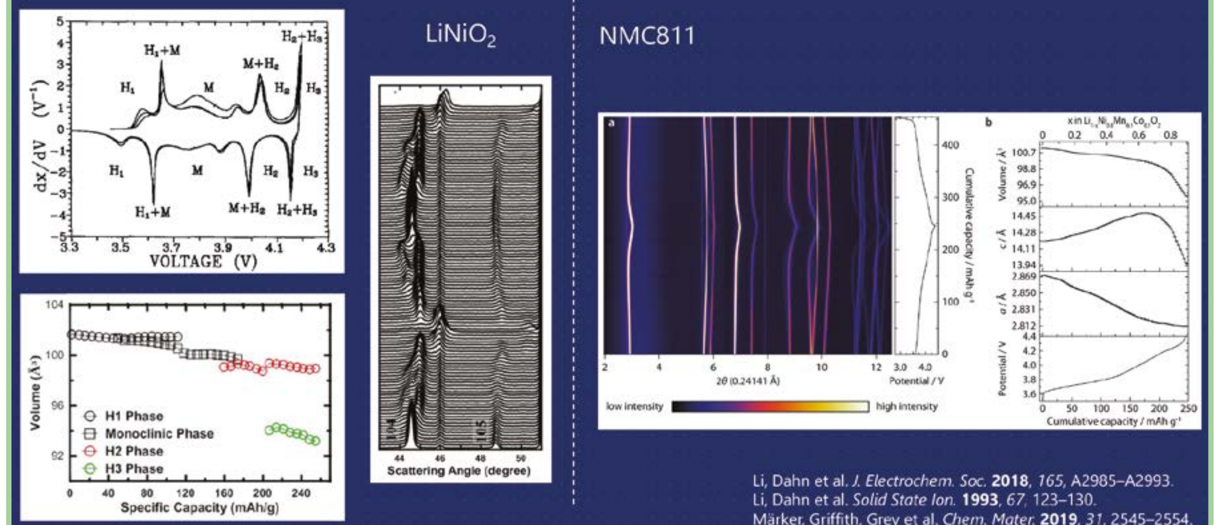
Lithium Iron (Mn) Phosphate ($LiFe(Mn)PO_4$ – LF(M)P)

Lithium Nickel Manganese Cobalt Aluminum Oxide ($Li(Ni,Mn,Co)O_2$ – NMCA)

Lithium-rich Disordered Rocksalt Oxides ($Li_{1+x}Nb_yTM_{1-2x}O_2$ – DRX)

Cathode chemistry

Challenges with Ni-rich layered oxides



Li, Dahn et al. *J. Electrochem. Soc.* **2018**, *165*, A2985–A2993.
Li, Dahn et al. *Solid State Ion.* **1993**, *67*, 123–130.
Märker, Griffith, Grey et al. *Chem. Mater.* **2019**, *31*, 2545–2554.

Cathode chemistry

Challenges with Ni-rich layered oxides

Cation migration: Li^+/Ni^{2+} antisite mixing during synthesis or cycling

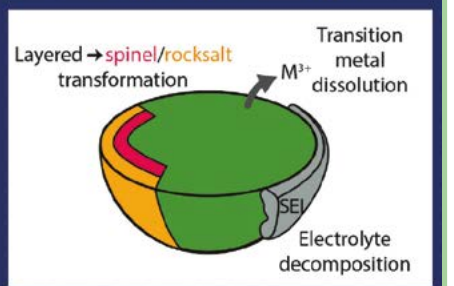
Phase transformation: layered ($LiMO_2$) → spinel (LiM_2O_{4-x} or M_3O_{4-x}) → rocksalt (MO)
- Loss of lithium and/or loss of oxygen
- May be surface reconstruction or bulk transformation

Particle fracture and disconnection from the current collector (loss of active material)
- Primary or secondary particles

Interfacial side reactions and impedance growth

Transition metal dissolution

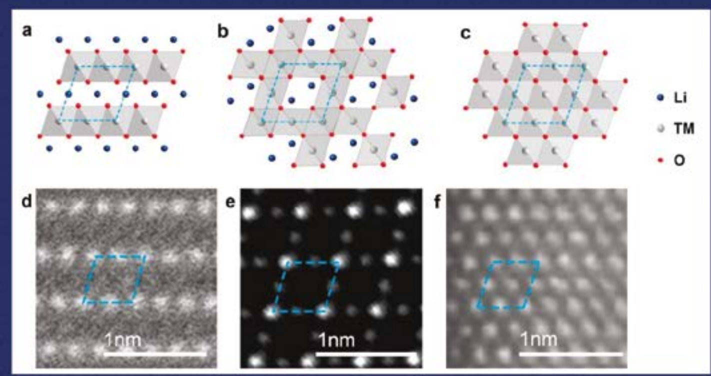
Current collector corrosion



Cathode chemistry

Challenges with Ni-rich layered oxides

layered ($LiMO_2$) → spinel (LiM_2O_{4-x} or M_3O_{4-x}) → rocksalt (MO)



Layered → spinel does not require oxygen loss but still associated with oxygen evolution so suggests oxygen-deficient spinel

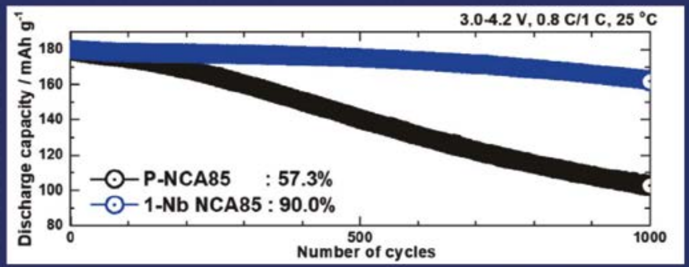
Rocksalt is least desirable, "electrochemically dead", though often amorphous

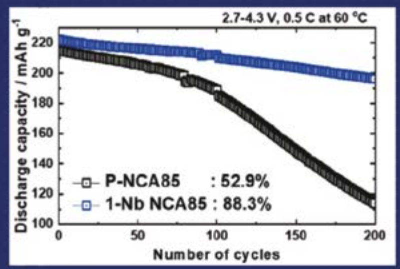
Similar process occurs thermally (> 200 °C, delithiated) and electrochemically (> 4.2 V)

Zhang, Liu, Piper, Whittingham, Zhou *Chem. Rev.* **2022**, *122*, 5641–568

Cathode chemistry
Enhancing cycle life

Nb^{5+} doping and $LiNbO_3$ coating of Ni-rich cathodes





Sun et al. *Adv. Energy Mater.* **2021**, *11*, 2100884.
Whittingham et al. *ACS Energy Lett.* **2021**, 6, 1377–1382.

Cathode chemistry
Mechanisms of favorable performance

Nb^{5+} doping and $LiNbO_3$ coating of Ni-rich cathodes

Doping stabilizes the layered cathode structure

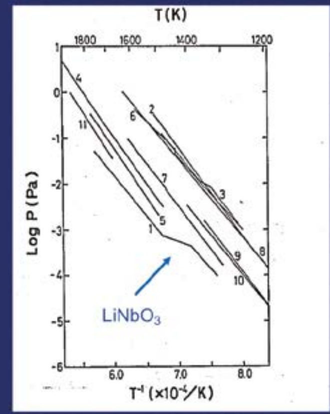
Nb grain boundary preferential enrichment leads to oriented, rod shaped primary particles

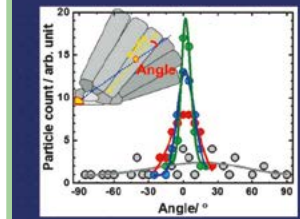
$LiNbO_3$ is a good ionic conductor, electronic insulator

100× higher σ_{Li^+} than $LiAlO_2$ or Li_2ZrO_3

$LiNbO_3$ coating prevents side reactions with the electrolyte and transition metal dissolution

$LiNbO_3$ has ultra low lithium vapor pressure





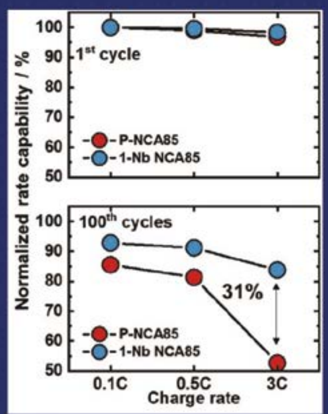
Sun et al. *Adv. Energy Mater.* **2021**, *11*, 2100884.
Whittingham et al. *ACS Energy Lett.* **2021**, 6, 1377–1382.
Uhlendorf et al. *Z. Phys. Chem.* **2017**, *231*, 1423–1442.
Hellstrom and Van Gool *Solid State Ionics* **1981**, 2, 59–64.
Yamawaki et al. *Advances in Ceramics*, 1990.

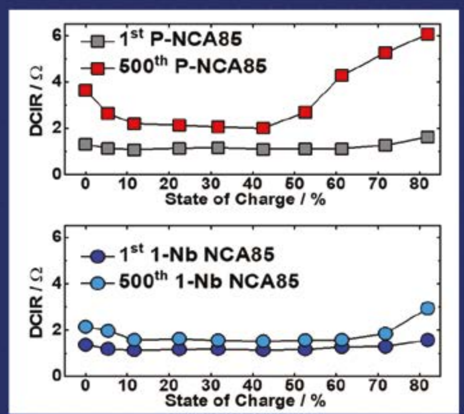
Cathode chemistry
Suppressing impedance growth

Nb^{5+} doping and $LiNbO_3$ coating of Ni-rich cathodes

Retains maximum power at all states of charge

Retains high charge rate over lifetime





Kim et al. *Adv. Energy Mater.* **2021**, *11*, 2100884.

Cathode chemistry
Enhancing energy, lifetime, and safety

Nb^{5+} doping and $LiNbO_3$ coating of Ni-rich cathodes

Sun et al. *Adv. Energy Mater.* **2021**, *11*, 2100884.

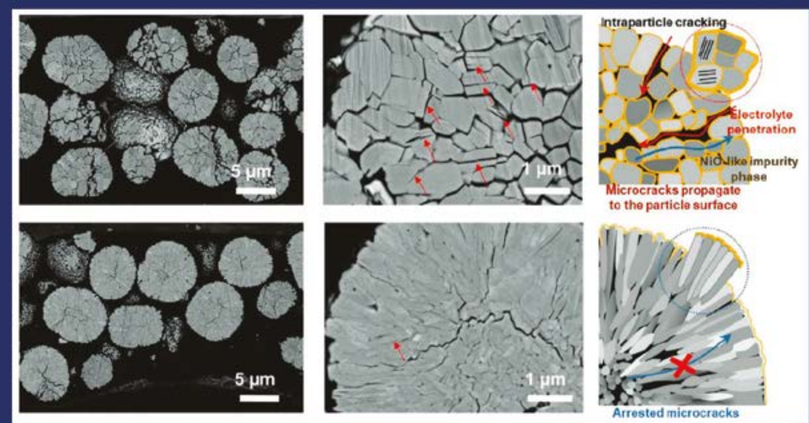
Doping stabilizes the layered cathode structure

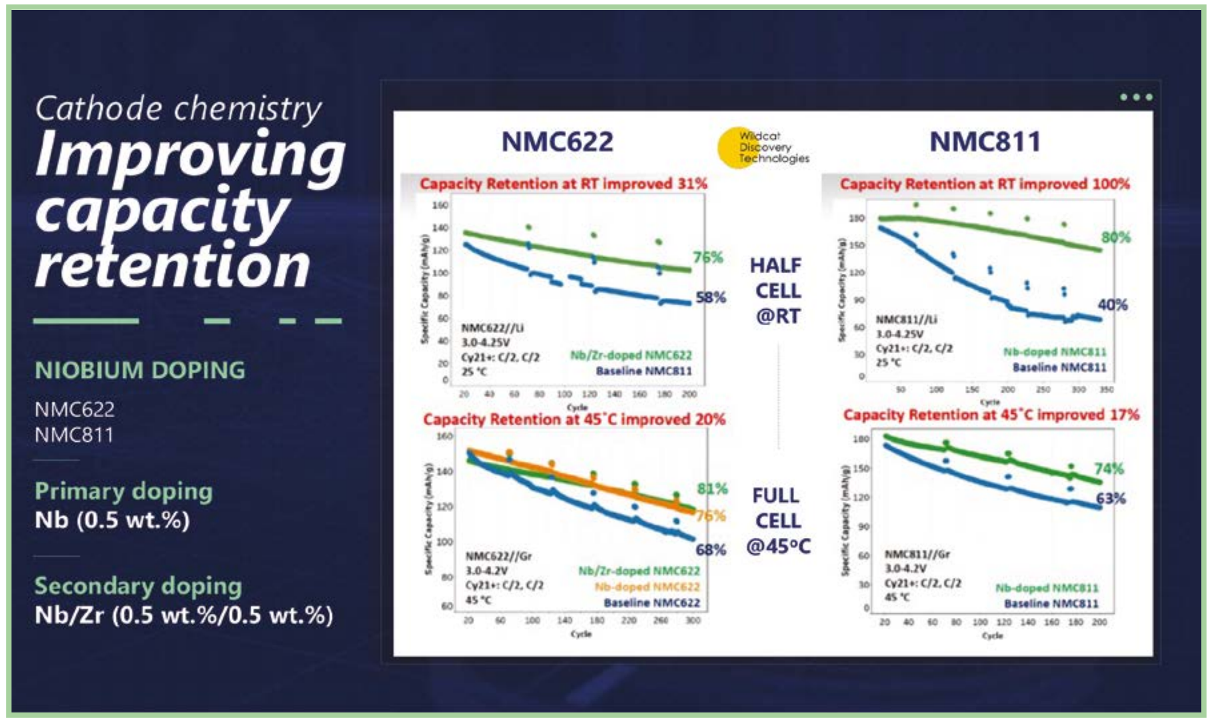
Lower interior porosity → Higher electrode density

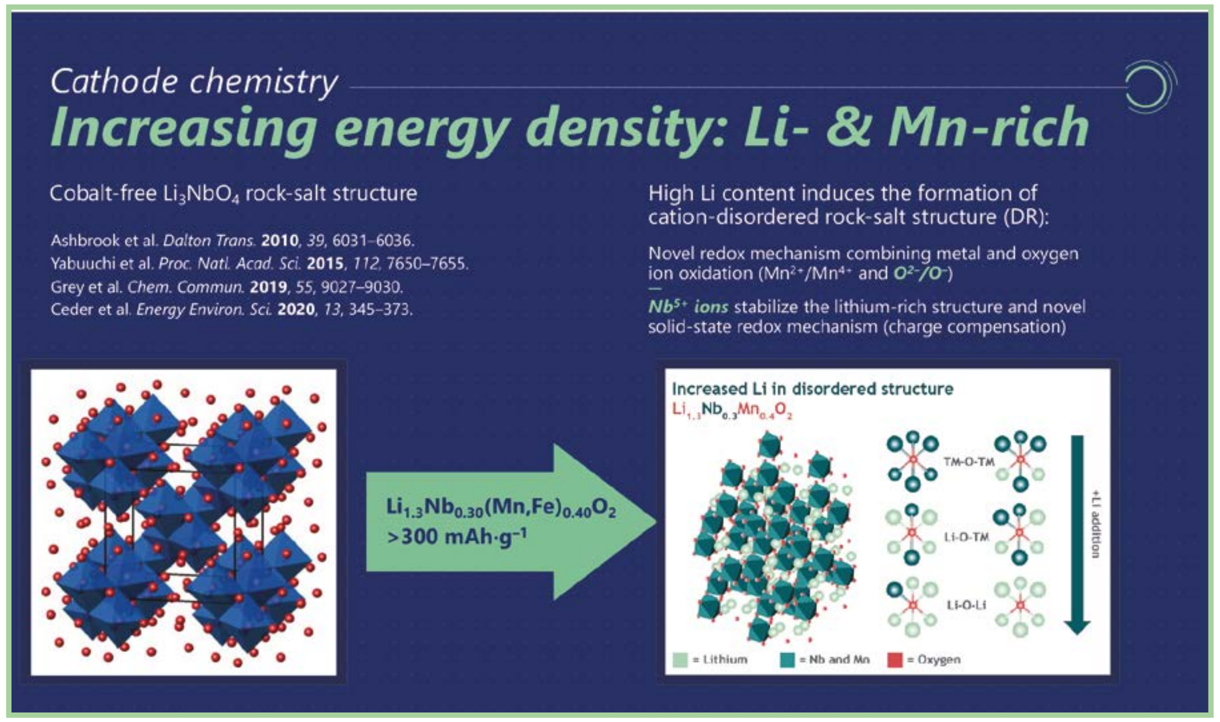
Alignment and doping mitigate particle cracking

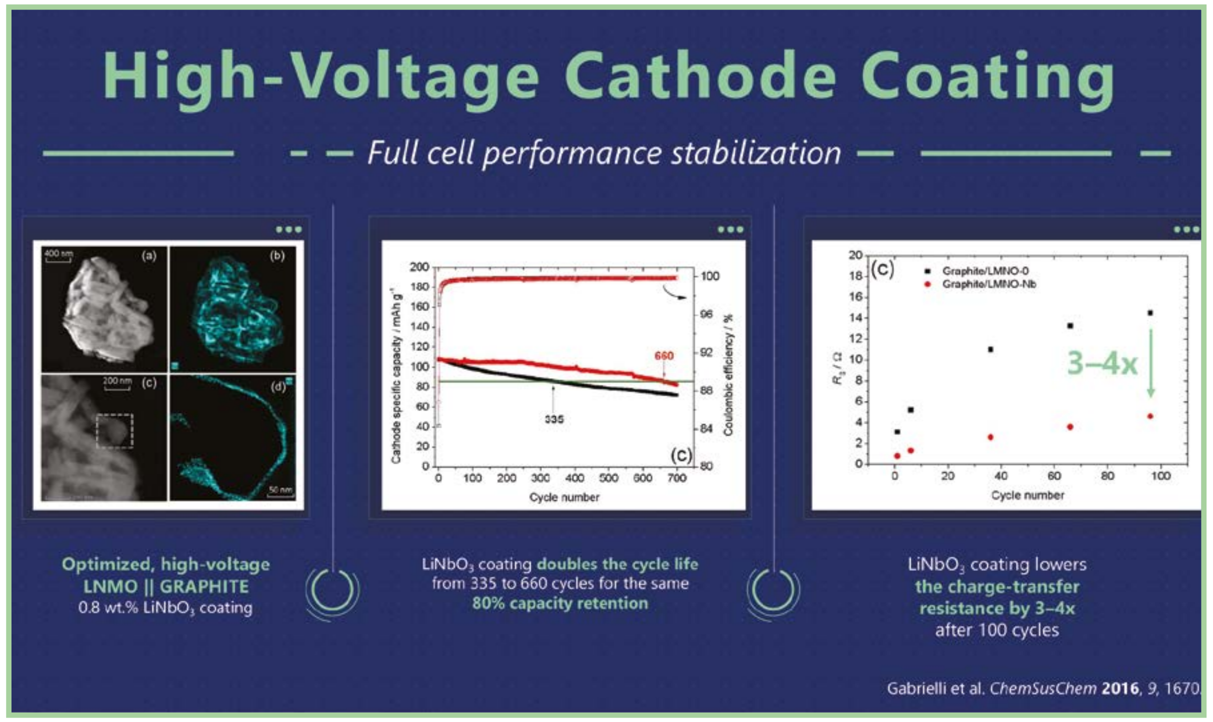
Without niobium

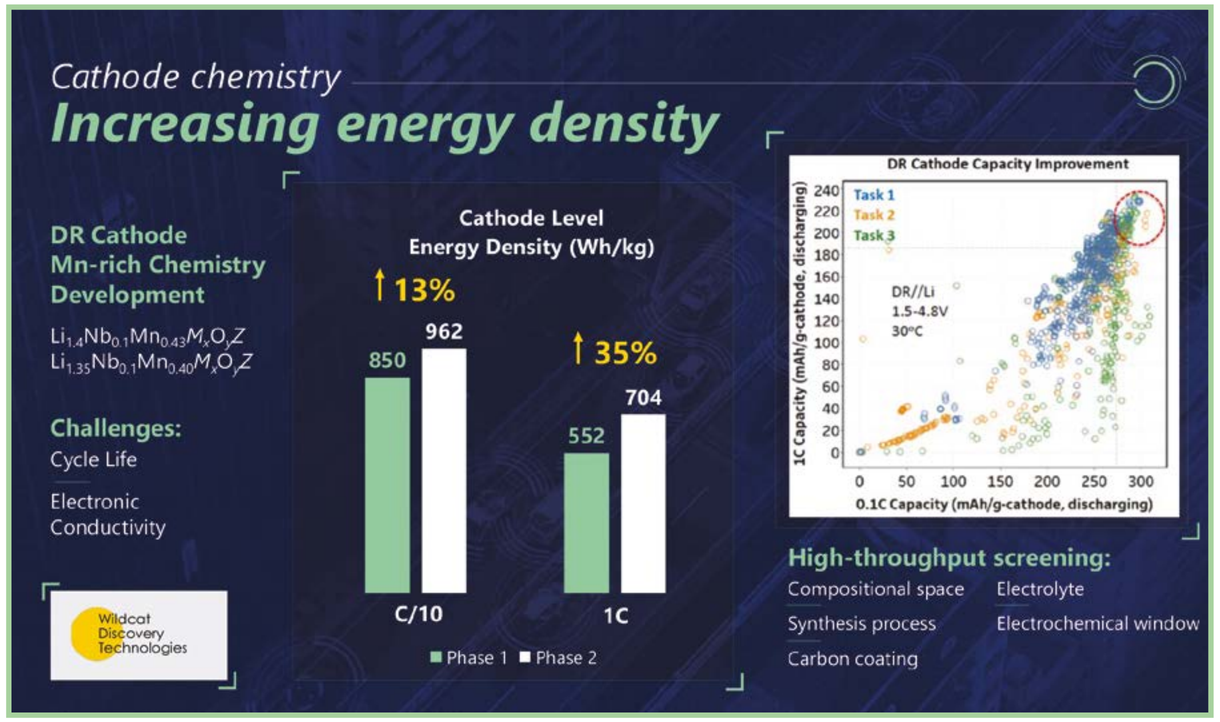
With niobium

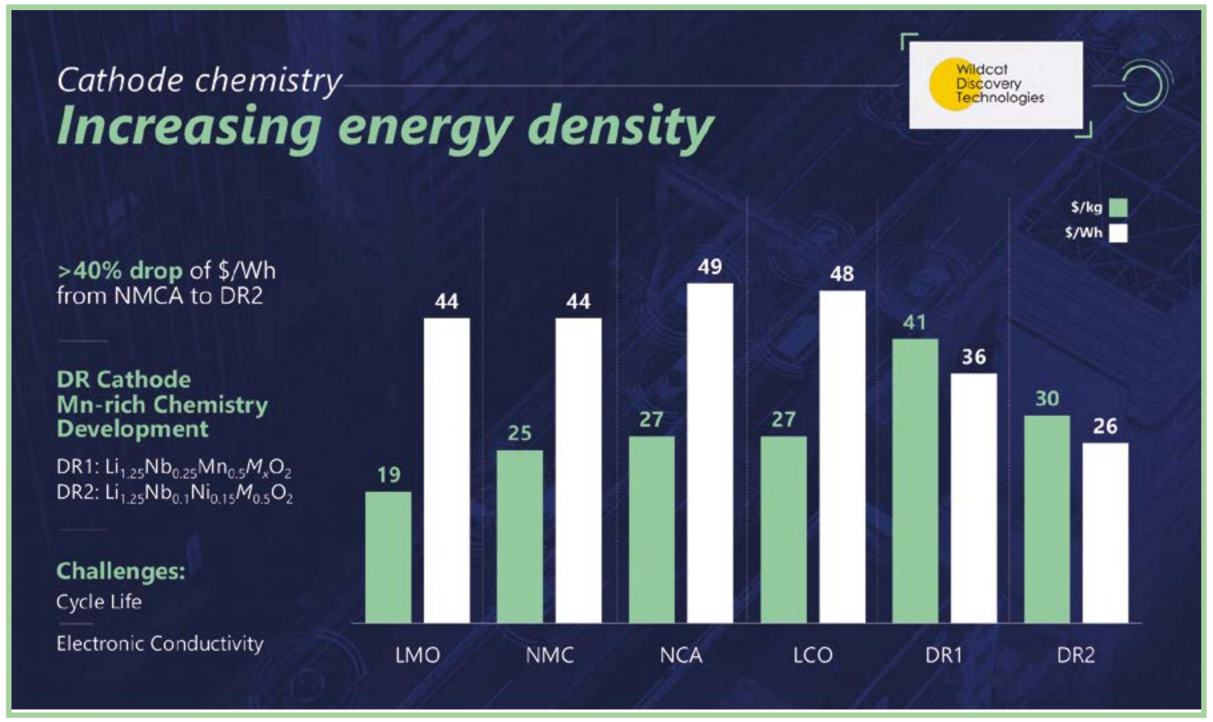


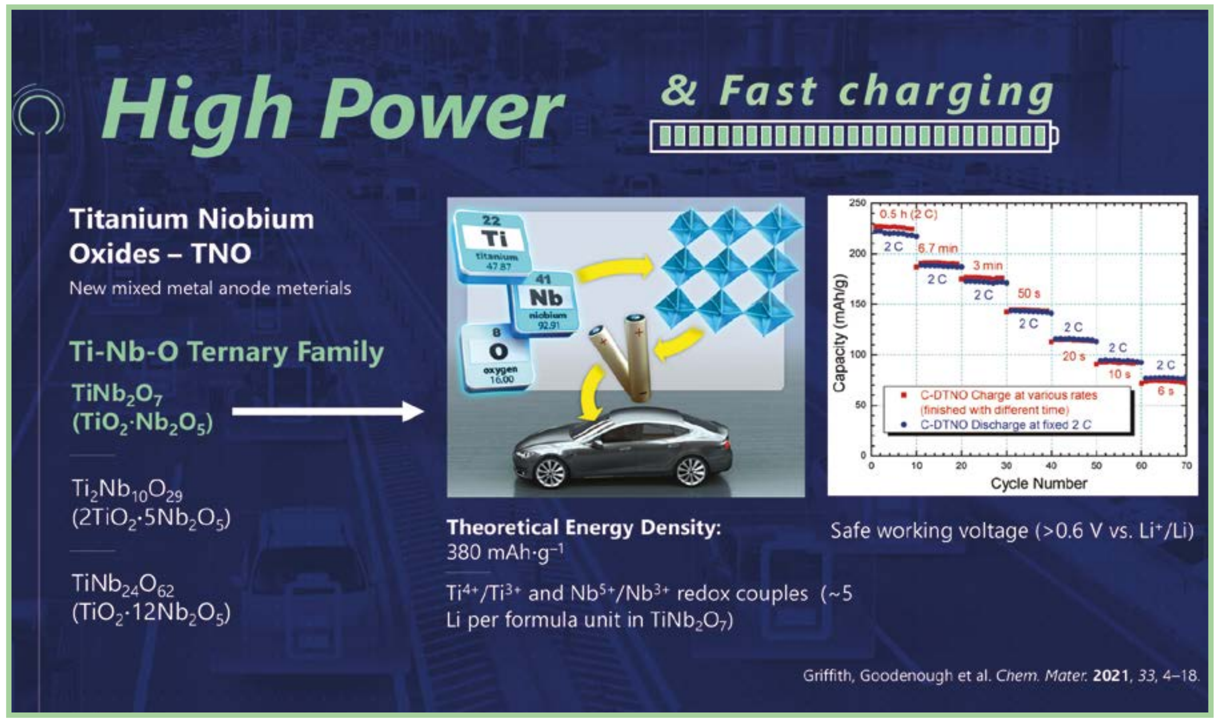

Cathode chemistry
Improving capacity retention
NIOBIUM DOPING
NMC622
NMC811
Primary doping
Nb (0.5 wt.%)
Secondary doping
Nb/Zr (0.5 wt.%/0.5 wt.%)
NMC622
NMC811
Capacity Retention at RT improved 31%
Capacity Retention at RT improved 100%
HALF CELL @RT
Capacity Retention at 45˚C improved 20%
Capacity Retention at 45˚C improved 17%
FULL CELL @45ºC
76%
58%
80%
40%
81%
76%
68%
74%
63%
Baseline NMC622
Baseline NMC811
Nb-doped NMC811
Nb/Zr-doped NMC622

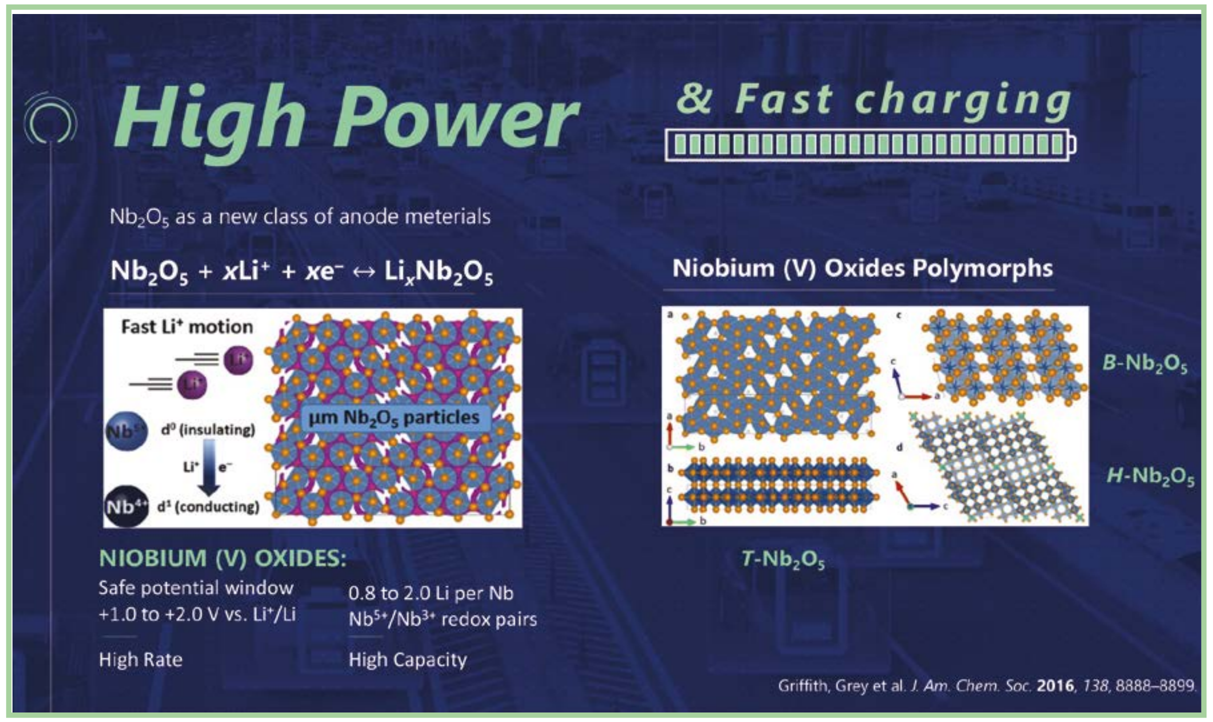

Cathode chemistry
Increasing energy density: Li- & Mn-rich
Cobalt-free Li_3NbO_4 rock-salt structure
Ashbrook et al. Dalton Trans. 2010, 39, 6031–6036.
Yabuuchi et al. Proc. Natl. Acad. Sci. 2015, 112, 7650–7655.
Grey et al. Chem. Commun. 2019, 55, 9027–9030.
Ceder et al. Energy Environ. Sci. 2020, 13, 345–373.
High Li content induces the formation of cation-disordered rock-salt structure (DR):
Novel redox mechanism combining metal and oxygen ion oxidation (Mn^{2+}/Mn^{4+} and O^{2-}/O^{-})
Nb^{5+} ions stabilize the lithium-rich structure and novel solid-state redox mechanism (charge compensation)
$Li_{1.3}Nb_{0.30}(Mn,Fe)_{0.40}O_2$
>300 mAh·g^{-1}
Increased Li in disordered structure
TM-O-TM
Li-O-TM
Li-O-Li
+Li addition
= Lithium
= Nb and Mn
= Oxygen

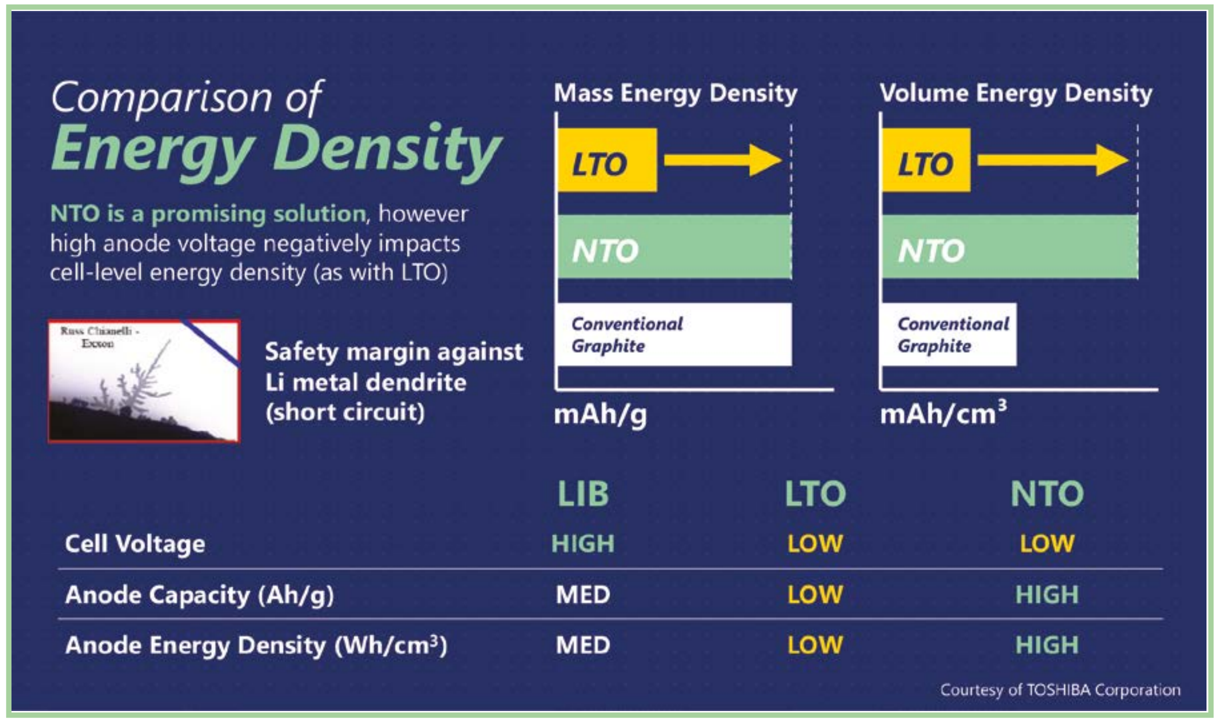

High-Voltage Cathode Coating
Full cell performance stabilization
Optimized, high-voltage LNMO || GRAPHITE
0.8 wt.% $LiNbO_3$ coating
$LiNbO_3$ coating doubles the cycle life from 335 to 660 cycles for the same 80% capacity retention
$LiNbO_3$ coating lowers the charge-transfer resistance by 3–4x after 100 cycles
3–4x
660
335
Cycle number
Graphite/LMNO-0
Graphite/LMNO-Nb
Gabrielli et al. ChemSusChem 2016, 9, 1670

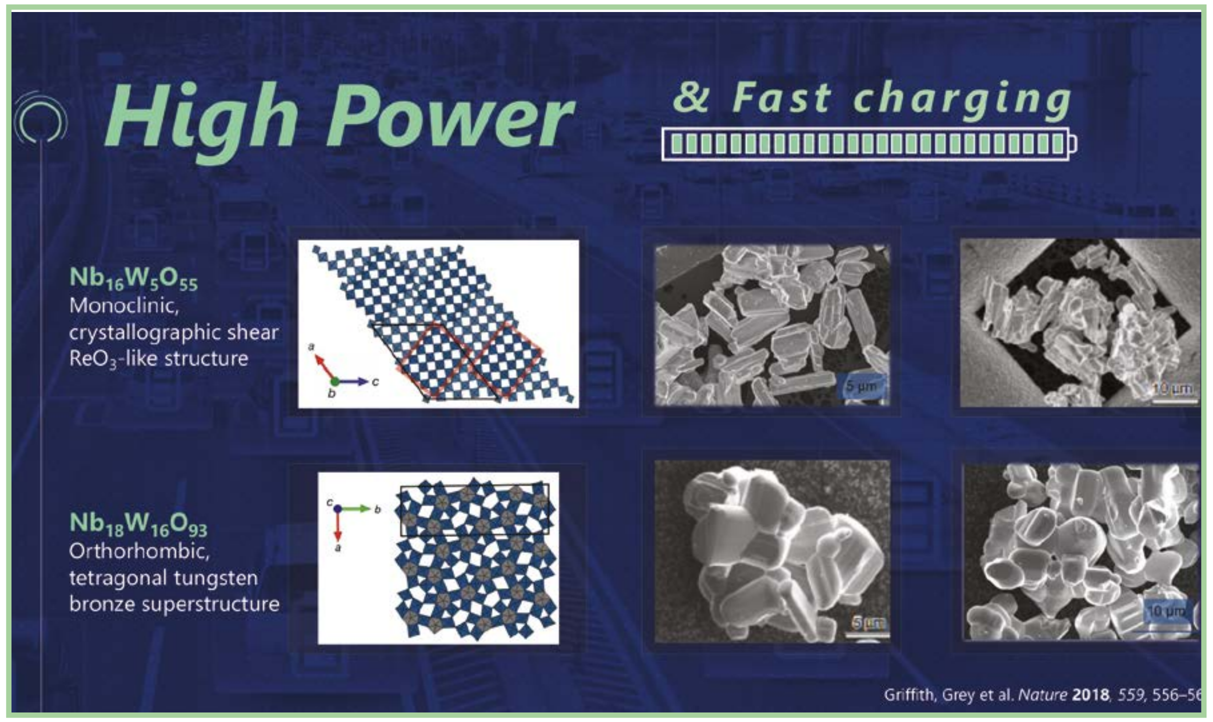

Cathode chemistry
Increasing energy density
DR Cathode Mn-rich Chemistry Development
$Li_{1.4}Nb_{0.1}Mn_{0.43}M_xO_yZ$
$Li_{1.35}Nb_{0.1}Mn_{0.40}M_xO_yZ$
Challenges:
Cycle Life
Electronic Conductivity
Cathode Level Energy Density (Wh/kg)
13%
35%
850
962
552
704
C/10
1C
Phase 1
Phase 2
DR Cathode Capacity Improvement
Task 1
Task 2
Task 3
DR//Li
1.5-4.8V
30ºC
1C Capacity (mAh/g-cathode, discharging)
0.1C Capacity (mAh/g-cathode, discharging)
High-throughput screening:
Compositional space
Electrolyte
Synthesis process
Electrochemical window
Carbon coating

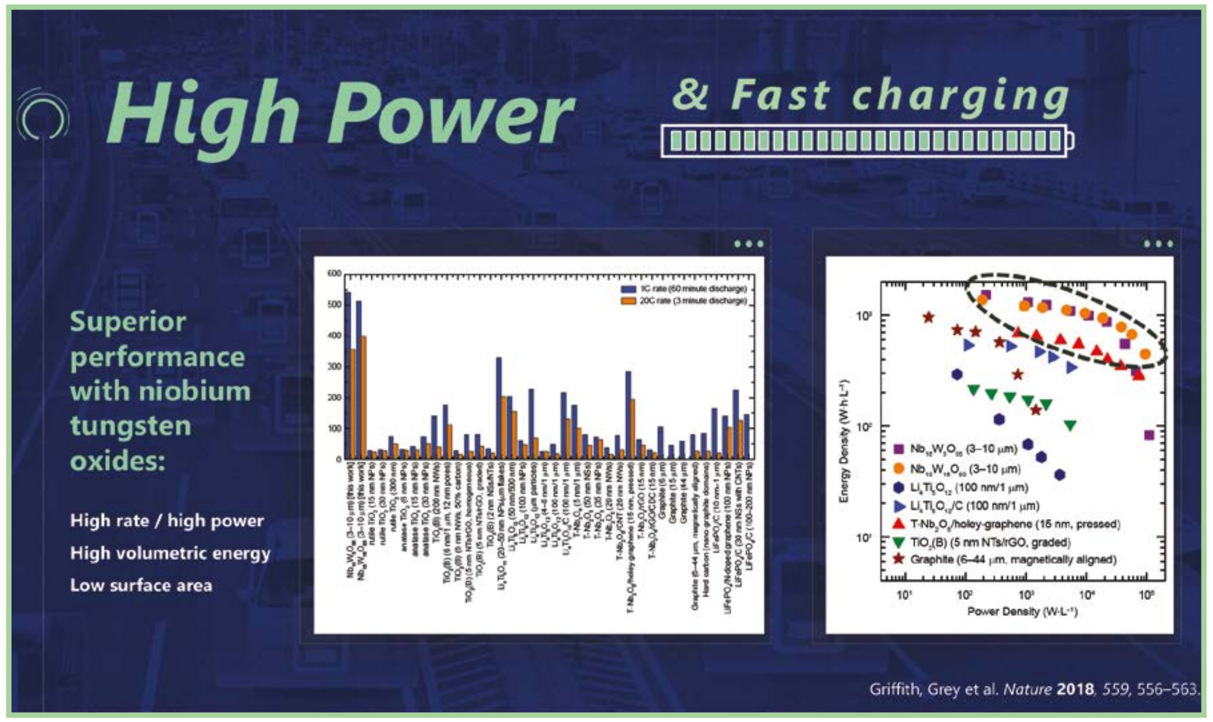

Cathode chemistry
Increasing energy density
Wildcat Discovery Technologies
>40% drop of $/Wh from NMCA to DR2
DR Cathode Mn-rich Chemistry Development
DR1: $Li_{1.25}Nb_{0.25}Mn_{0.5}M_xO_2$
DR2: $Li_{1.25}Nb_{0.1}Ni_{0.15}M_{0.5}O_2$
Challenges:
Cycle Life
Electronic Conductivity
$/kg
$/Wh
19
44
25
44
27
49
27
48
41
36
30
26
LMO
NMC
NCA
LCO
DR1
DR2


High Power
& Fast charging
Titanium Niobium Oxides – TNO
New mixed metal anode meterials
Ti-Nb-O Ternary Family
$TiNb_2O_7$ ($TiO_2 \cdot Nb_2O_5$)
$Ti_2Nb_{10}O_{29}$ ($2TiO_2 \cdot 5Nb_2O_5$)
$TiNb_{24}O_{62}$ ($TiO_2 \cdot 12Nb_2O_5$)
Ti
Nb
O
Capacity (mAh/g)
Cycle Number
Theoretical Energy Density:
380 mAh·g^{-1}
Safe working voltage (>0.6 V vs. Li^+/Li)
Ti^{4+}/Ti^{3+} and Nb^{5+}/Nb^{3+} redox couples (~5 Li per formula unit in $TiNb_2O_7$)
Griffith, Goodenough et al. Chem. Mater. 2021, 33, 4–18.

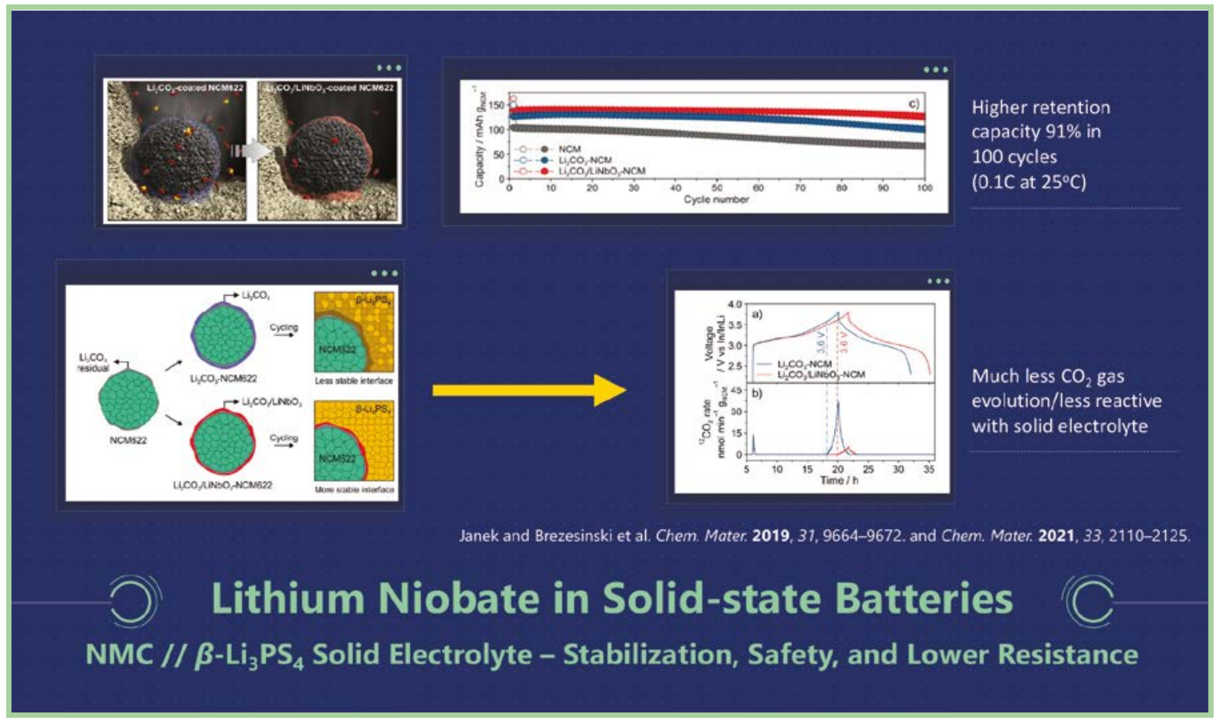

High Power
& Fast charging
Nb_2O_5 as a new class of anode meterials
$Nb_2O_5 + xLi^+ + xe^- \leftrightarrow Li_xNb_2O_5$
Fast Li^+ motion
µm Nb_2O_5 particles
d^0 (insulating)
d^1 (conducting)
Niobium (V) Oxides Polymorphs
B-Nb_2O_5
H-Nb_2O_5
T-Nb_2O_5
NIOBIUM (V) OXIDES:
Safe potential window +1.0 to +2.0 V vs. Li^+/Li
0.8 to 2.0 Li per Nb
Nb^{5+}/Nb^{3+} redox pairs
High Rate
High Capacity
Griffith, Grey et al. J. Am. Chem. Soc. 2016, 138, 8888–8899.

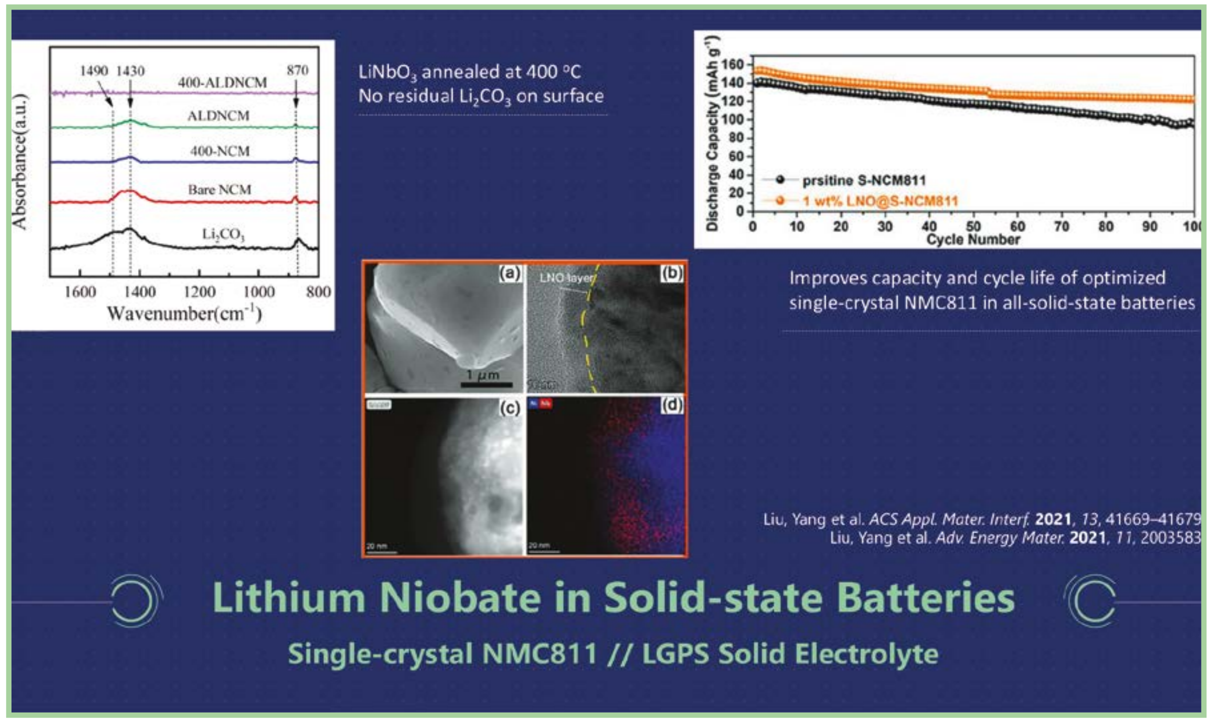

Comparison of
Energy Density
NTO is a promising solution, however high anode voltage negatively impacts cell-level energy density (as with LTO)
Safety margin against Li metal dendrite (short circuit)
Mass Energy Density
Volume Energy Density
LTO
NTO
Conventional Graphite
mAh/g
mAh/cm^3
LIB LTO NTO
Cell Voltage HIGH LOW LOW
Anode Capacity (Ah/g) MED LOW HIGH
Anode Energy Density (Wh/cm^3) MED LOW HIGH
Courtesy of TOSHIBA Corporation

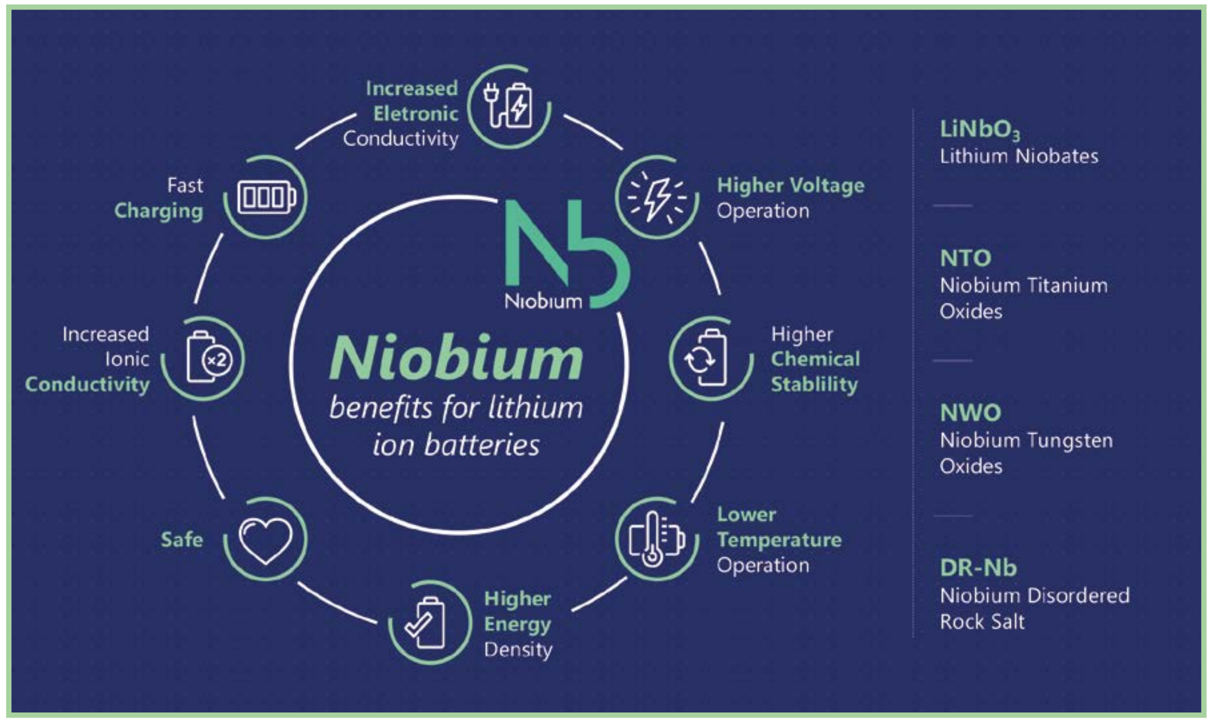




2022 International Conference on Niobium Based Batteries
5TH EDITION







2022 International Conference on Niobium Based Batteries

Notes

Notes

2022 International Conference on Niobium Based Batteries

Notes

5TH EDITION

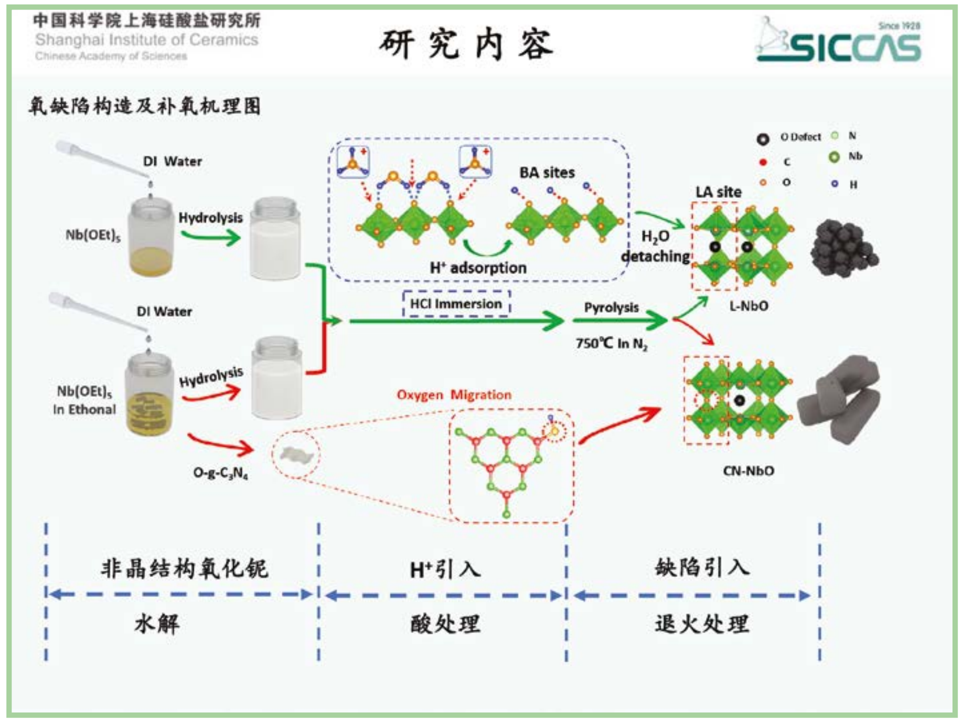
Prof. Dr. Chilin Li

Shanghai Institute of Ceramics, Chinese Academy of Sciences

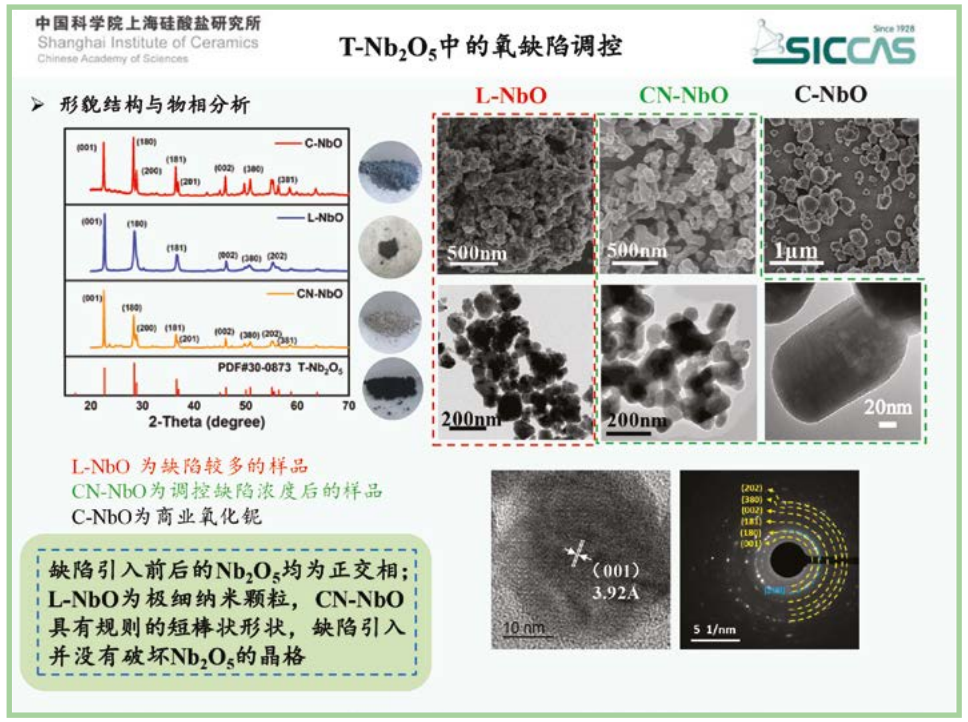
李驰麟，中国科学院上海硅酸盐研究所研究员，博士生导师，课题组长，入选上海市优秀学术带头人、上海市高层次人才计划、中科院杰出人才计划，在氟基电池、固态电池、锂/镁金属电池、快充电池等方面作出系列原创成果。在SCI. ADV.、NAT. COMMUN.、J. AM. CHEM. SOC.、ANGEW.CHEM.、ADV. MATER.、ENERGY ENVIRON. SCI.等发表期刊论文110余篇。授权和申请PCT国际发明专利和中国发明专利20余项。

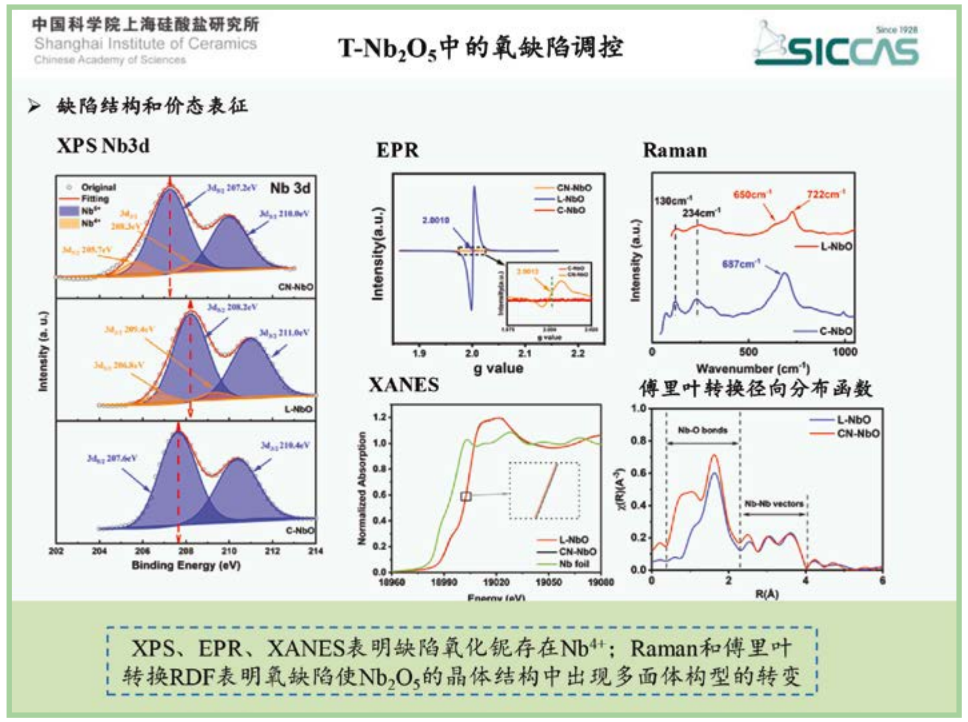
Dr. Chilin Li, researcher of Shanghai Institute of Silicate, Chinese Academy of Sciences and project leader. He was selected as Shanghai's excellent academic leader, Shanghai high-level talent plan, and Chinese Academy of Sciences outstanding talent plan and made a series of achievements in fluorine-based batteries, solid-state batteries, lithium/magnesium metal batteries, and fast charging batteries field. He has published more than 110 journal papers in SCI Adv., Nat. Commun., J. Am. Chem. Soc., Angew. Chem., Adv. Mater and Energy Environ. Sci. Prof. Chilin Li also authorized and applied for more than 20 PCT international invention patents and Chinese invention patents.

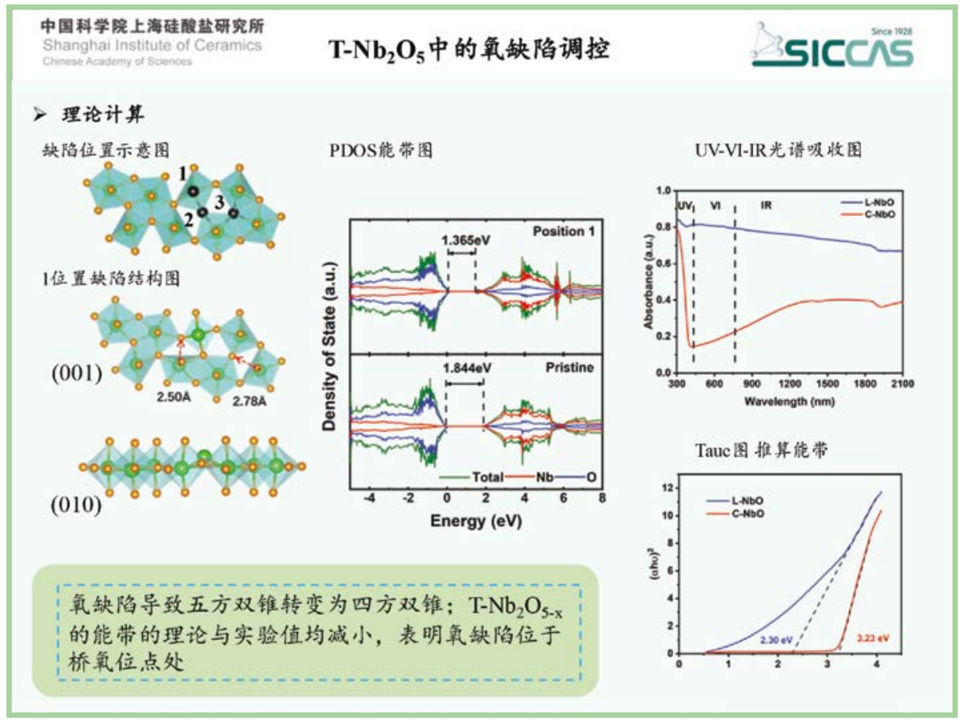
2022 International Conference on Niobium Based Batteries
5TH EDITION



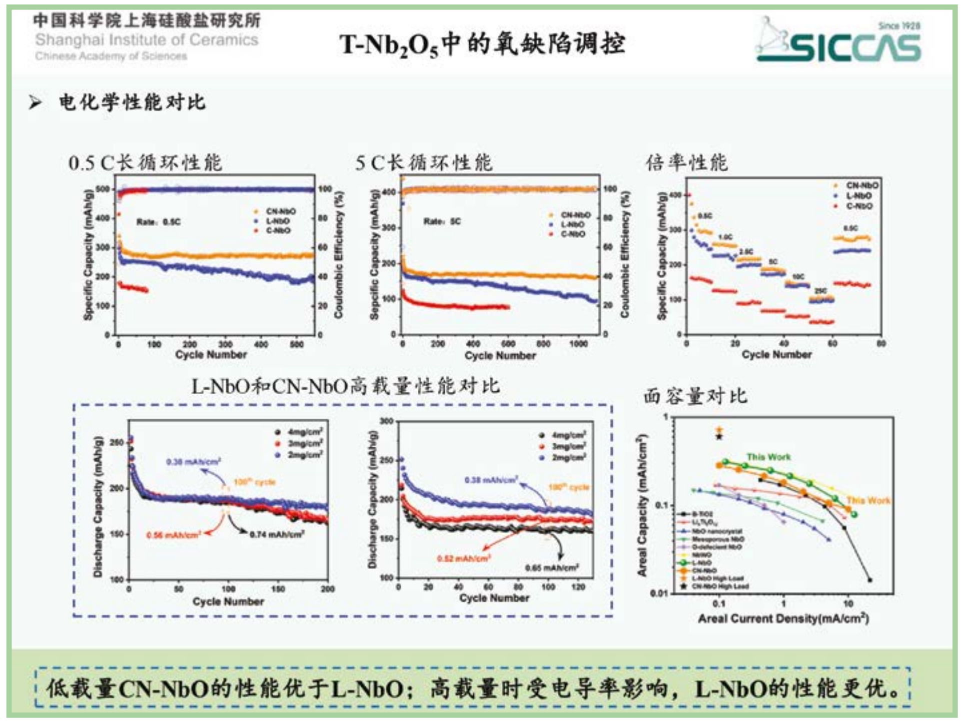
2022 International Conference on Niobium Based Batteries

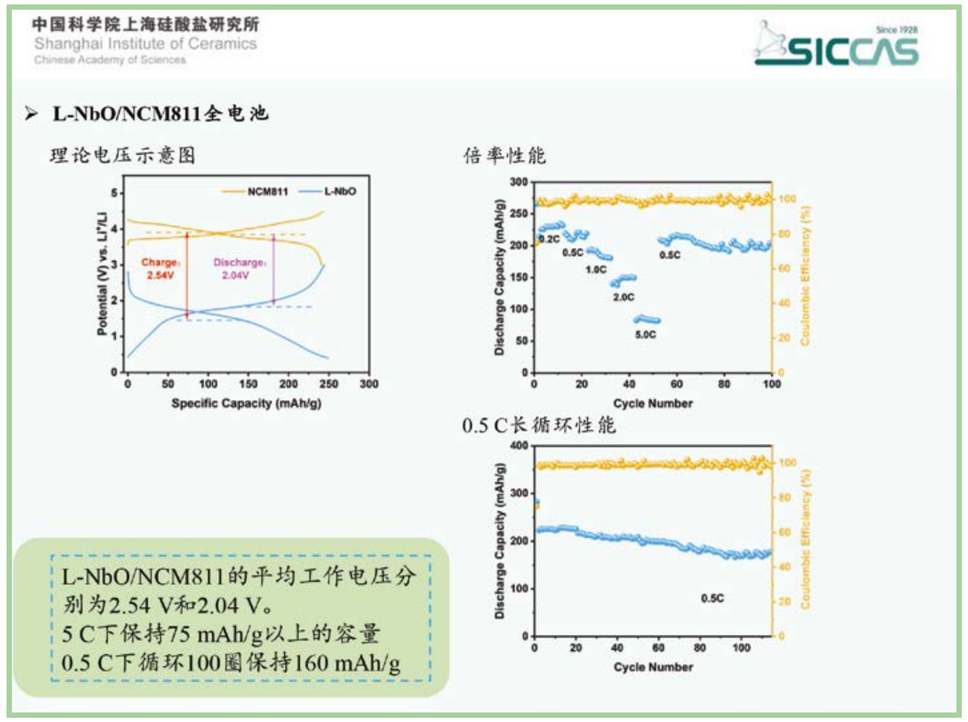


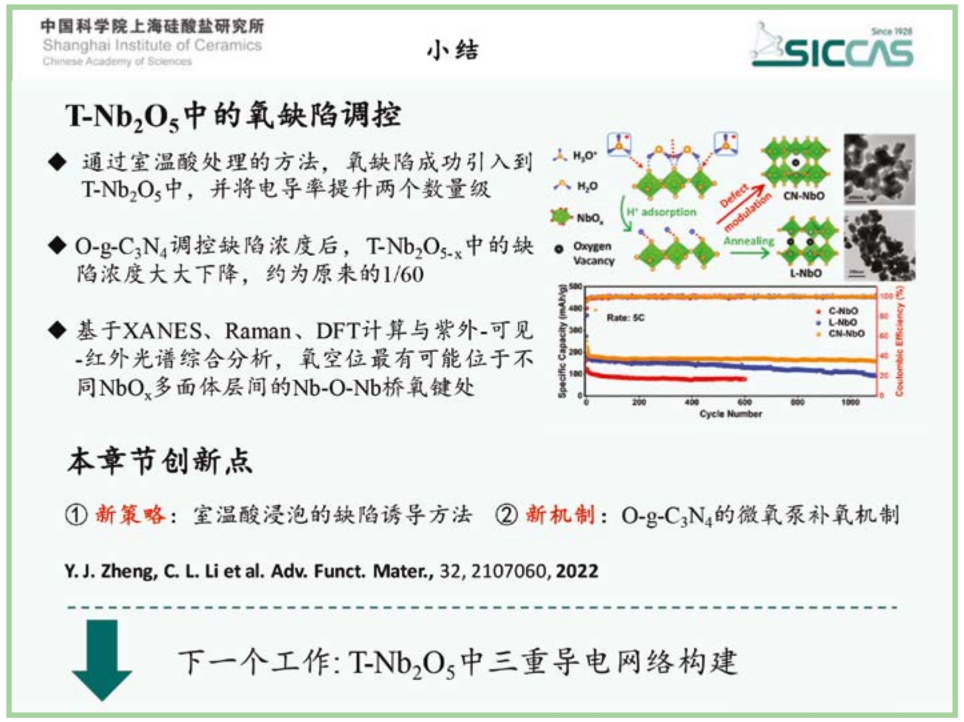


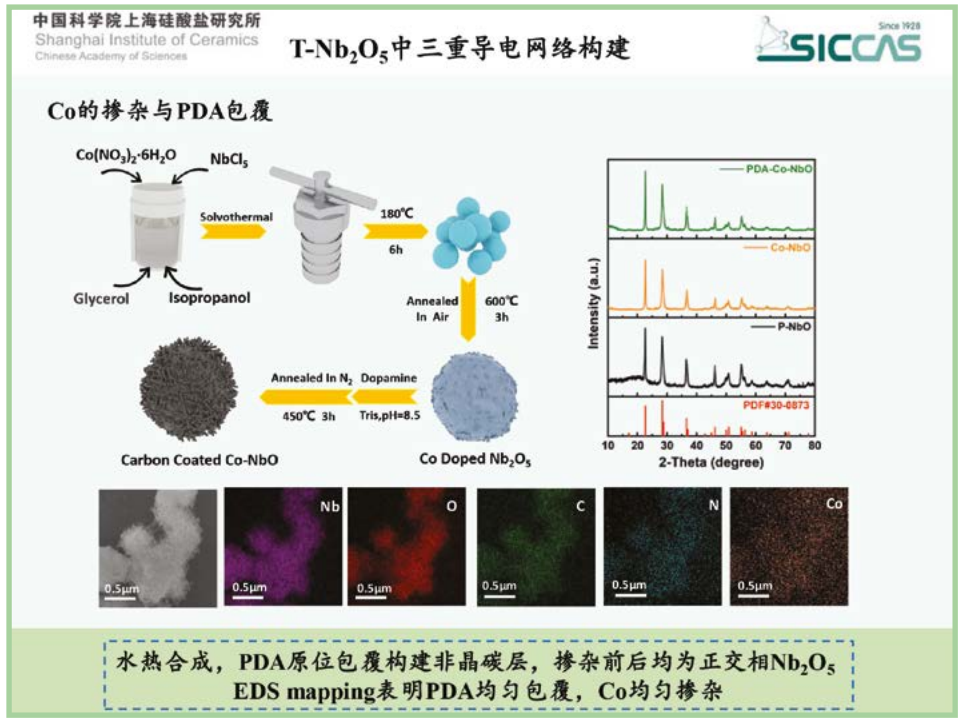

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb2O5中的氧缺陷调控
SICCAS
理论计算
缺陷位置示意图
1位置缺陷结构图
(001)
(010)
PDOS能带图
Position 1
Pristine
1.365eV
1.844eV
Density of State (a.u.)
Energy (eV)
UV-VI-IR光谱吸收图
Absorbance (a.u.)
Wavelength (nm)
L-NbO
C-NbO
Tauc图推算能带
2.30 eV
3.23 eV
氧缺陷导致五方双锥转变为四方双锥；T-Nb2O5-x的能带的理论与实验值均减小，表明氧缺陷位于桥氧位点处

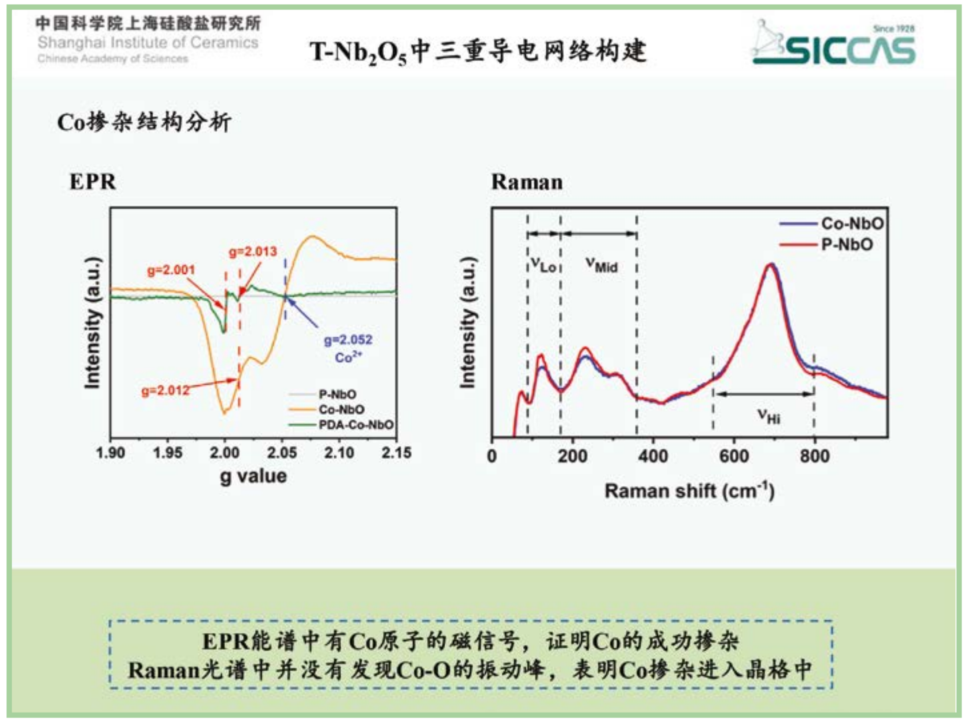

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb2O5中的氧缺陷调控
SICCAS
动力学性能对比
赝电容性能
极化差对比
CV扩散系数对比
GITT扩散系数对比
阻抗对比
电压极化、扩散系数以及阻抗表明L-NbO的动力学性能更好

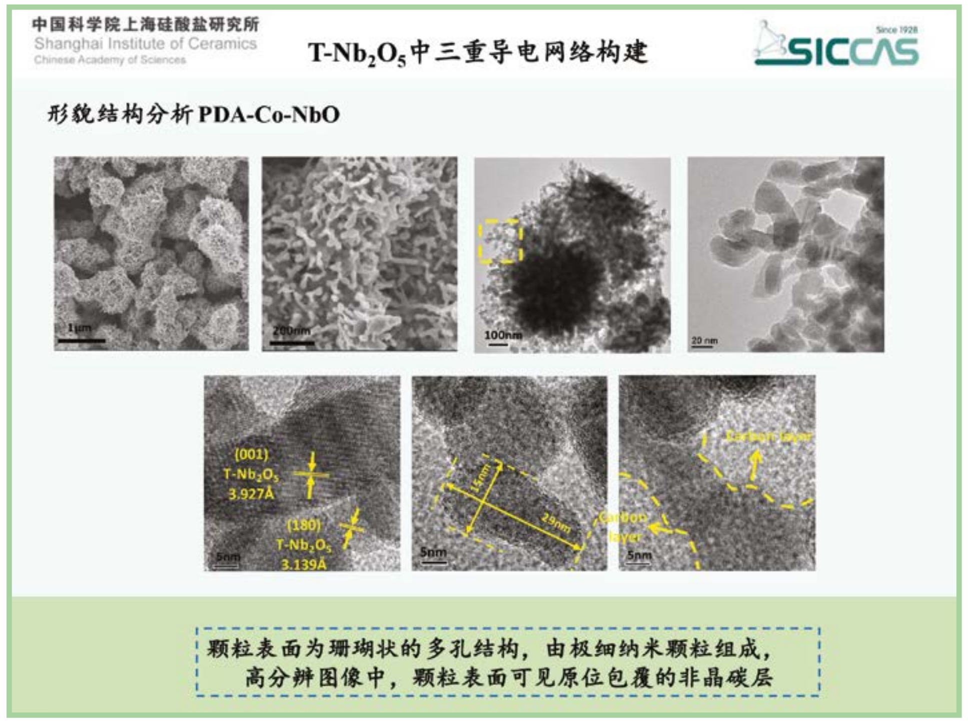

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb2O5中的氧缺陷调控
SICCAS
电化学性能对比
0.5 C长循环性能
5 C长循环性能
倍率性能
L-NbO和CN-NbO高载量性能对比
面容量对比
Cycle Number
Areal Current Density(mA/cm2)
低载量CN-NbO的性能优于L-NbO；高载量时受电导率影响，L-NbO的性能更优。

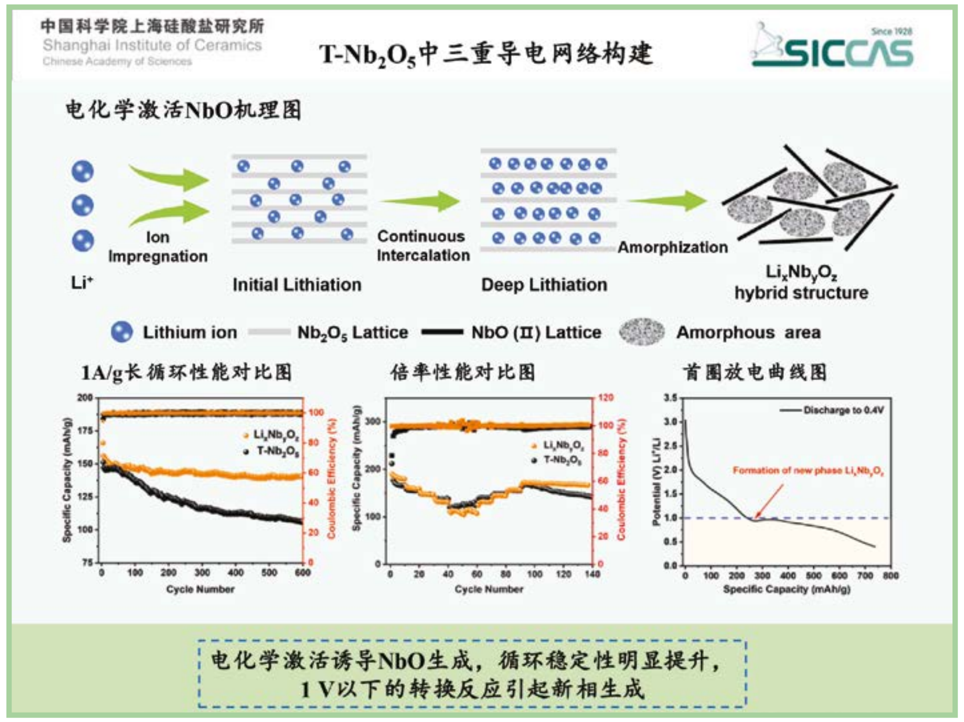

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
SICCAS
L-NbO/NCM811全电池
理论电压示意图
倍率性能
0.5 C长循环性能
NCM811
L-NbO
Charge: 2.54V
Discharge: 2.04V
Specific Capacity (mAh/g)
Cycle Number
L-NbO/NCM811的平均工作电压分别为2.54 V和2.04 V。
5 C下保持75 mAh/g以上的容量
0.5 C下循环100圈保持160 mAh/g

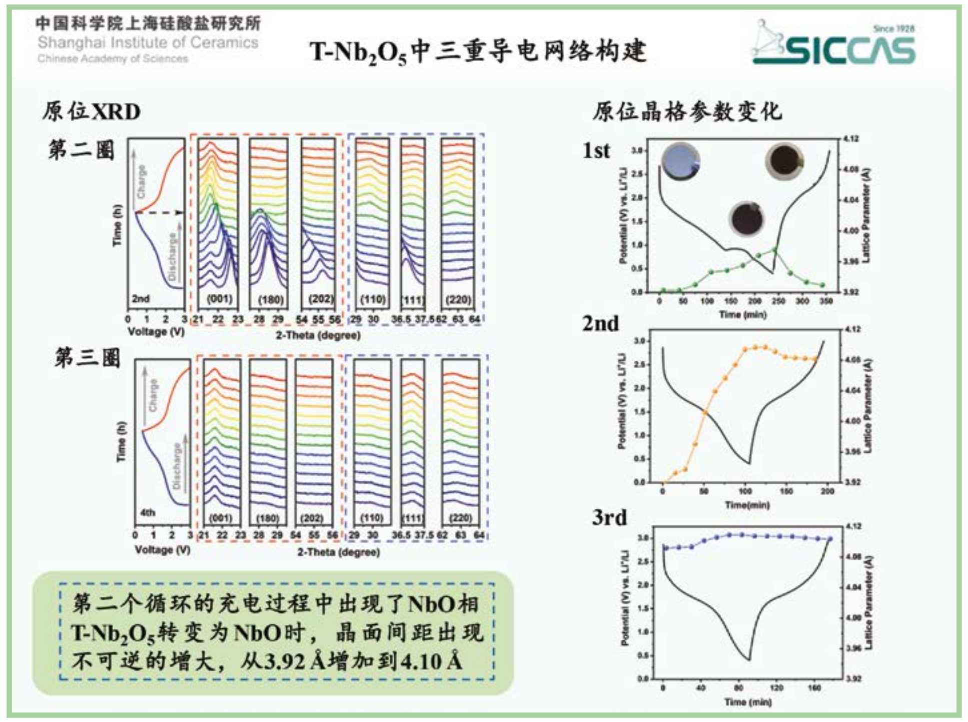

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
小结
SICCAS
T-Nb$_2$O$_5$中的氧缺陷调控
◆ 通过室温酸处理的方法，氧缺陷成功引入到T-Nb$_2$O$_5$中，并将电导率提升两个数量级
◆ O-g-C$_3$N$_4$调控缺陷浓度后，T-Nb$_2$O$_{5-x}$中的缺陷浓度大大下降，约为原来的1/60
◆ 基于XANES、Raman、DFT计算与紫外-可见-红外光谱综合分析，氧空位最有可能位于不同NbO$_x$多面体层间的Nb-O-Nb桥氧键处
本章节创新点
① 新策略：室温酸浸泡的缺陷诱导方法 ② 新机制：O-g-C$_3$N$_4$的微氧泵补氧机制
Y. J. Zheng, C. L. Li et al. Adv. Funct. Mater., 32, 2107060, 2022
下一个工作：T-Nb$_2$O$_5$中三重导电网络构建

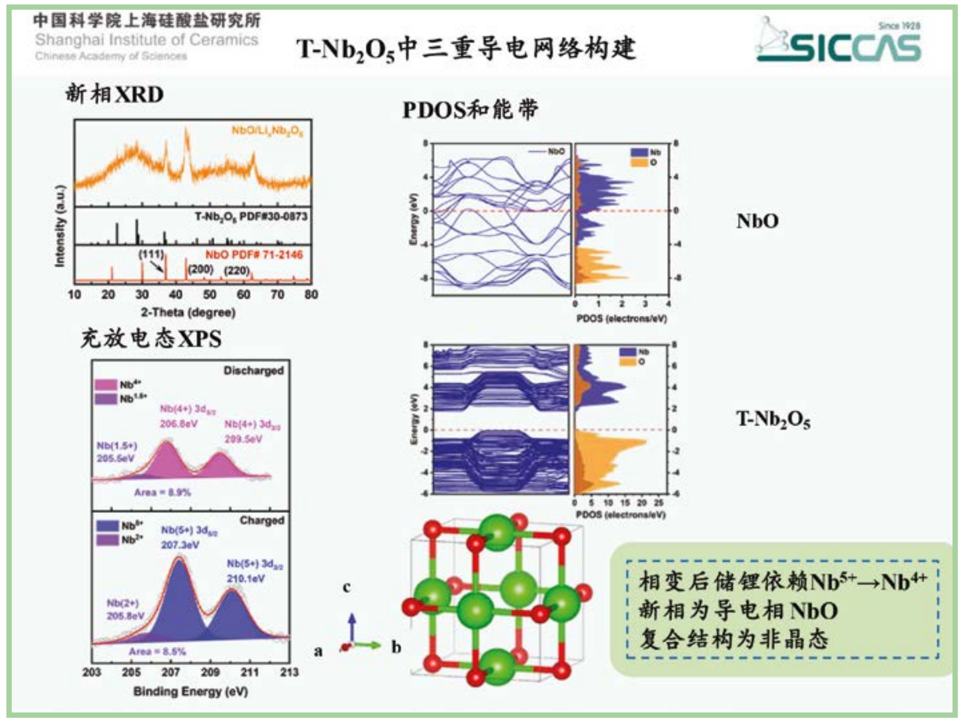

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
Co的掺杂与PDA包覆
Co(NO$_3$)$_2$·6H$_2$O
NbCl$_5$
Solvothermal
180℃
6h
Glycerol
Isopropanol
Annealed In Air
600℃ 3h
Annealed In N$_2$
450℃ 3h
Dopamine
Tris,pH=8.5
Carbon Coated Co-NbO
Co Doped Nb$_2$O$_5$
PDA-Co-NbO
Co-NbO
P-NbO
PDF#30-0873
Intensity (a.u.)
2-Theta (degree)
Nb
O
C
N
Co
水热合成，PDA原位包覆构建非晶碳层，掺杂前后均为正交相Nb$_2$O$_5$
EDS mapping表明PDA均匀包覆，Co均匀掺杂

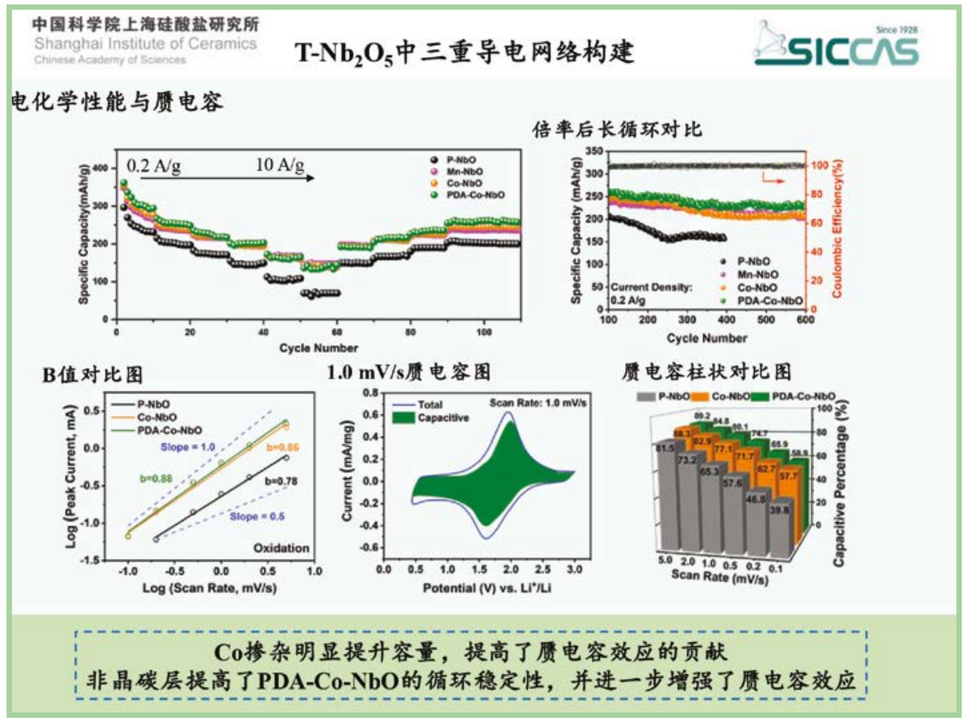

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
Co掺杂结构分析
EPR
Raman
g=2.001
g=2.013
g=2.052
Co^{2+}
g=2.012
P-NbO
Co-NbO
PDA-Co-NbO
Intensity (a.u.)
g value
Co-NbO
P-NbO
ν_{Lo}
ν_{Mid}
ν_{Hi}
Raman shift (cm^{-1})
EPR能谱中有Co原子的磁信号，证明Co的成功掺杂
Raman光谱中并没有发现Co-O的振动峰，表明Co掺杂进入晶格中

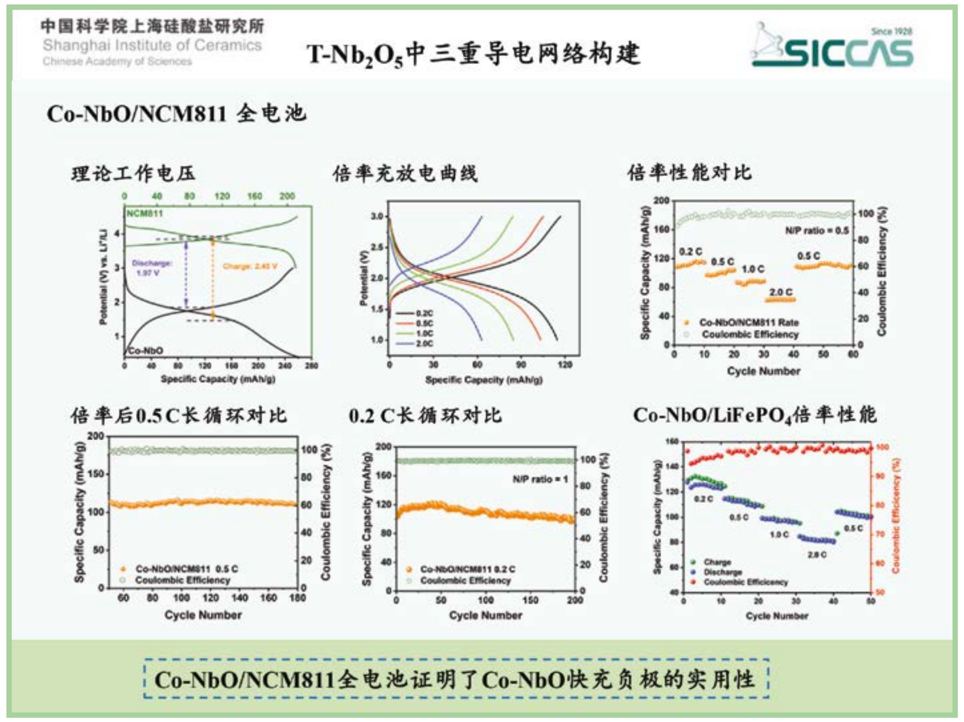

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
形貌结构分析PDA-Co-NbO
(001) T-Nb$_2$O$_5$ 3.927Å
(180) T-Nb$_2$O$_5$ 3.139Å
颗粒表面为珊瑚状的多孔结构，由极细纳米颗粒组成，
高分辨图像中，颗粒表面可见原位包覆的非晶碳层

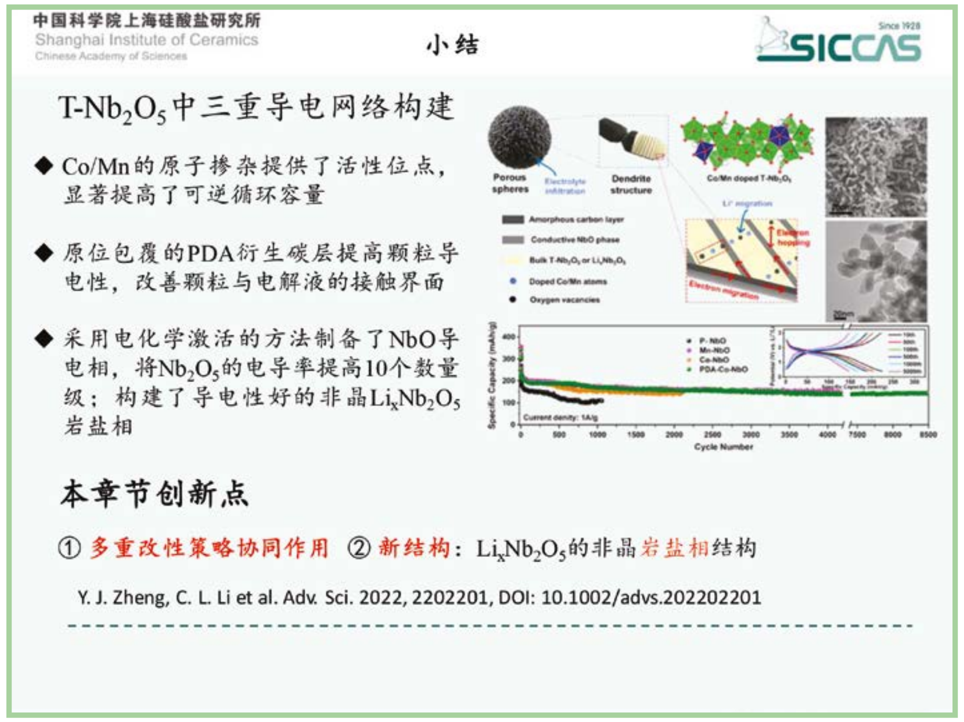

中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
电化学激活NbO机理图
Li$^+$
Ion Impregnation
Initial Lithiation
Continuous Intercalation
Deep Lithiation
Amorphization
Li$_x$Nb$_y$O$_z$ hybrid structure
Lithium ion
Nb$_2$O$_5$ Lattice
NbO (II) Lattice
Amorphous area
1A/g长循环性能对比图
倍率性能对比图
首圈放电曲线图
Cycle Number
Specific Capacity (mAh/g)
Formation of new phase Li$_x$Nb$_y$O$_z$
Discharge to 0.4V
电化学激活诱导NbO生成，循环稳定性明显提升，
1 V以下的转换反应引起新相生成


中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
原位XRD
第二圈
第三圈
原位晶格参数变化
1st
2nd
3rd
Voltage (V)
2-Theta (degree)
Time (min)
第二个循环的充电过程中出现了NbO相
T-Nb$_2$O$_5$转变为NbO时，晶面间距出现
不可逆的增大，从3.92 Å增加到4.10 Å


中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
新相XRD
2-Theta (degree)
PDOS和能带
NbO
T-Nb$_2$O$_5$
充放电态XPS
Discharged
Charged
Binding Energy (eV)
相变后储锂依赖Nb^{5+}→Nb^{4+}
新相为导电相NbO
复合结构为非晶态


中国科学院上海硅酸盐研究所
Shanghai Institute of Ceramics
Chinese Academy of Sciences
T-Nb$_2$O$_5$中三重导电网络构建
SICCAS
电化学性能与赝电容
倍率后长循环对比
0.2 A/g
10 A/g
Cycle Number
B值对比图
1.0 mV/s赝电容图
赝电容柱状对比图
Log (Scan Rate, mV/s)
Potential (V) vs. Li$^+$/Li
Scan Rate (mV/s)
Co掺杂明显提升容量，提高了赝电容效应的贡献
非晶碳层提高了PDA-Co-NbO的循环稳定性，并进一步增强了赝电容效应





2022 International Conference on Niobium Based Batteries
5TH EDITION

Notes

Notes

Notes

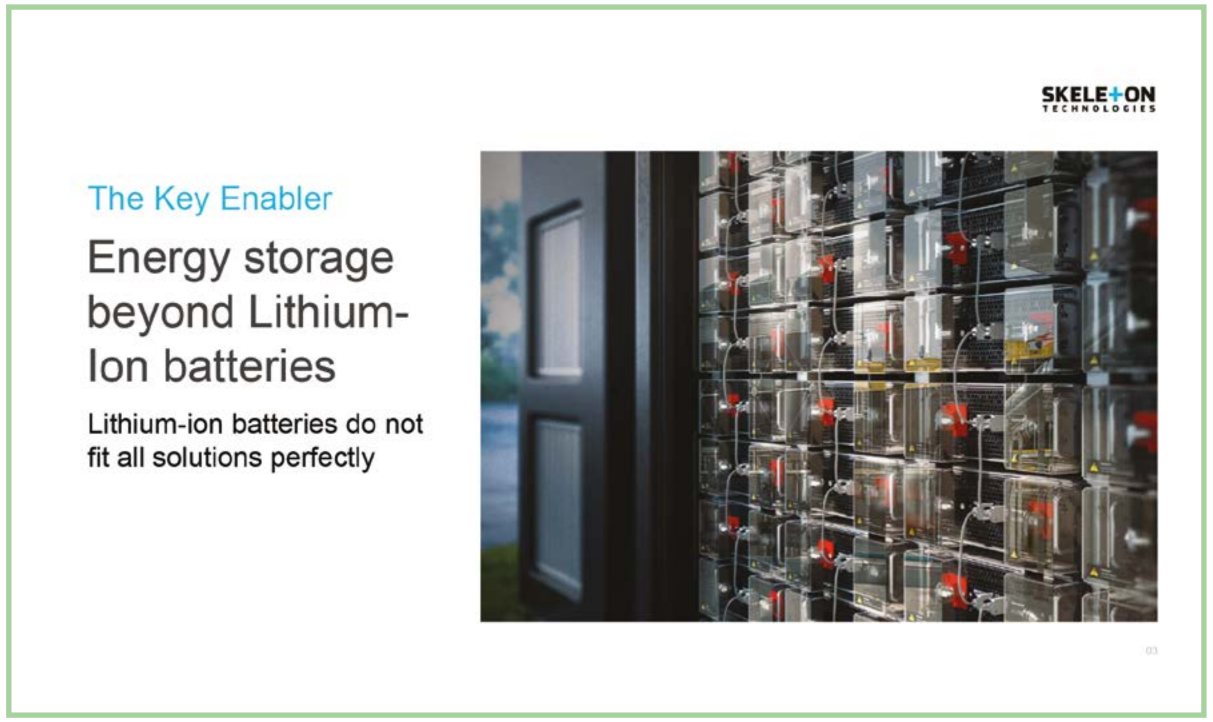
Dr. Sebastian Pohlmann

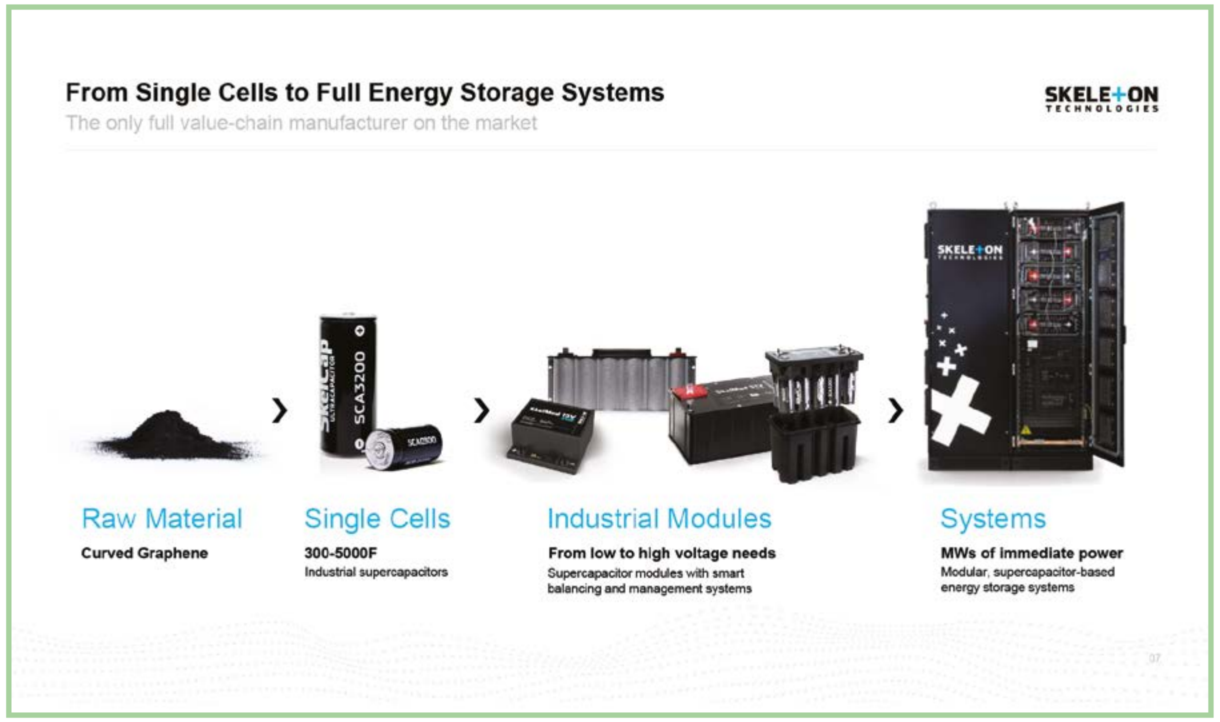
VP Automotive and Business Development - Skeleton Technologies

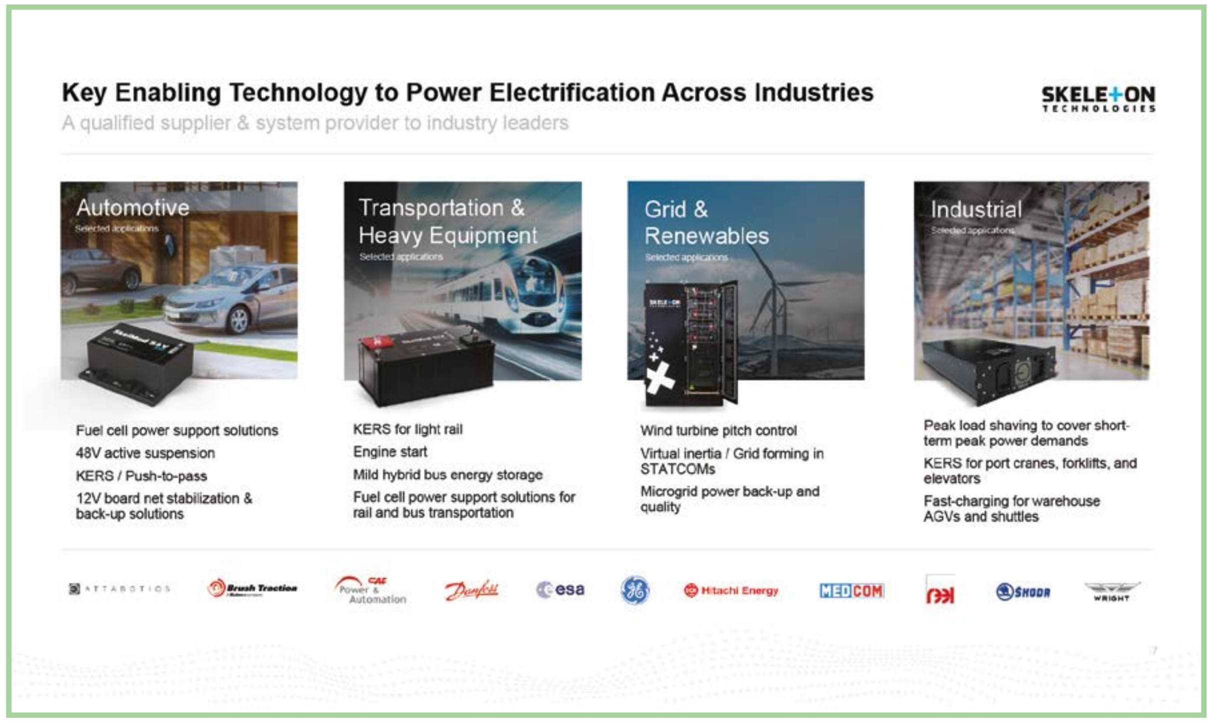
SEBASTIAN POHLMANN博士是SKELETON TECHNOLOGIES汽车和业务开发副总裁，他领导汽车商业活动，并将下一代超级电容器引入未来应用。在SKELETON工作的5年中，他还领导了2年的开发团队，使SKELETON的“弯曲石墨烯”技术更接近应用。POHLMANN博士于2014年在明斯特大学获得物理化学博士学位，并撰写和合作撰写了超过12份出版物和专利。

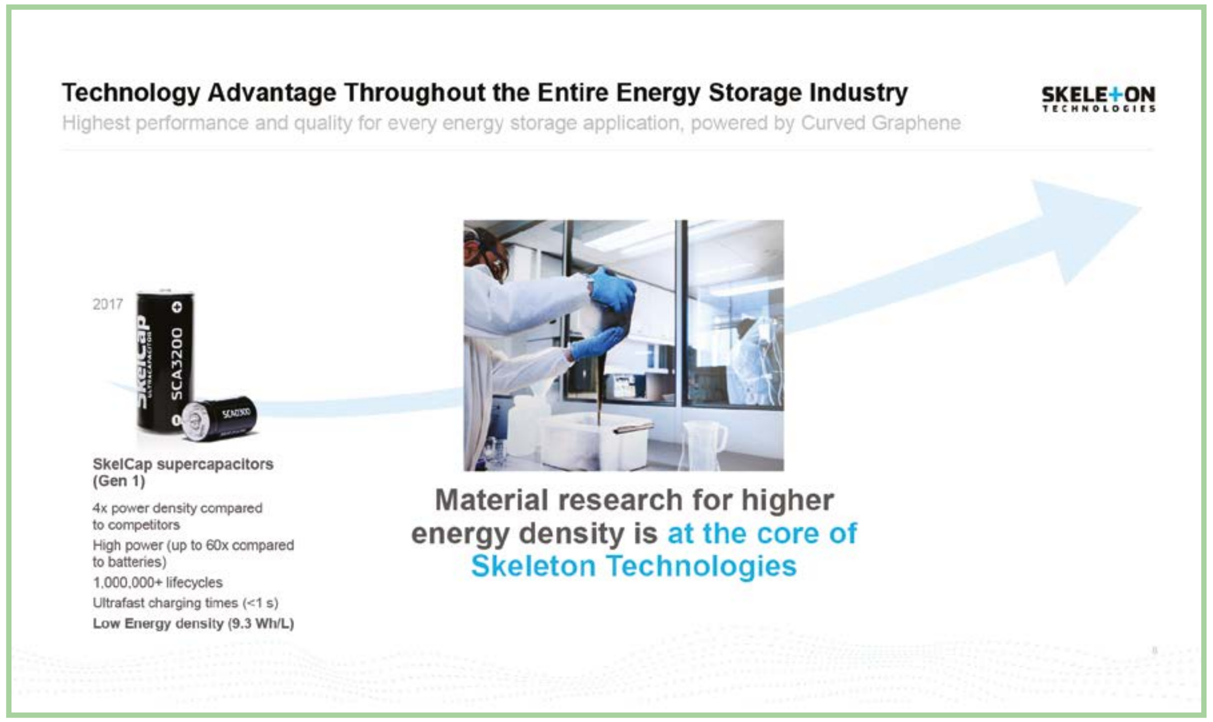
Dr. Sebastian Pohlmann is Vice President Automotive & Business Development at Skeleton Technologies, where he leads automotive commercial activities and brings next generation ultracapacitors into future applications. During his 5 years at Skeleton, he also led the development team for 2 years, bringing Skeleton's "Curved Graphene" technology closer to application. Dr. Pohlmann obtained his PhD in Physical Chemistry in 2014 at the University of Münster and has authored and co-authored over 12 publications and patents.

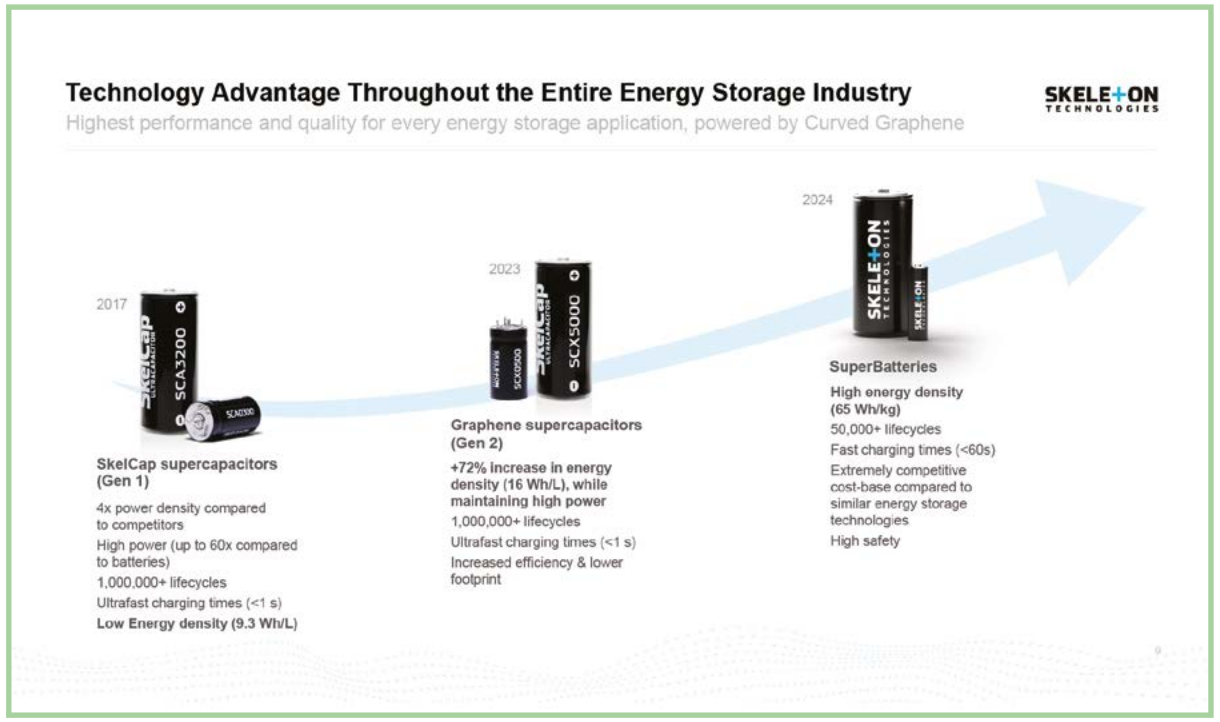
2022 International Conference on Niobium Based Batteries

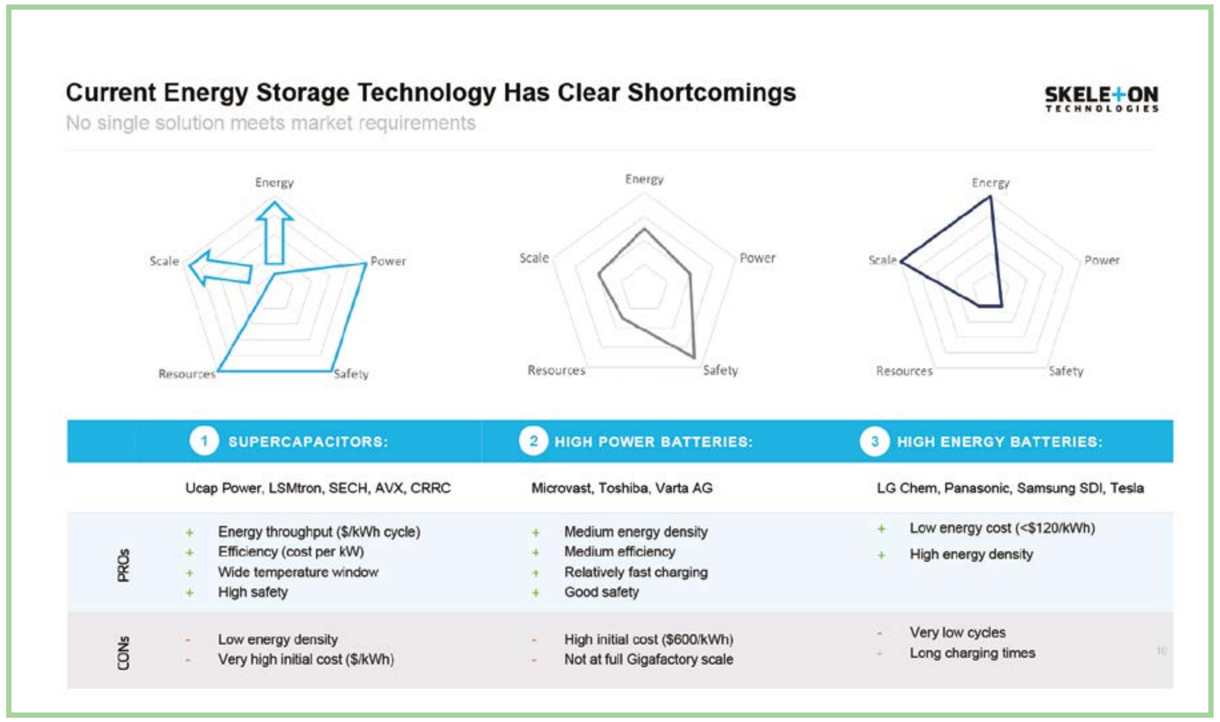





Key Enabling Technology to Power Electrification Across Industries
A qualified supplier & system provider to industry leaders
SKELETON TECHNOLOGIES
Automotive
Selected applications
Fuel cell power support solutions
48V active suspension
KERS / Push-to-pass
12V board net stabilization & back-up solutions
Transportation & Heavy Equipment
Selected applications
KERS for light rail
Engine start
Mild hybrid bus energy storage
Fuel cell power support solutions for rail and bus transportation
Grid & Renewables
Selected applications
Wind turbine pitch control
Virtual inertia / Grid forming in STATCOMs
Microgrid power back-up and quality
Industrial
Selected applications
Peak load shaving to cover short-term peak power demands
KERS for port cranes, forklifts, and elevators
Fast-charging for warehouse AGVs and shuttles
Brush Traction
CAF Power & Automation
Danfoss
esa
Hitachi Energy
MEDCOM
SKODA
WRIGHT


Technology Advantage Throughout the Entire Energy Storage Industry
Highest performance and quality for every energy storage application, powered by Curved Graphene
SKELETON TECHNOLOGIES
2017
SkelCap supercapacitors (Gen 1)
4x power density compared to competitors
High power (up to 60x compared to batteries)
1,000,000+ lifecycles
Ultrafast charging times (<1 s)
Low Energy density (9.3 Wh/L)
Material research for higher energy density is at the core of Skeleton Technologies


Technology Advantage Throughout the Entire Energy Storage Industry
Highest performance and quality for every energy storage application, powered by Curved Graphene
SKELETON TECHNOLOGIES
2017
SkelCap supercapacitors (Gen 1)
4x power density compared to competitors
High power (up to 60x compared to batteries)
1,000,000+ lifecycles
Ultrafast charging times (<1 s)
Low Energy density (9.3 Wh/L)
2023
Graphene supercapacitors (Gen 2)
+72% increase in energy density (16 Wh/L), while maintaining high power
1,000,000+ lifecycles
Ultrafast charging times (<1 s)
Increased efficiency & lower footprint
2024
SuperBatteries
High energy density (65 Wh/kg)
50,000+ lifecycles
Fast charging times (<60s)
Extremely competitive cost-base compared to similar energy storage technologies
High safety


Current Energy Storage Technology Has Clear Shortcomings
No single solution meets market requirements
SKELETON TECHNOLOGIES
Energy
Power
Safety
Resources
Scale
1 SUPERCAPACITORS:
2 HIGH POWER BATTERIES:
3 HIGH ENERGY BATTERIES:
Ucap Power, LSMtron, SECH, AVX, CRRC
Microvast, Toshiba, Varta AG
LG Chem, Panasonic, Samsung SDI, Tesla
PROs
+ Energy throughput ($/kWh cycle)
+ Efficiency (cost per kW)
+ Wide temperature window
+ High safety
+ Medium energy density
+ Medium efficiency
+ Relatively fast charging
+ Good safety
+ Low energy cost (<$120/kWh)
+ High energy density
CONs
- Low energy density
- Very high initial cost ($/kWh)
- High initial cost ($600/kWh)
- Not at full Gigafactory scale
- Very low cycles
- Long charging times

2022 International Conference on Niobium Based Batteries

Where is high power required?

Defining requirements

SKELETON TECHNOLOGIES

Critical requirements in the application's power profile

Fast charging:	High utilization, no dedicated charging storage
High power discharge:	Pack size dependent on power density
High RMS current:	Lifetime dependent on power density and low ESR

Critical requirements independent of power profile

Safety:	Less overhead, wider application field
Sustainability:	Emission footprint, end-of-life costs
Supply chain security:	Price stability

Industrial grid solutions| Data centre UPS

CHALLENGE: High safety, footprint and high power

SKELETON TECHNOLOGIES

Fast charging

High power discharge

High RMS current

Safety

Sustainability

Supply chain security

BACKGROUND

- Data centers have extreme reliability, availability and maintainability requirements
- Uncontrolled power loss can mean losing the work of millions of euros in data loss.
- Uninterruptable Power Supplies (UPS) needed to prevent shut down of mission critical loads in case of grid issues
- UPS aim to provide 15 – 30min of power before gensets or fuel cells

KEY CHALLENGES

- Low lifetime in lead acid requires constant system substitution.
- Very high safety and reliability requirements incompatible with standard Li-ion
- Only options are high priced (LTO) or oversized (NMC/LFP)

BENEFITS

- Increased lifetime and high power capabilities
- Extended system energy storage lifespan up to 8 times and reduce maintenance cost.
- Increased intrinsically safety of the system at cell, module and system level.

How does the classic Li-ion battery compare?

Low cost and high energy density are pressuring other technologies

SKELETON TECHNOLOGIES

Competition in power

Fast charging:

High power discharge:

High RMS current:

Oversizing vs cost advantage

A LIB with 400 kWh @ **100 EUR/kWh** is a cheaper solution than a high power battery with 100 kWh @ **500 EUR/kWh**

Price per kWh determines required "oversizing gap"

LIB are challenged on safety, sustainability and supply chain

Safety:

Sustainability:

Supply chain security:

Mining Solutions | Surface Full Electric Haul Trucks

CHALLENGE: Electrification with lowest impact on TCO

SKELETON TECHNOLOGIES

Fast charging

High power discharge

High RMS current

Safety

Sustainability

Supply chain security

BACKGROUND

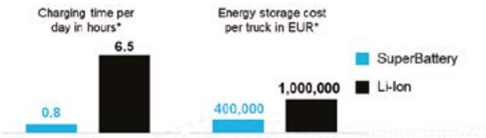
- All-electric mines require electrified hauling
- Electrification should have no impact on the haul cycle
- Battery-electric haul trucks require up to 400 kWh capacity per roundtrip

KEY CHALLENGES

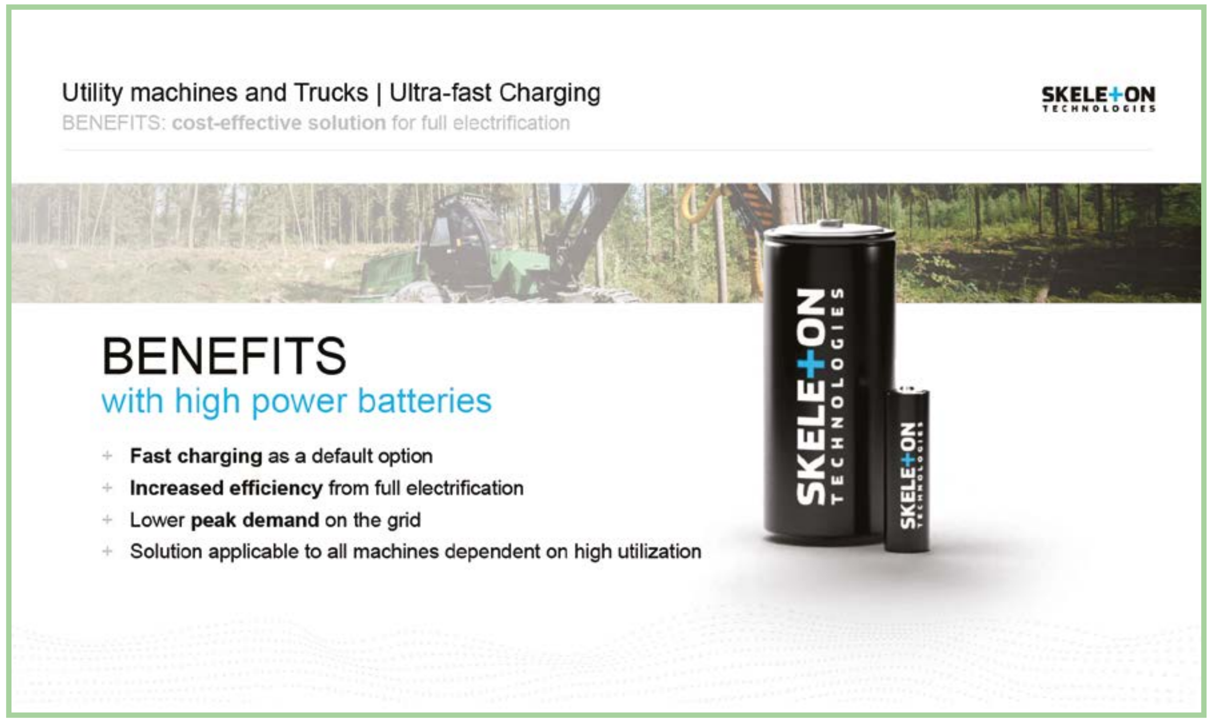
- Trolley solutions require a catenary – resulting in high CAPEX with frequent interruptions for extensions as the mine grows
- Battery-electric trucks require long charging times and large battery capacities when charged stationary
- Battery swap not possible due to large battery size

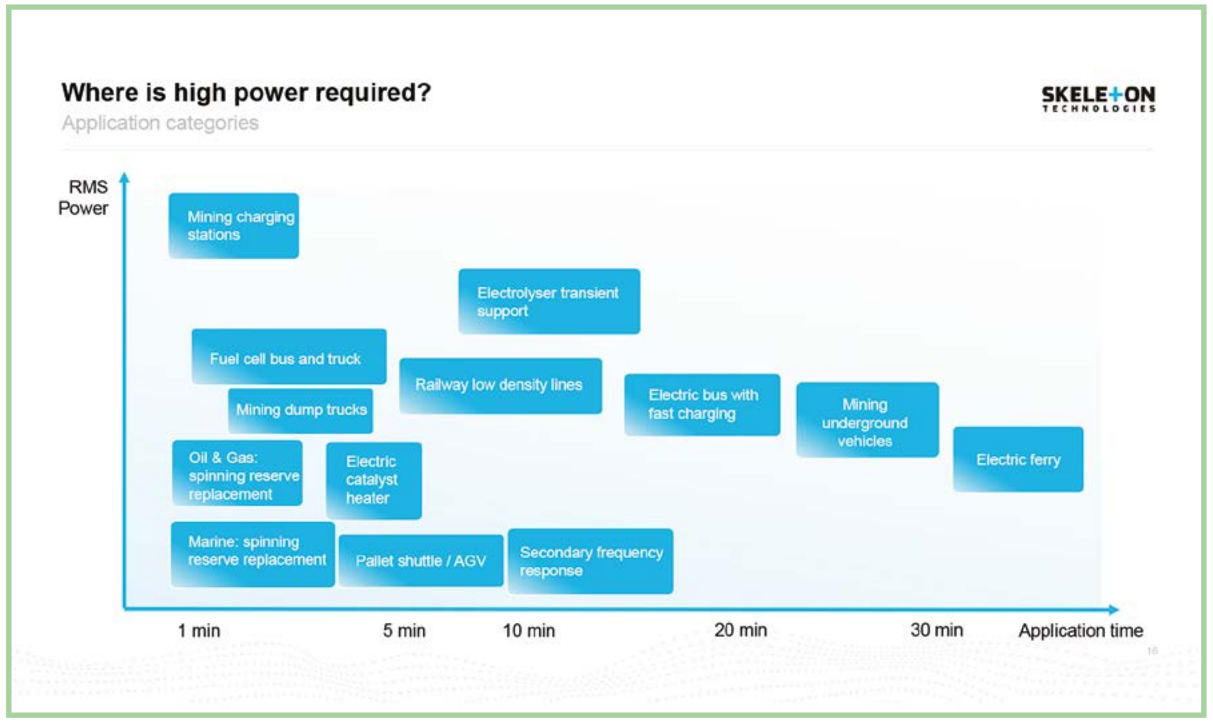
SOLUTION

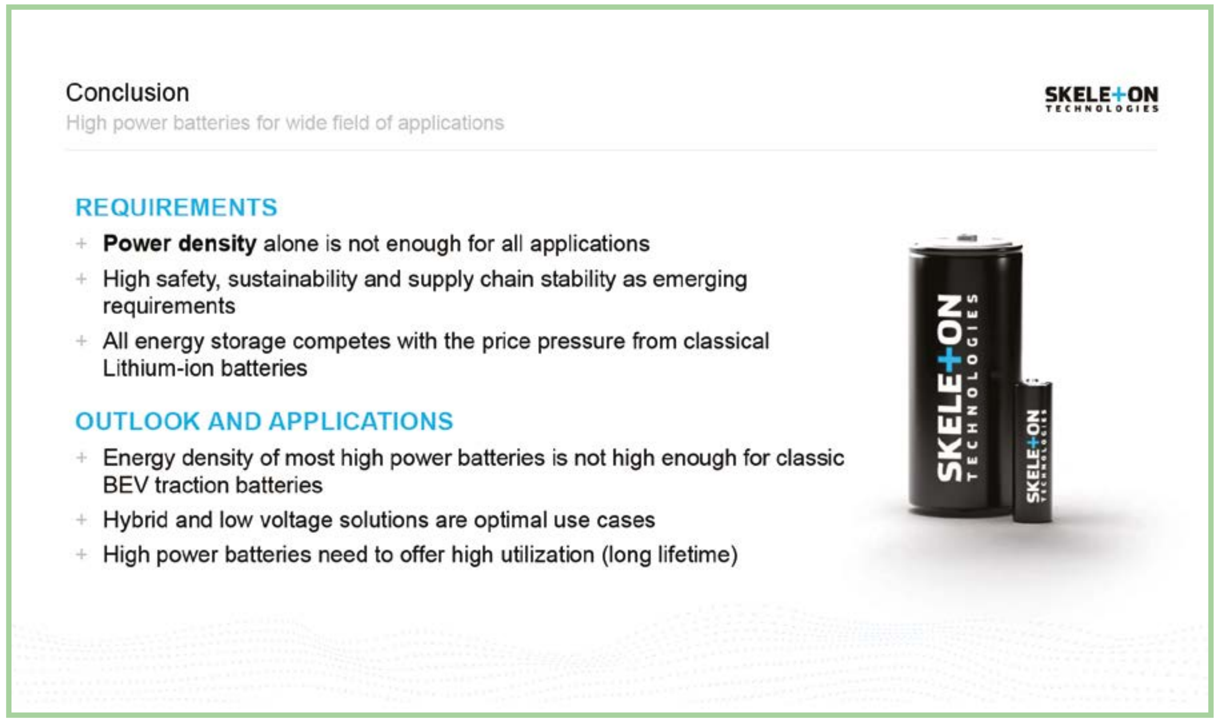
- Fast charging **high power battery system** on board
- **Charging in <2 min** depending on power connection
- Charging station supported by SuperBattery for high power availability

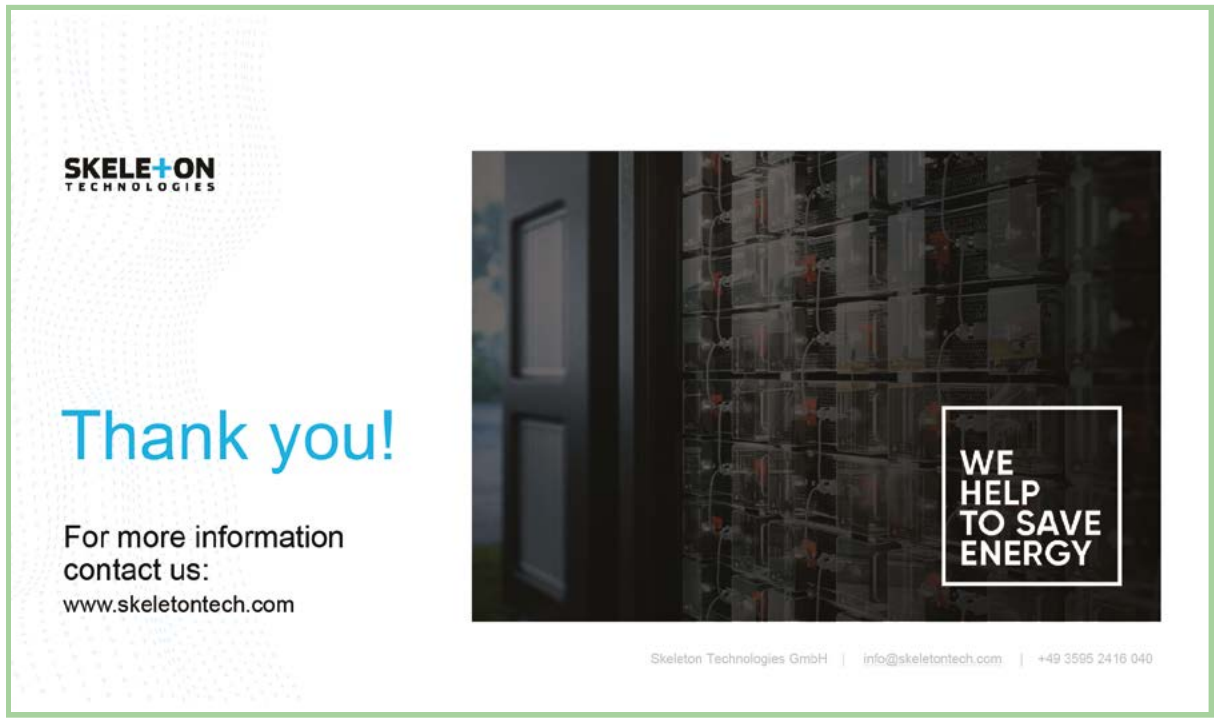


*calculated for a 30 min charge for LIB with 5000 cycles, including overhead for additional trucks to compensate for charging time


Utility machines and Trucks | Ultra-fast Charging
BENEFITS: cost-effective solution for full electrification
SKELETON TECHNOLOGIES
BENEFITS
with high power batteries
Fast charging as a default option
Increased efficiency from full electrification
Lower peak demand on the grid
Solution applicable to all machines dependent on high utilization


Where is high power required?
Application categories
SKELETON TECHNOLOGIES
RMS Power
Mining charging stations
Electrolyser transient support
Fuel cell bus and truck
Railway low density lines
Electric bus with fast charging
Mining underground vehicles
Mining dump trucks
Electric ferry
Oil & Gas: spinning reserve replacement
Electric catalyst heater
Marine: spinning reserve replacement
Pallet shuttle / AGV
Secondary frequency response
1 min
5 min
10 min
20 min
30 min
Application time


Conclusion
High power batteries for wide field of applications
SKELETON TECHNOLOGIES
REQUIREMENTS
Power density alone is not enough for all applications
High safety, sustainability and supply chain stability as emerging requirements
All energy storage competes with the price pressure from classical Lithium-ion batteries
OUTLOOK AND APPLICATIONS
Energy density of most high power batteries is not high enough for classic BEV traction batteries
Hybrid and low voltage solutions are optimal use cases
High power batteries need to offer high utilization (long lifetime)


SKELETON TECHNOLOGIES
Thank you!
For more information contact us:
www.skeletontech.com
WE HELP TO SAVE ENERGY
Skeleton Technologies GmbH | info@skeletontech.com | +49 3595 2416 040

Notes

2022 International Conference on Niobium Based Batteries
5TH EDITION

Notes

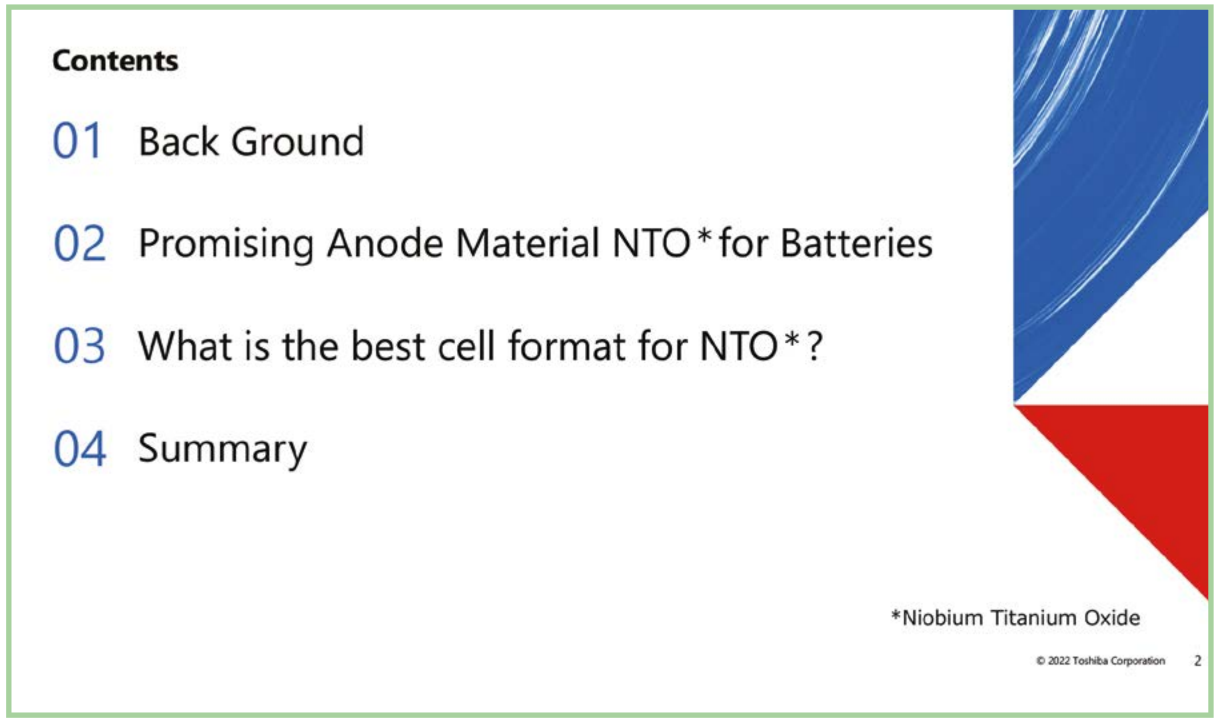
2022 International Conference on Niobium Based Batteries

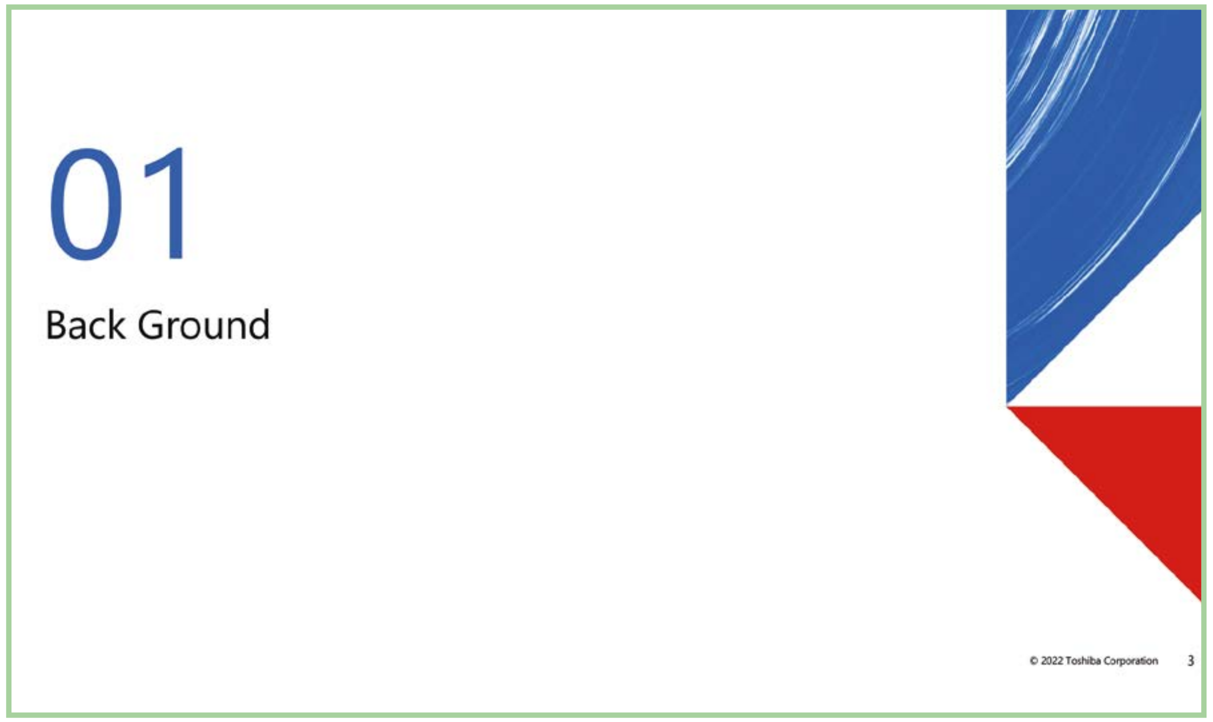
Dr. Yasuhiro Harada

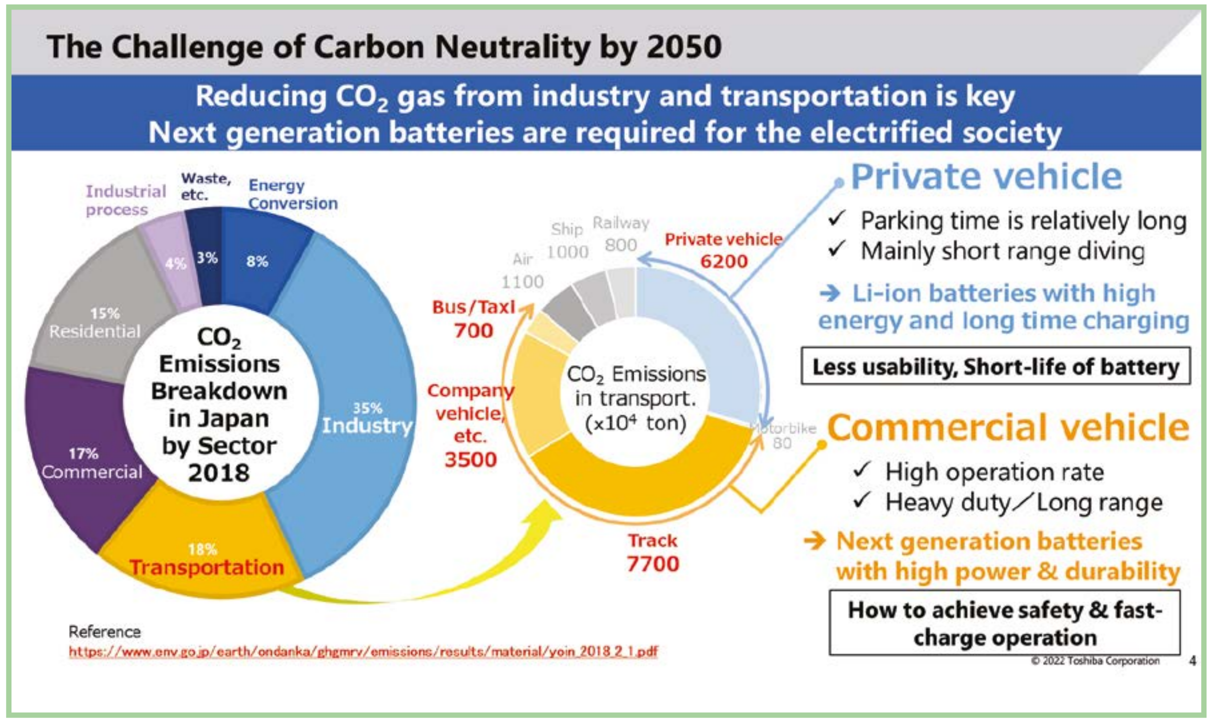
Senior Fellow - Nano Materials & Frontier Research Laboratories Corporate Research & Development Center, Toshiba Corporation, Japan

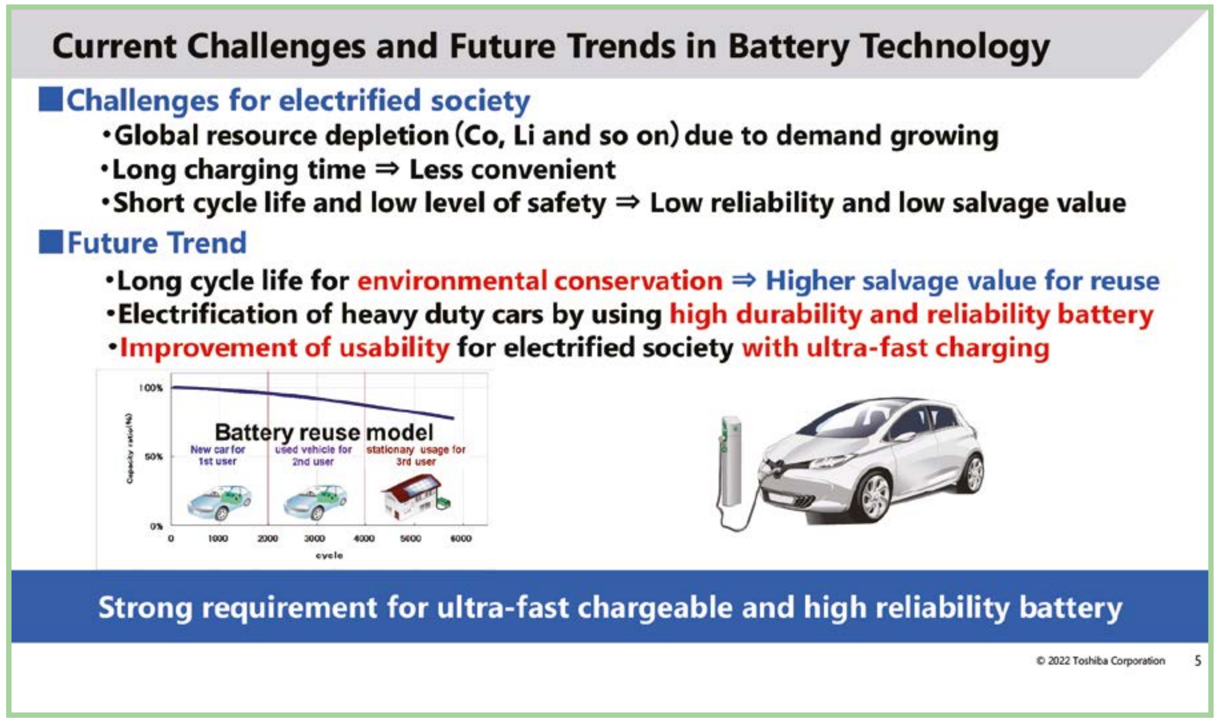
YASUHIRO HARADA目前是东芝公司研发中心的高级研究员。他2001毕业于东京理科大学无机化学专业获得博士学位，并于2002年加入东芝。他从事新电池材料的研究已有19年。他于2020年被日本文部科学省授予科学技术奖。他目前的工作重点是开发新的电池技术。

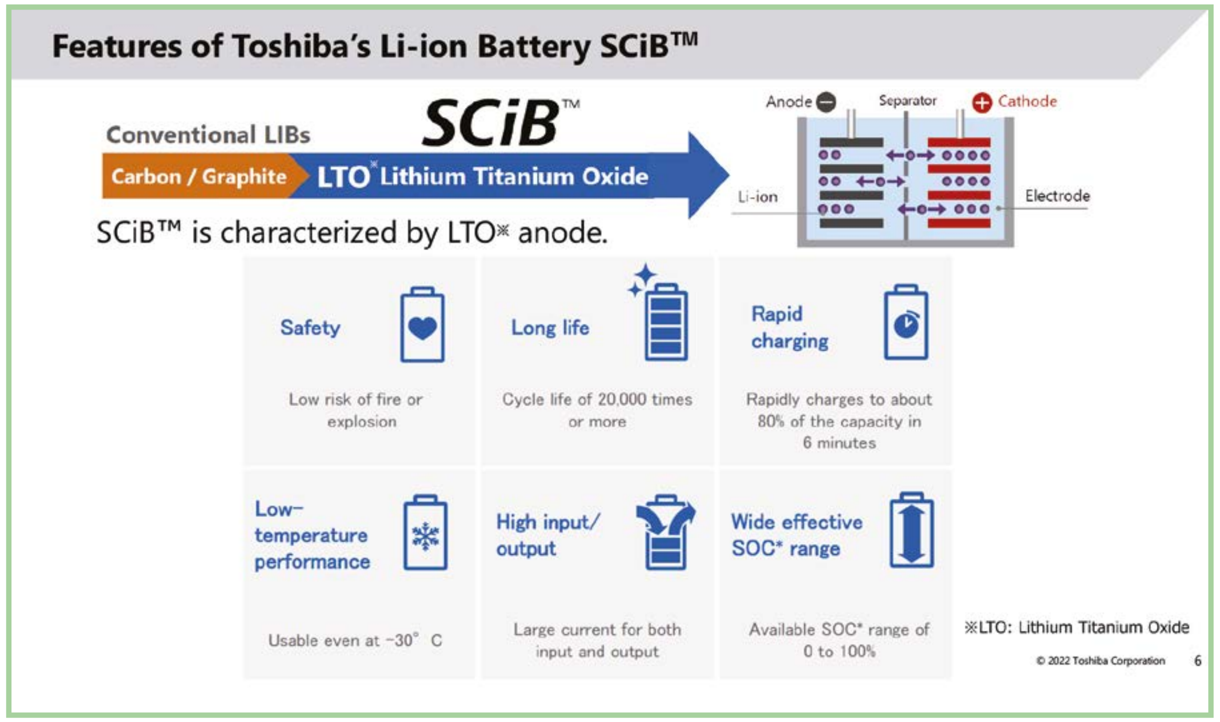
Yasuhiro Harada is currently a Senior Fellow at Toshiba corporate R&D center. He received his Ph.D. in inorganic chemistry from Tokyo University of Science in 2001. He joined Toshiba in 2002. He has been working on new battery materials for 19 years. He was awarded the Commendation for Science and Technology by Japan Minister of Education, Culture, Sports, Science and Technology, 2020. His current work is focused on the development of new battery technologies.




01
Back Ground
© 2022 Toshiba Corporation 3


The Challenge of Carbon Neutrality by 2050
Reducing CO_2 gas from industry and transportation is key
Next generation batteries are required for the electrified society
Industrial process
Waste, etc.
Energy Conversion
4%
3%
8%
15% Residential
CO_2 Emissions Breakdown in Japan by Sector 2018
35% Industry
17% Commercial
18% Transportation
Ship
Railway
Air 1000
800
1100
Private vehicle 6200
Bus/Taxi 700
Company vehicle, etc. 3500
CO_2 Emissions in transport. ($\times10^4$ ton)
Motorbike 80
Track 7700
Private vehicle
✓ Parking time is relatively long
✓ Mainly short range diving
→ Li-ion batteries with high energy and long time charging
Less usability, Short-life of battery
Commercial vehicle
✓ High operation rate
✓ Heavy duty/Long range
→ Next generation batteries with high power & durability
How to achieve safety & fast-charge operation
Reference
https://www.env.go.jp/earth/ondanka/ghgmrv/emissions/results/material/yoin_2018_2_1.pdf
© 2022 Toshiba Corporation 4


Current Challenges and Future Trends in Battery Technology
■Challenges for electrified society
・Global resource depletion (Co, Li and so on) due to demand growing
・Long charging time ⇒ Less convenient
・Short cycle life and low level of safety ⇒ Low reliability and low salvage value
■Future Trend
・Long cycle life for environmental conservation ⇒ Higher salvage value for reuse
・Electrification of heavy duty cars by using high durability and reliability battery
・Improvement of usability for electrified society with ultra-fast charging
Battery reuse model
New car for 1st user
Used vehicle for 2nd user
stationary usage for 3rd user
100%
50%
0%
0
1000
2000
3000
4000
5000
6000
cycle
Strong requirement for ultra-fast chargeable and high reliability battery
© 2022 Toshiba Corporation 5


Features of Toshiba's Li-ion Battery SCiB™
Conventional LIBs
SCiB™
Carbon / Graphite
LTO Lithium Titanium Oxide
SCiB™ is characterized by LTO※ anode.
Anode
Separator
Cathode
Li-ion
Electrode
Safety
Low risk of fire or explosion
Long life
Cycle life of 20,000 times or more
Rapid charging
Rapidly charges to about 80% of the capacity in 6 minutes
Low-temperature performance
Usable even at -30° C
High input/ output
Large current for both input and output
Wide effective SOC* range
Available SOC* range of 0 to 100%
※LTO: Lithium Titanium Oxide
© 2022 Toshiba Corporation 6

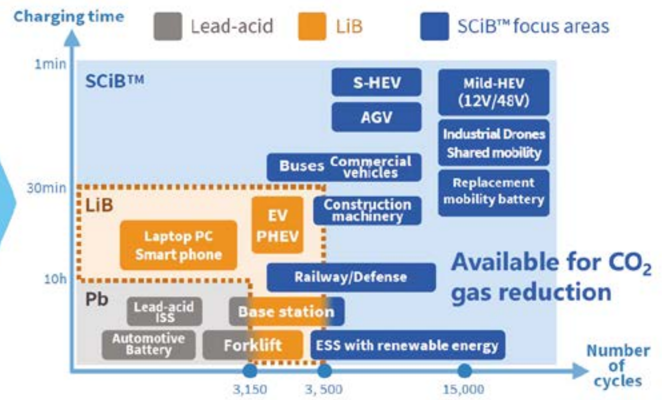
2022 International Conference on Niobium Based Batteries

Target Market Segment for SCiB™

Focus on heavy-duty areas where SCiB™ can be useful, rather than simple energy storage applications

SCiB™ Characteristics

Target Markets



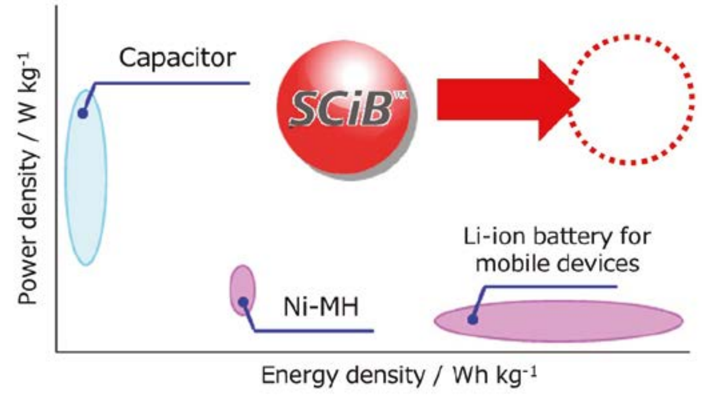
© 2022 Toshiba Corporation 7

02

Promising Anode Material
Niobium **T**itanium **O**xide

© 2022 Toshiba Corporation 8

Target Energy Density for Next Generation Battery



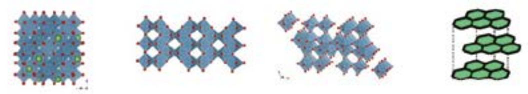
Lack of sufficient energy density is the biggest weakness of Toshiba's battery.

Toshiba's challenge is to enhance the energy density which is mainly determined by capacity and electrode potential of the anode material.

© 2022 Toshiba Corporation 9

Candidates for High-capacity Oxide Anode Material

Table. Titanium-based oxide anode materials and Graphite

Anode materials	LTO※	TiO_2(B)	NTO*	Graphite
Crystal structure	Spinel	monoclinic	monoclinic	Hexagonal
				
Redox couples	Ti^{4+}/Ti^{3+}	Ti^{4+}/Ti^{3+}	Ti^{4+}/Ti^{3+} Nb^{5+}/Nb^{3+}	C_6/C_6^-
Density (g/cm^3)	3.41	3.73	4.34	2.25
Capacity* (mAh/g)	170	335	387	372
Capacity* (mAh/cm^3)	580	1250	1680	837
Potential (V vs. Li)	1.55	1.6	1.6	0.2

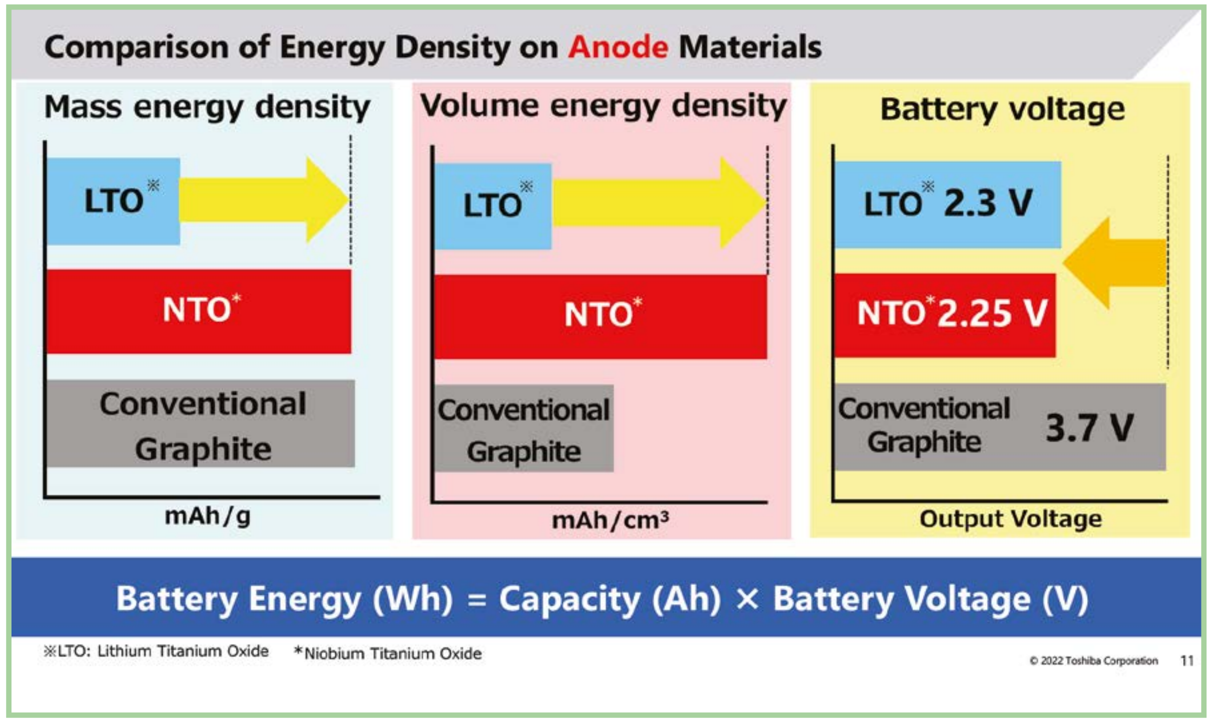
* Theoretical capacity

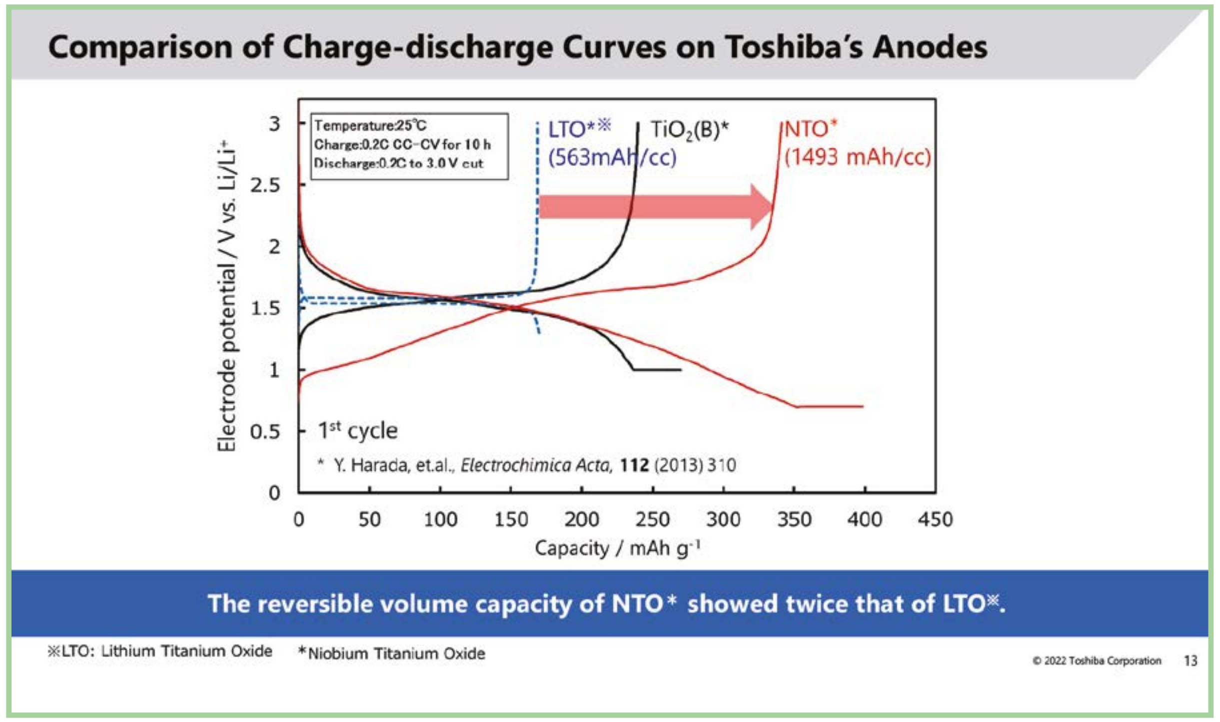
※LTO: Lithium Titanium Oxide
*Niobium Titanium Oxide

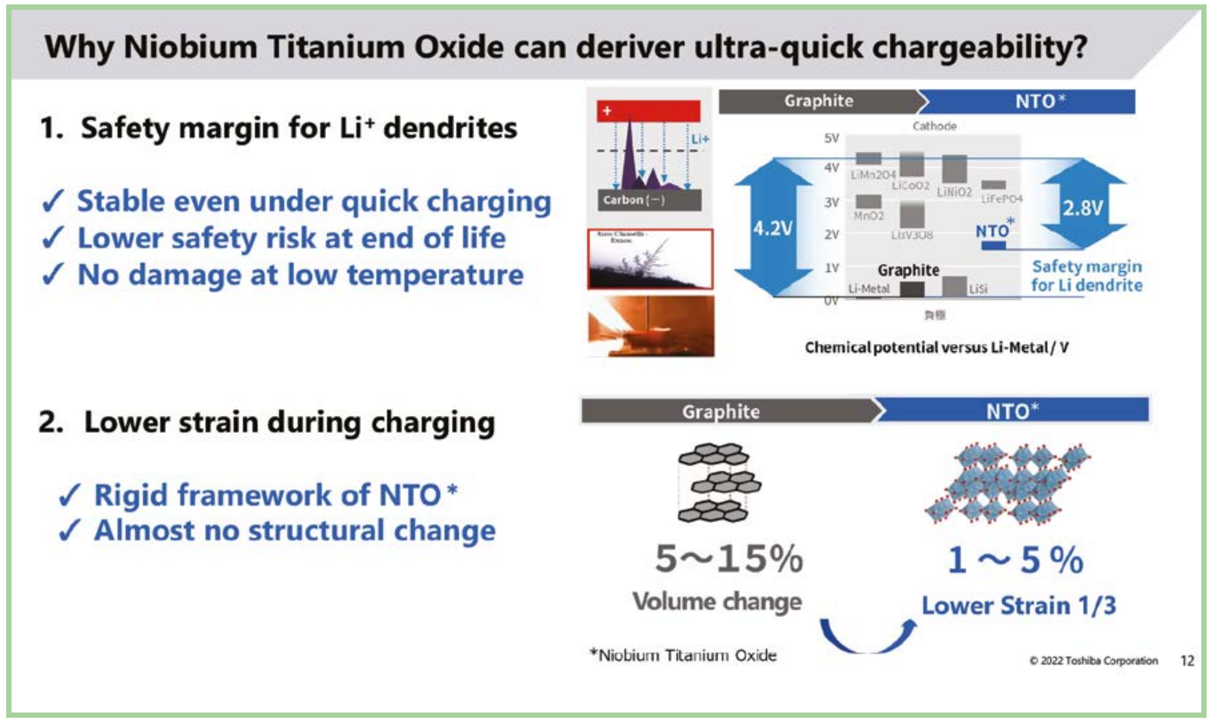
NTO* would be the only material that can deriver high capacity with the same redox potential as LTO※.
NTO* has unique redox couples such as not only Ti but also Nb, which enables to react 3 electrons.

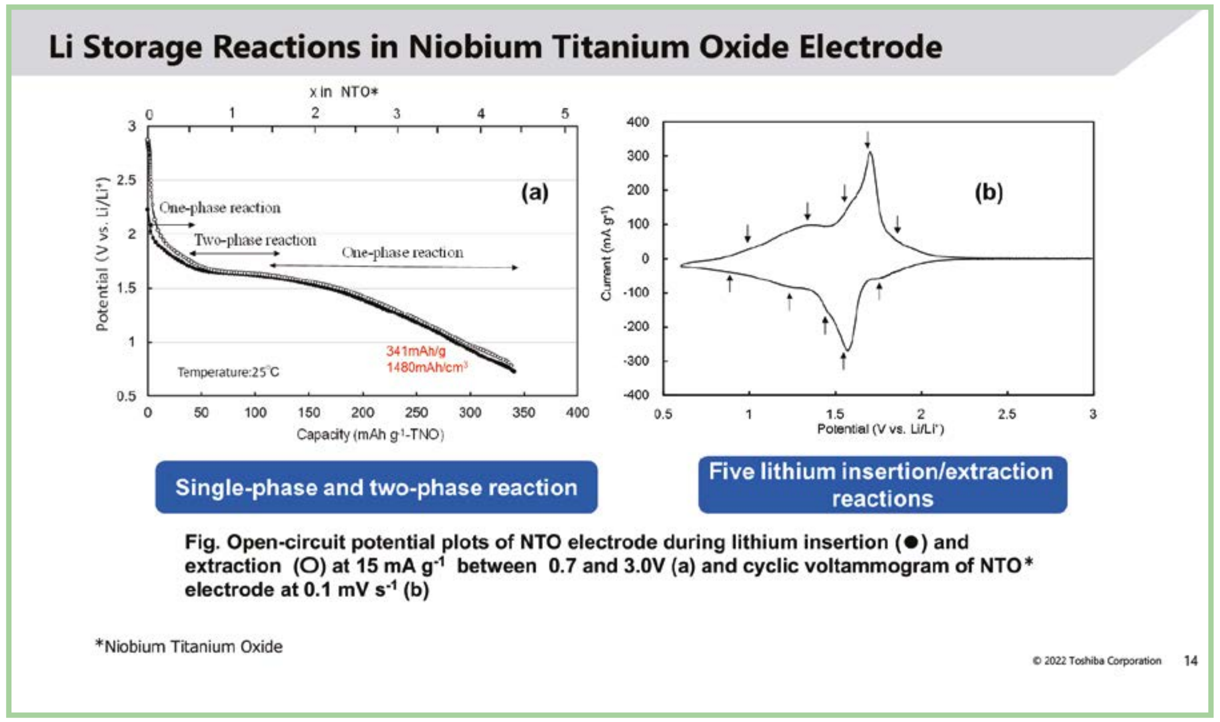
© 2022 Toshiba Corporation 10

2022 International Conference on Niobium Based Batteries
5TH EDITION



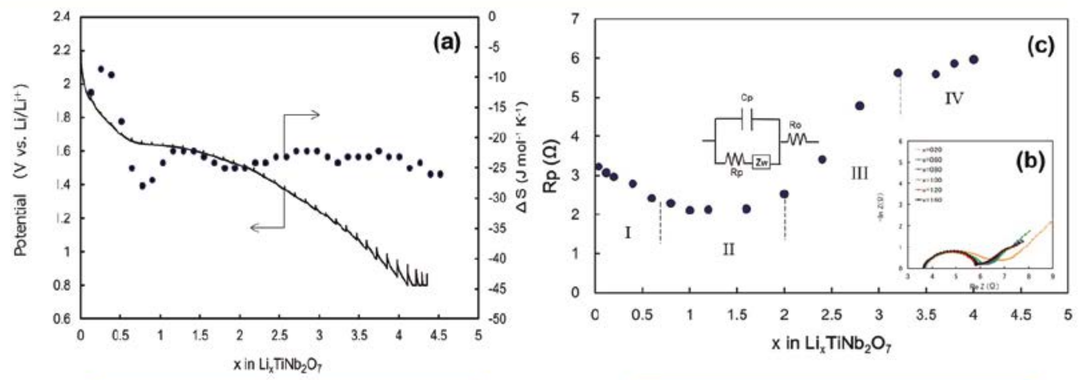






2022 International Conference on Niobium Based Batteries

ΔS and *Rp* on Li Insertion into Niobium Titanium Oxide Electrodes



ΔS during lithium insertion indicates exothermal heat effect

Interface resistance varied as lithium insertion proceeded

Fig. Galvanostatic potential curve with open-circuit potential and ΔS (a), impedance spectra (b), and *Rp* (c) of the NTO* electrodes during lithium insertion at 25℃.

*Niobium Titanium Oxide

© 2022 Toshiba Corporation 15

03

What is the best cell format for **N**iobium **T**itanium **O**xide

*Niobium Titanium Oxide

© 2022 Toshiba Corporation 17

Cell Thickness Change During Charge-Discharge

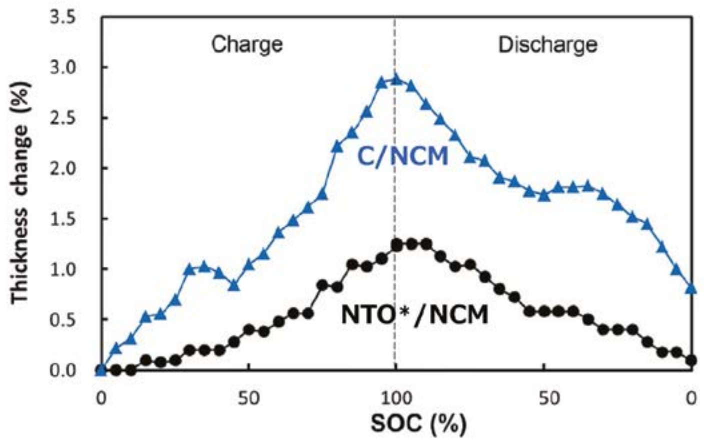


Fig. Change in thickness of NTO*/NCM (●) and graphite/NCM (▲) battery during charge and discharge at 0.2 C rate.

*Niobium Titanium Oxide

© 2022 Toshiba Corporation 16

Specifications of 32 Ah Prototype Prismatic Cell

TENTATIVE

Cathode	NCM
Anode	NTO*
Case	Aluminum prismatic
Dimension (mm)	W116 x D22.3 x H106 mm
Weight (g)	Approx. 570
Max. charge voltage	3.0
Min. discharge voltage	1.5
Nominal voltage (V)	2.25
Designed Capacity (Ah)	**31.6**
Operating temperature	-30 to 60℃
AC impedance (mΩ)	0.54
DC impedance for 0.2 sec (mΩ)	0.98
Energy density	**260 Wh/l**, 124 Wh/kg
10 s output power density	2.8 kW/l, 1.28 kW/kg (SOC50%)
10 s input power density	**6.0 kW/l**, 2.76 kW/kg (SOC50%)

*Niobium Titanium Oxide

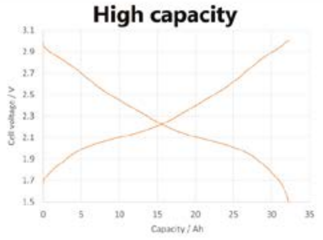
© 2022 Toshiba Corporation 18

Performances of Prismatic Cell Format

TENTATIVE

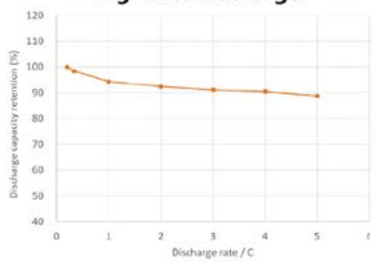
32Ah Prismatic Format

High capacity

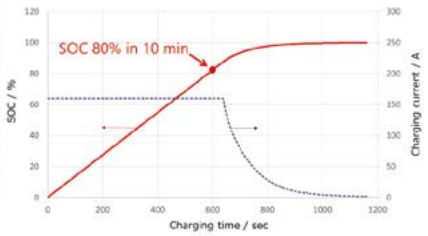


High input power

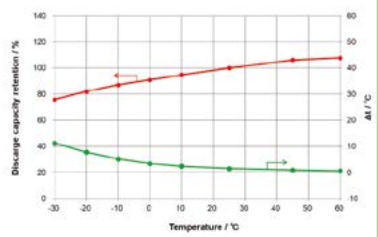
High rate discharge



Super-quick charge



Low temp. performance



© 2022 Toshiba Corporation 19

Found Issue for Prismatic Cell Preparation

TENTATIVE

(a)w/o Clamping (b) Clamping

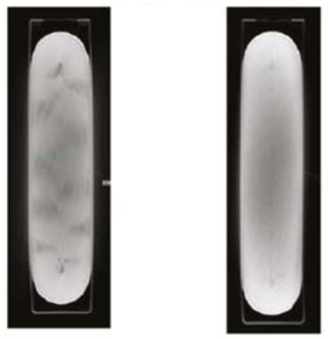


Fig. X-ray CT images for (a) non-clamped and (b)clamped cell.

Fig. Appearance of test cell with clamping zig.

Winding coil requires sufficient clamping during 1st cell formation

© 2022 Toshiba Corporation 20

Target Specification of Niobium Titanium Oxide Cell

TENTATIVE

Good valance between energy and power can be expected by using pouch cell with stacking electrode

※LTO: Lithium Titanium Oxide *Niobium Titanium Oxide

	20Ah LTO※	32Ah NTO*	LFP	NTO* Large Pouch
Capacity	23Ah	31.6Ah	100Ah	55Ah
Anode/Cathode	LTO/NCM	NTO/NCM	C/LFP	NTO/NCM
Electrode/Shell	Winding/Can	Winding/Can	Winding/Can	Stacking/Pouch
Input power	★★★ 5 kW/L	★★★ 6.0 kW/L	⯨ 0.7 kW/L	★★★ 6.5-7.4 kW/L※1
Output power	★★★ 4.0 kW/L	★★ 2.8 kW/L	⯨ 0.4 kW/L	★★⯨ 3.0-3.8 kW/L※1
Energy density	★ 202 Wh/L	★★⯨ 260 Wh/L	★★★ 280 Wh/L	★★★ 300-340 Wh/L※2
Initial cost	★	★	★★★	TBD

※1 : Depending on tab structure ※2 : Volume w/o sealing and tabs

© 2022 Toshiba Corporation 21

Specification of Large Pouch Cell

TENTATIVE

55Ah Large pouch cell using Niobium Titanium Oxide can be successfully produced

Cell Specification

Capacity	55 Ah
Input power	7,400wh/L (Designed value)
Output power	3,900Wh/L (Designed value)
Energy density※	348 Wh/L※ (133 Wh/kg)

※ Volume calculated without tab and sealing area.

55Ah class pouch cell

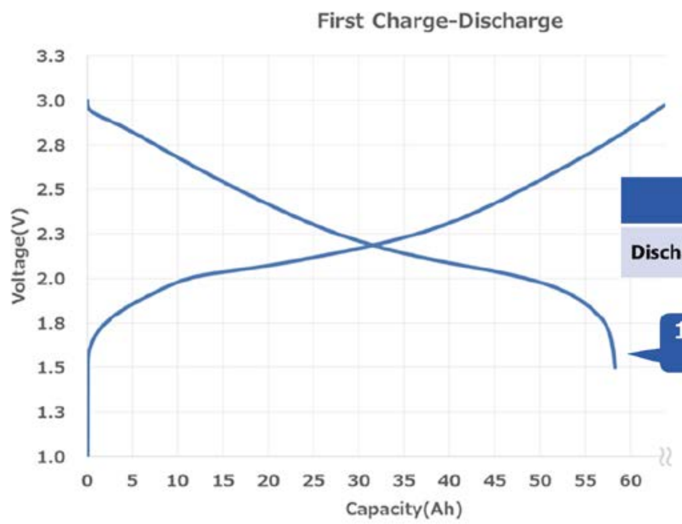
Cell appearance of after capacity check process

© 2022 Toshiba Corporation 22

2022 International Conference on Niobium Based Batteries

55Ah Large Pouch Cell Charge-Discharge Curve

TENTATIVE



	Designed	Measured
Discharge capacity (Ah)	56.8	58.3

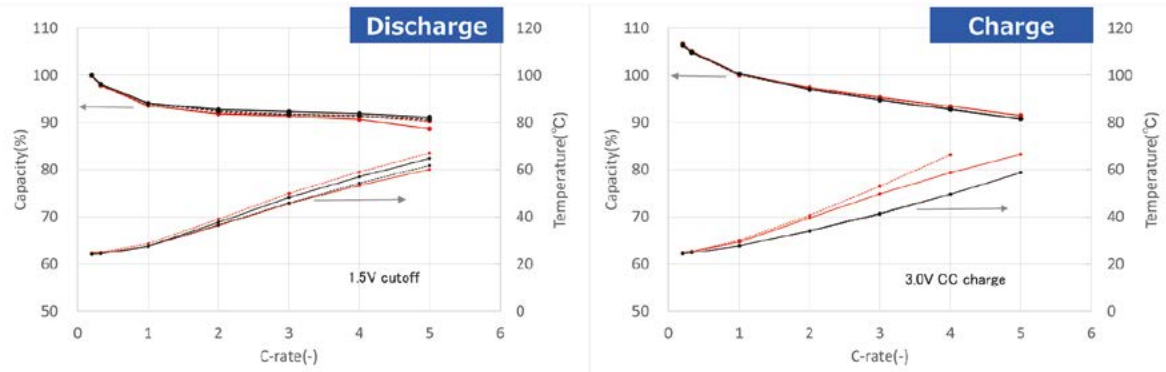
1st Discharge 58.3 Ah

© 2022 Toshiba Corporation 23

Rate Capability

TENTATIVE

90% capacity retention is available even at 5C (275A) rate @25℃

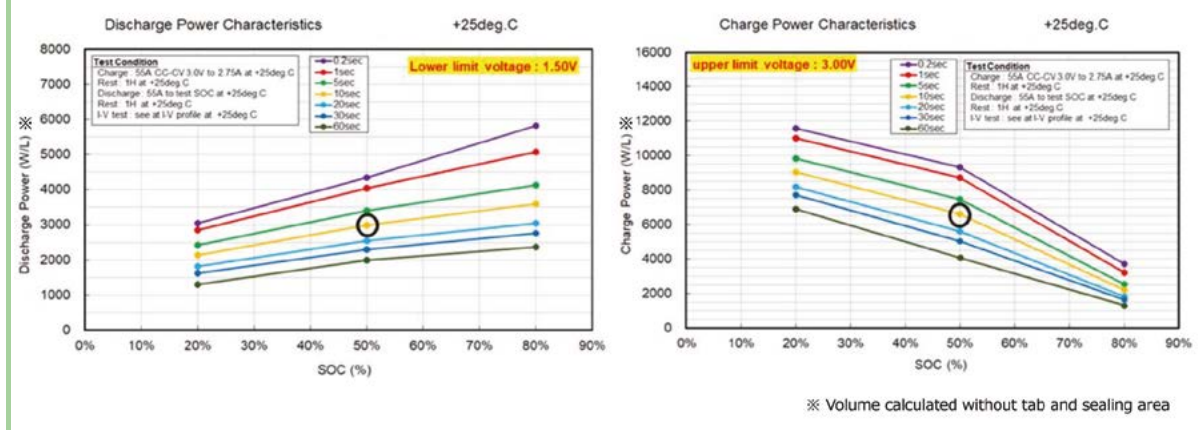


© 2022 Toshiba Corporation 25

Power Capability

TENTATIVE

Trial produced pouch cell showed higher 10 sec power than prismatic
Output 2983 W/L※ (Prismatic x1.23), Input 6605 W/L※ (x1.13)



※ Volume calculated without tab and sealing area

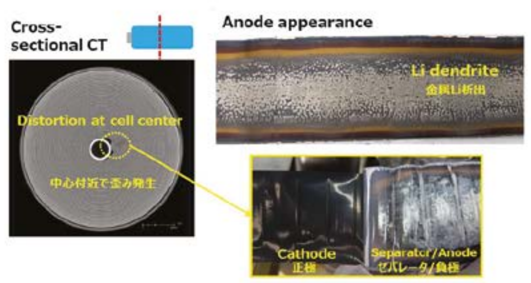
© 2022 Toshiba Corporation 24

Safety Test Results

TENTATIVE

Niobium Titanium Oxide 55Ah Cell

FYI: LFP Cell



Lithium dendrite risk after long cycling

© 2022 Toshiba Corporation 26

Summary

01 NTO* anode material has double the volumetric capacity of graphite, which is a promising candidate for alternative anode to LTO※.

02 The best scenario of NTO* cell design seems to be pouch cell format with stacking electrode. However, reliability and durability of pouch cell format for long term usage should be tested.

03 This new high energy density battery containing Nb makes it possible to expand the cruising range of EVs comparable to LFP chemistry battery with a short charging time within 10 minutes, and is expected to improve the usability of commercial EVs.

※LTO: Lithium Titanium Oxide *Niobium Titanium Oxide

© 2022 Toshiba Corporation 27

2022 International Conference on Niobium Based Batteries

5TH EDITION

Notes

Notes

Notes

Dr. Rahul Fotedar

Morrow Batteries AS

RAHUL FOTEDAR博士是MORROW BATTERIES AS的首席技术官和联合创始人之一。RAHUL拥有图明钦大学化学硕士学位和苏黎世大学电池材料专业博士学位。他曾在奥斯陆的能源技术研究所担任职员科学家，在那里他开创了他们在二次电池领域的研究。2013年，他共同创立了石墨烯电池公司，这是一家专注于开发主要用于无重金属电池的技术的初创公司。在加入MORROW之前，他在HILTI CORPORATION担任高级细胞技术专家多年，领导分化细胞技术的开发和产业化活动。

Dr. Rahul Fotedar is the Chief Technology Officer and one of the co-founders of Morrow Batteries AS. Rahul holds a Masters degree in Chemistry from TU München and a PhD degree specializing on battery materials from ETH Zürich. He has previously worked as staff scientist in Institute of Energy Technology near Oslo where he pioneered their research activities in the field of secondary batteries. In 2013, he co-founded Graphene Batteries AS, a startup focused on developing technologies primarily for heavy metal free batteries. Prior to joining Morrow he was working for many years as an expert in advanced cell technology in Hilti Corporation leading activities on developing and industrializing differentiated cell technologies.

2022 International Conference on Niobium Based Batteries

5TH EDITION

Commercialization of Next-gen Batteries Based on Niobium Based Chemistries

Dr. Rahul Fotedar
Morrow Batteries AS

Abstract

Morrow Batteries, through close collaboration with industrial partners, including Echion Technologies, Haldor Topsoe, Arkema and others, has developed a cell design utilizing a niobium-based anode material with an ultralong cycle life (projected to reach well over 10 000 cycles in the final cell). Coupled with a high voltage LNMO cathode, this cell not only offers superior cycle life and highly competitive energy density, but also excellent safety and sustainability. Morrow has previously demonstrated these features in lab-produced cells, whereas the focus has now shifted to upscaling – making larger cells using industrial equipment. The final product has the potential to revolutionize existing applications and open completely new application areas.

Notes

2022 International Conference on Niobium Based Batteries

5TH EDITION

Notes

Excellent Paper Award Recognition for Research on Niobium Based Batteries

Winning Paper Presentation

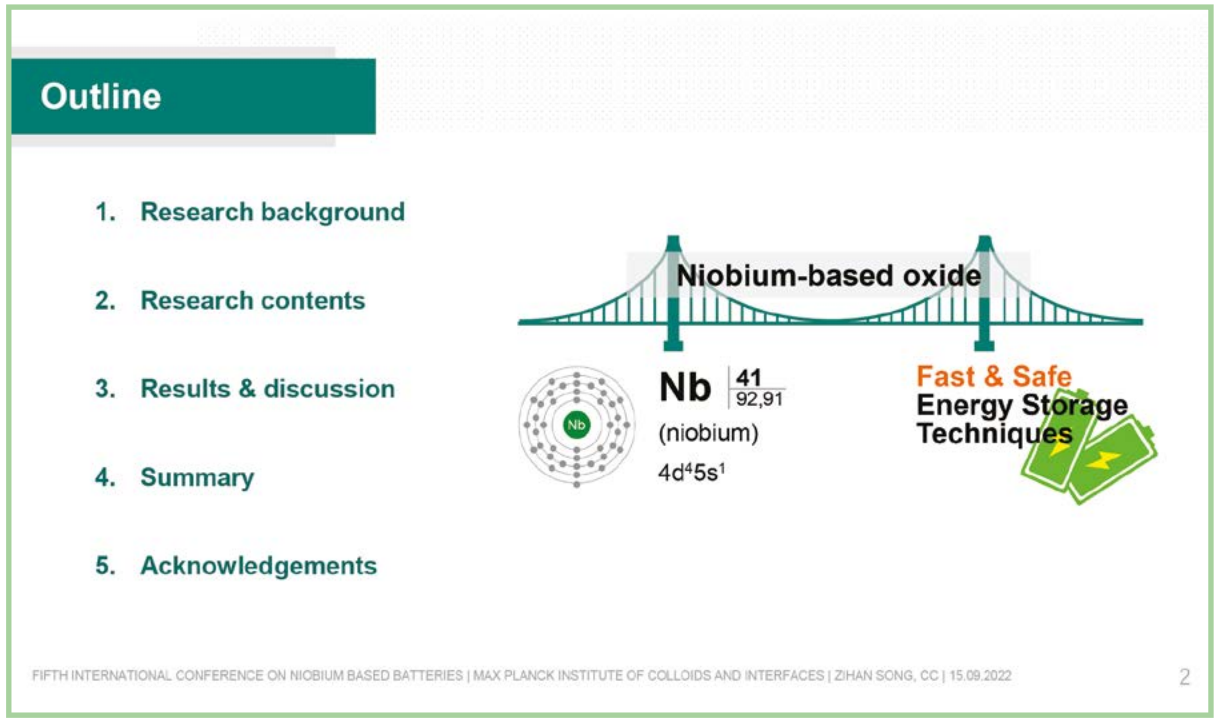
Ultrafast and Stable Li-(De)intercalation in a Large Single Crystal H-Nb_2O_5 Anode via Optimizing the Homogeneity of Electron and Ion Transport

Advanced Materials, 2020, 32 (22): e2001001. DOI: 10.1002/adma.202001001

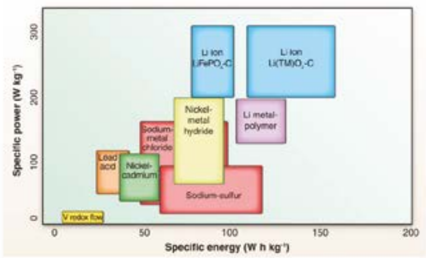
- Zihan Song
- Hui Li
- Wei Liu
- Hongzhang Zhang
- Jingwang Yan
- Yongfu Tang
- Jianyu Huang
- Huamin Zhang
- Xianfeng Li

2022 International Conference on Niobium Based Batteries

5TH EDITION



1. Research background ---- Anode materials for fast chargeable LIBs



Dunn B , Kamath H , Tarascon J M. *Science*, 2011, 334(6058):928-935.

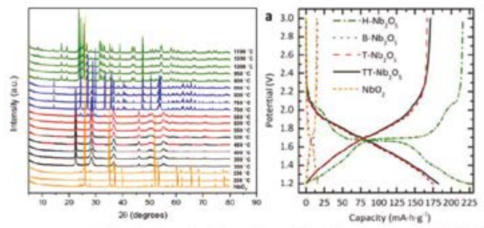
- **Graphite**
  Low Li (de)intercalation potential of < 0.2 V vs Li^+/Li
  Particle fracture and the risk of Li dendrite formation;
  Leading to short circuits and potentially fires and explosions;
- **$Li_4Ti_5O_{12}$ (Lithium titanate, LTO)**
  An average potential of 1.55 V vs Li^+/Li
  High-rate Li (de)intercalation without the risk of Li dendrites;
  Low specific capacity (theoretically 175 mAh g^{-1})

Ideal high-rate anode materials:
- Good electronic conductivity
- Fast Li-ion diffusion kinetics
- Safe (de)intercalation potential range
- High specific capacity

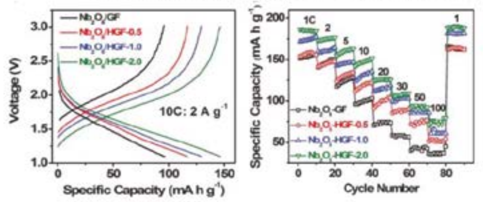
FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 3

1. Research background ---- Niobium-based anode materials

- **Nb_2O_5**
  Various modifications with different heating conditions and preparation procedures:
  $T-Nb_2O_5$, $M-Nb_2O_5$, $H-Nb_2O_5$, etc.
  - **$T-Nb_2O_5$**
    - "Intercalation pseudocapacitive" material —— fast Li storage kinetics;
    - Low electronic conductivity;
    - Limited specific capacity (~200 mAh g^{-1}).
  - **$H-Nb_2O_5$**
    - Higher specific capacity (> 250 mAh g^{-1});
    - Safe operation potential (~1.6 V vs Li^+/Li);
    - Fast Li storage kinetics;
    - Poor cycling stability.



Griffith K J, *et al*. *J. Am. Chem. Soc*. 2016, 138, 8888-8899



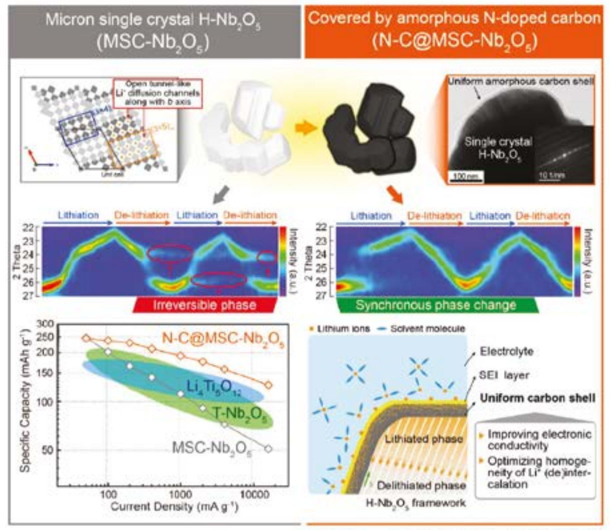
Sun H., *et al*. *Science*. 2017, 356, 599–604

FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 4

2022 International Conference on Niobium Based Batteries
5TH EDITION

2. Research contents ---- $H-Nb_2O_5$ for fast and stable Li storage

- Characteristics of synthesized micrometer single crystal $H-Nb_2O_5$ ($MSC-Nb_2O_5$);
- Understanding on the electrochemical Li storage behaviors of $MSC-Nb_2O_5$;
- Investigating the Li storage mechanism of $MSC-Nb_2O_5$ via operando/in-situ characterization methods;
- Interfacial modification with amorphous N-doped carbon shell ($N-C@MSC-Nb_2O_5$) and the improvement in fast Li storage performance.

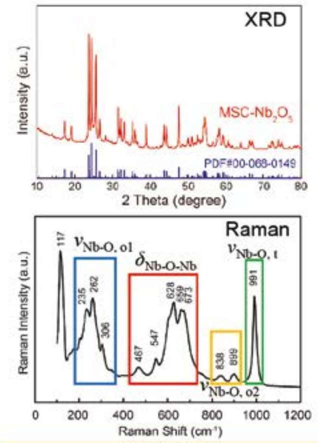


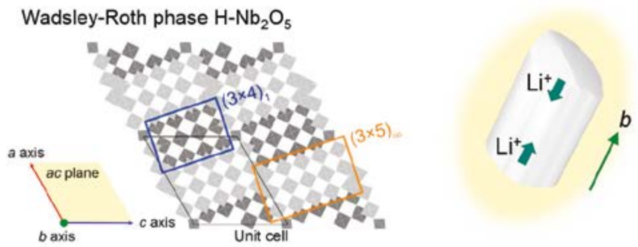
Zihan Song, *et al*. *Adv. Mater.*, **2020**, 2001001.

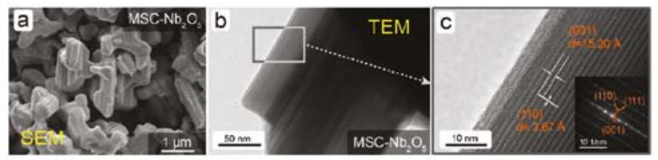
FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 5

3. Results & discussion ---- Characteristics of $MSC-Nb_2O_5$

- **Structural and morphological features of micrometer single-crystal $H-Nb_2O_5$ ($MSC-Nb_2O_5$)**







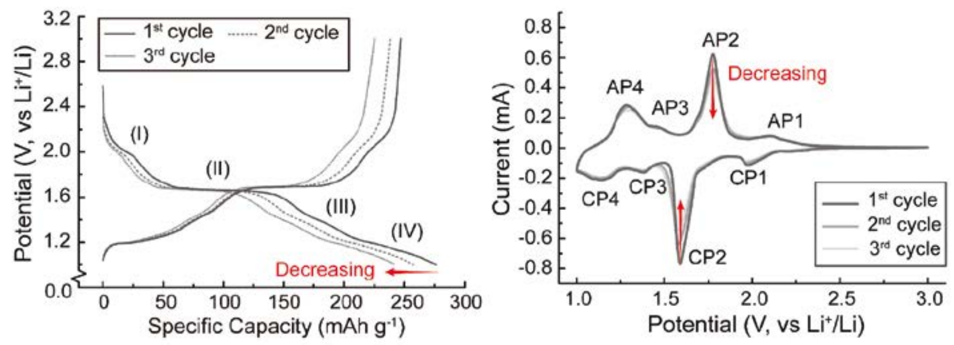
- $MSC-Nb_2O_5$ has continuous and fast Li^+ diffusion channels parallel to *b* axis.

FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 6

2022 International Conference on Niobium Based Batteries

3. Results & discussion ---- Electrochemical analysis

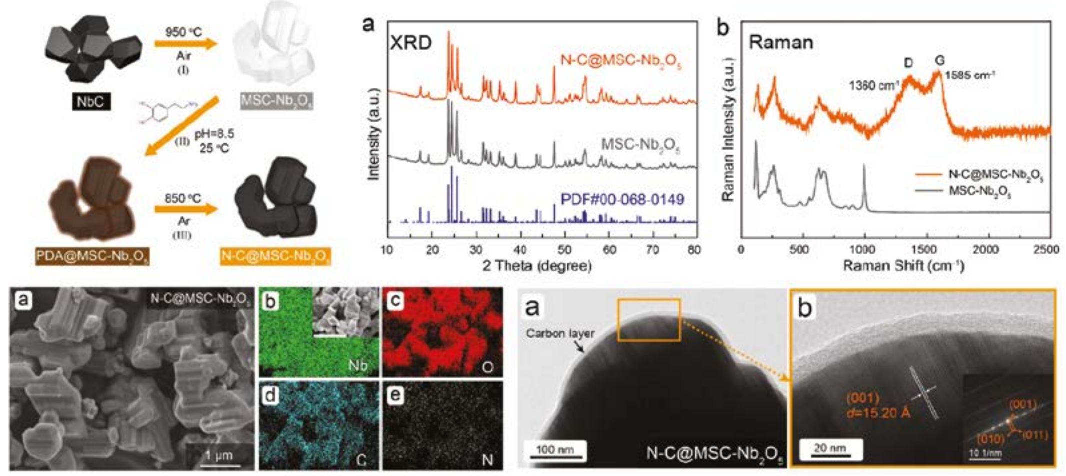
- Electrochemical Li storage behavior of MSC-Nb_2O_5



- High initial capacity of approximately 250 mAh g^{-1} and low polarization voltage of about 0.03V ;
- Rapid fading of capacity in the first 3 cycles, as well as that of response peak currents in CV.

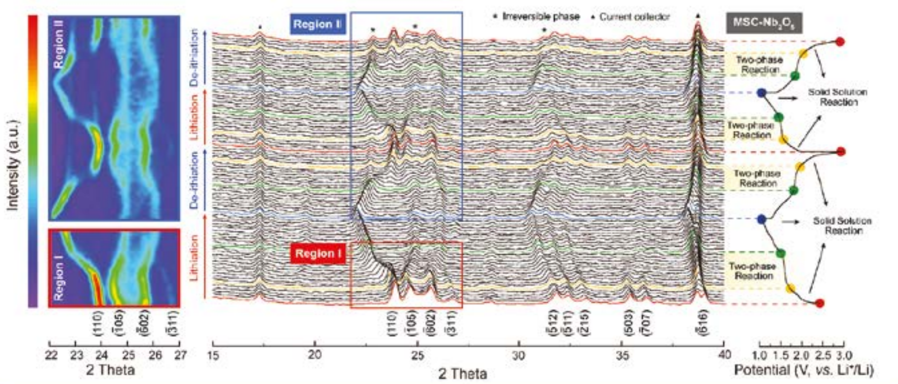
3. Results & discussion ---- Characteristics of N-C@MSC-Nb_2O_5

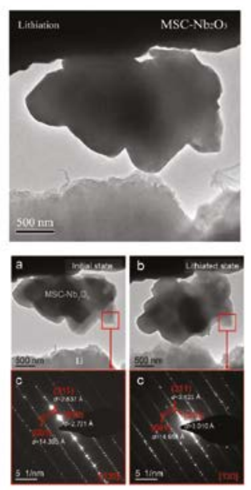
- Interfacial modification with amorphous N-doped carbon shell (N-C@MSC-Nb_2O_5)



3. Results & discussion ---- Investigation of Li storage mechanism

- Operando/in-situ characterizations of MSC-Nb_2O_5 during lithiation/de-lithiation processes

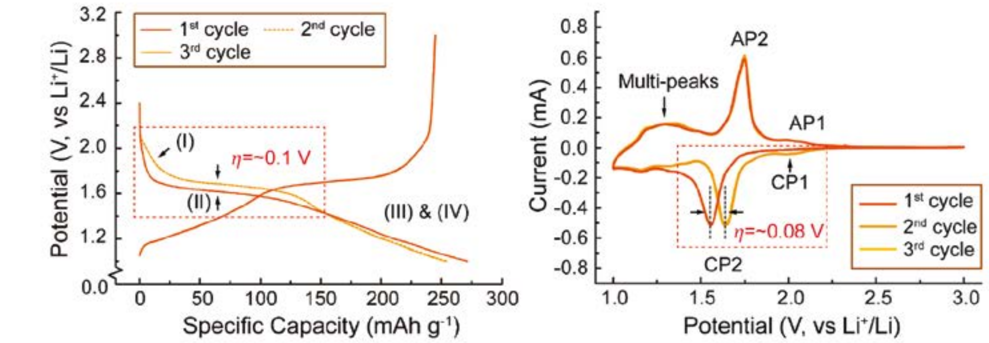




- The orientation of Li^+ diffusion in H-Nb_2O_5 is parallel with crystal expansion vector;
- Irreversible phases are observed during delithiation process.

3. Results & discussion ---- Electrochemical analysis

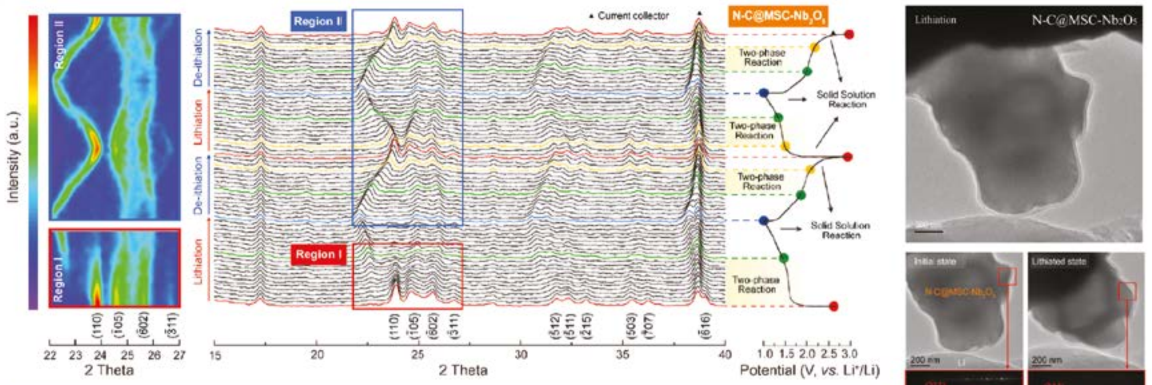
- Electrochemical Li storage behavior of N-C@MSC-Nb_2O_5



- The charge/discharge curves show improved cycling stability with smooth and slopy plateaus;
- An increased overpotential in the first lithiation process due to the modification of interfacial charge transport feature by introduced an amorphous N-doped carbon shell.

3. Results & discussion ---- Investigation of Li storage mechanism

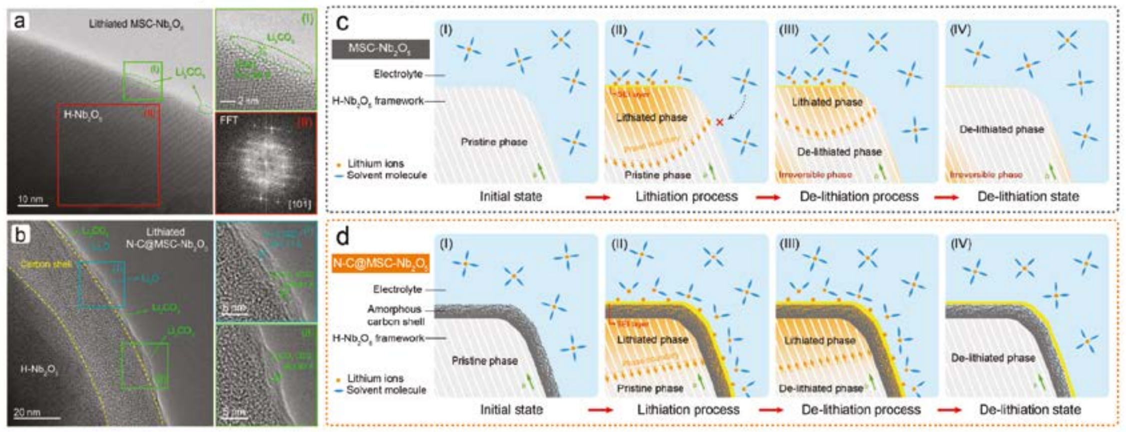
◻ Operando/in-situ characterizations of N-C@MSC-Nb_2O_5 during lithiation/de-lithiation processes



- ➢ Reversible phase transition without the formation of irreversible phases;
- ➢ Optimized homogeneity of Li-(de)intercalation in both interface and bulk phase.

3. Results & discussion ---- Investigation of Li storage mechanism

◻ Ex-situ TEM images of lithiated samples



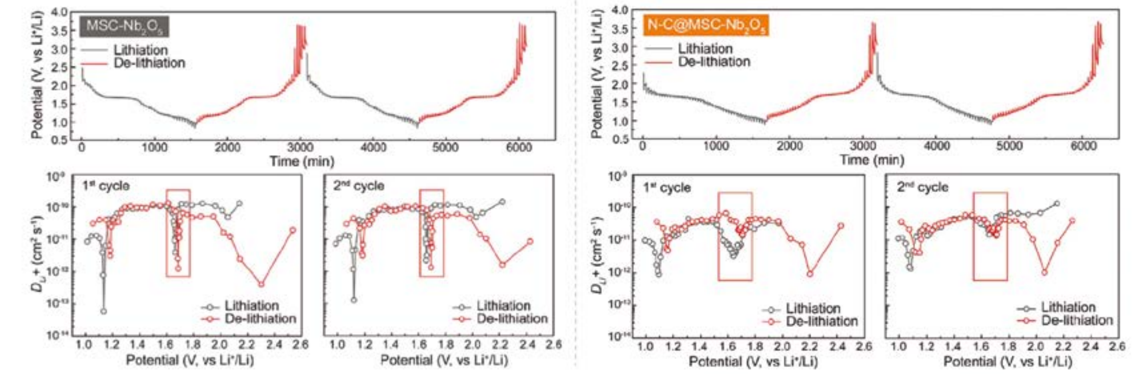
➢ The uniform amorphous carbon shell removes the anisotropy of charge transport of H-Nb_2O_5 in the interfacial region and facilitate the delivery of desolvated Li^+ between electrolyte and active facets of H-Nb_2O_5.

2022 International Conference on Niobium Based Batteries

5TH EDITION

3. Results & discussion ---- Electrochemical reaction kinetics

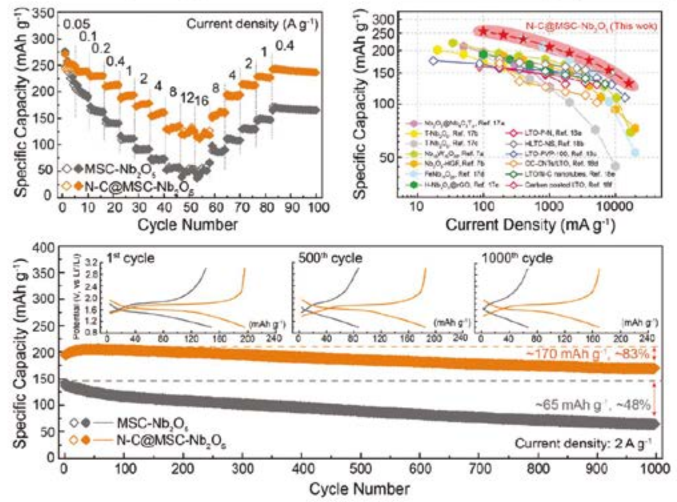
◻ Investigation of electrochemical reaction kinetics of MSC-Nb_2O_5 and N-C@MSC-Nb_2O_5



- ➢ The Li^+ chemical diffusion coefficients of H-Nb_2O_5 are in the range of 10^{-12}~10^{-10} $cm^2\ s^{-1}$;
- ➢ The Li storage kinetics of H-Nb_2O_5 are improved due to unfirm phase transitions in bulk particles.

3. Results & discussion ---- Improved Li storage performance

◻ The comparison of rate and cycling performances between MSC-Nb_2O_5 and N-C@MSC-Nb_2O_5



4. Summary

- The parallel orientations of ion diffusion and crystal expansion vectors of single crystal $H\text{-}Nb_2O_5$ ensures an instinct feature of fast Li storage even in micrometer-sized particles;
- The anisotropy of charge transport of $H\text{-}Nb_2O_5$ in the interfacial regions leads to nonuniform Li^+ flux and phase transition during electrochemical process, causing a degradation of practical performance;
- Interfacial modification with conductive amorphous phase not only optimizes the electronic conductivity, but also performs as a media to minimize the barrier of solvation/desolvation and improves the electrochemical reaction kinetics via facilitating the delivery of desolvated Li^+ between electrolyte and active facets of $H\text{-}Nb_2O_5$.

FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 15

5. Acknowledgements

- Prof. Xianfeng Li, DICP
- Prof. Hongzhang Zhang, DICP
- Prof. Wei Liu, DICP
- Prof. Huamin Zhang, DICP
- Prof. Jingwang Yan

- Prof. Yongfu Tang, YSU
- Hui Li, YSU

This work was supported by:
- National Natural Science Foundation of China
- Youth Innovation Promotion Association of CAS
- Youth Innovation Foundation of DICP
- National Key Research and Development Project

Division of Energy storage (DNL17)

FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 16

2022 International Conference on Niobium Based Batteries

Thank you
For Your Attention

Division of Energy Storage (DNL17)
Dalian Institute of Chemical Physics, Chinese Academy of Sciences
Zhongshan Road 457, Dalian 116023, China
E-mail: zhanghz@dicp.ac.cn; lixianfeng@dicp.ac.cn

Official Account in Wechat
"储能技术研究部"
Website: www.energystorage.dicp.ac.cn

Main Authors

Zihan Song (宋子晗) received his B.S. degree in Applied Chemistry from Tianjin University in 2015. and his Ph.D. degree in Chemical Engineering from University of Chinese Academy of Sciences in 2020. He is currently a postdoctoral researcher in Max Planck Institute of Colloids and Interfaces. His research interest focuses on electrode materials and interfaces for high-energy rechargeable batteries.
***E-mail:** Zihan.Song@mpikg.mpg.de

Hongzhang Zhang (张洪章) is currently a professor in the Division of Energy Storage, Dalian Institute of Chemical Physics (DICP), Chinese Academy of Sciences (CAS) and serves as the group leader of Innovative Battery Technology. He received his B.S. degree from Shandong University in 2008. He received his Ph.D. degree from University of Chinese Academy of Sciences in 2013. His research interests focus on the development of novel batteries with high energy and power density.
***E-mail:** zhanghz@dicp.ac.cn

Xianfeng Li (李先锋) received his Ph.D. degree in Polymer Chemistry and Physics from Jilin University. He was appointed as a full professor at DICP, CAS, in 2012. He currently serves as the head of the energy storage division at DICP. His research interest includes key materials and core technologies of flow batteries (vanadium flow battery, zinc-based flow batteries, and novel flow battery systems), innovation battery technologies (lead carbon battery, supercapacitor and lithium/sodium/potassium/zinc-based battery), the structure design and simulation of batteries as well as battery systems, the testing and evaluation, the industrial development and application demonstration.
***E-mail:** lixianfeng@dicp.ac.cn

FIFTH INTERNATIONAL CONFERENCE ON NIOBIUM BASED BATTERIES | MAX PLANCK INSTITUTE OF COLLOIDS AND INTERFACES | ZIHAN SONG, CC | 15.09.2022 18

Excellent Paper Award Recognition for Research on Niobium Based Batteries

2nd Place Paper Presentation

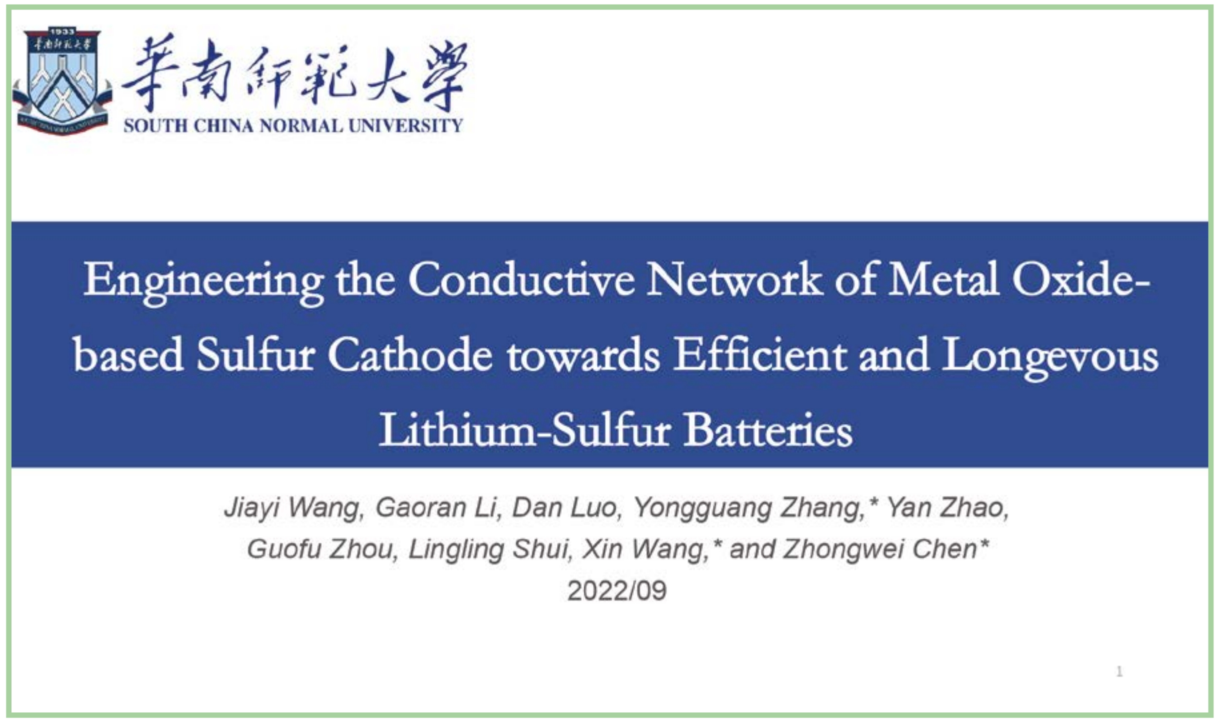
Engineering the Conductive Network of Metal Oxide-Based Sulfur Cathode towards Efficient and Longevous Lithium-Sulfur Batteries

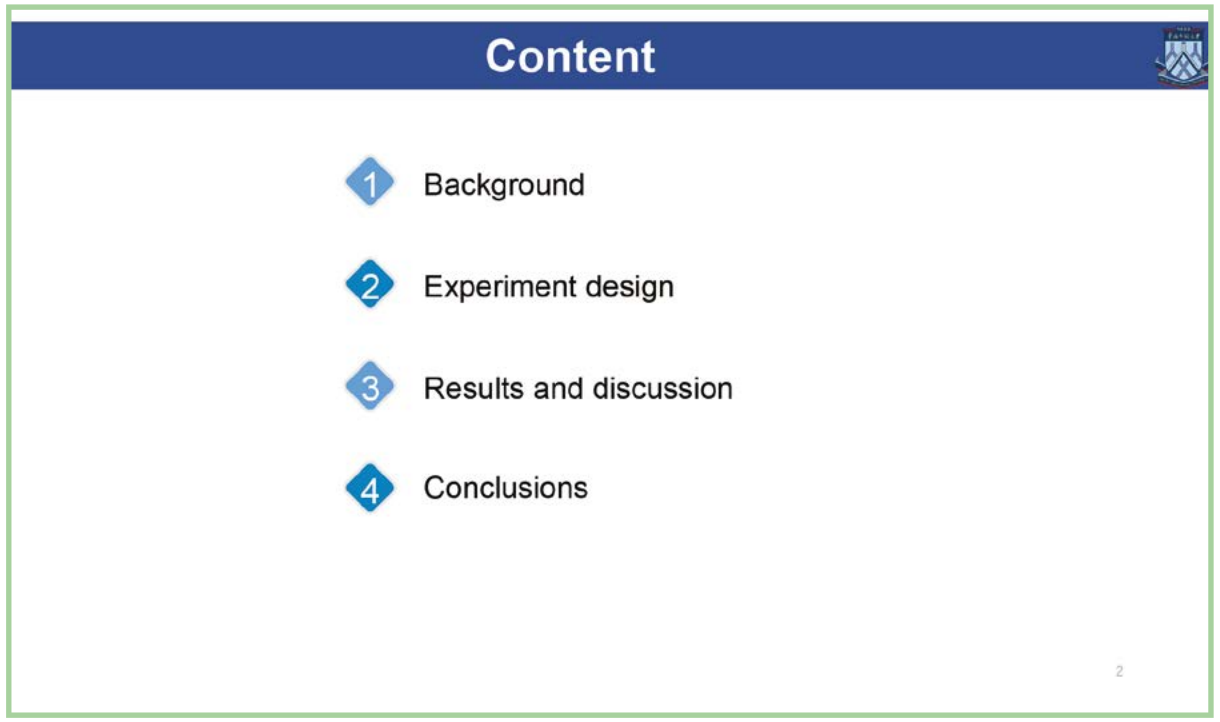
Advanced Energy Materials, 2020, 10(41): e2002076.
DOI:10.1002/aenm.202002076

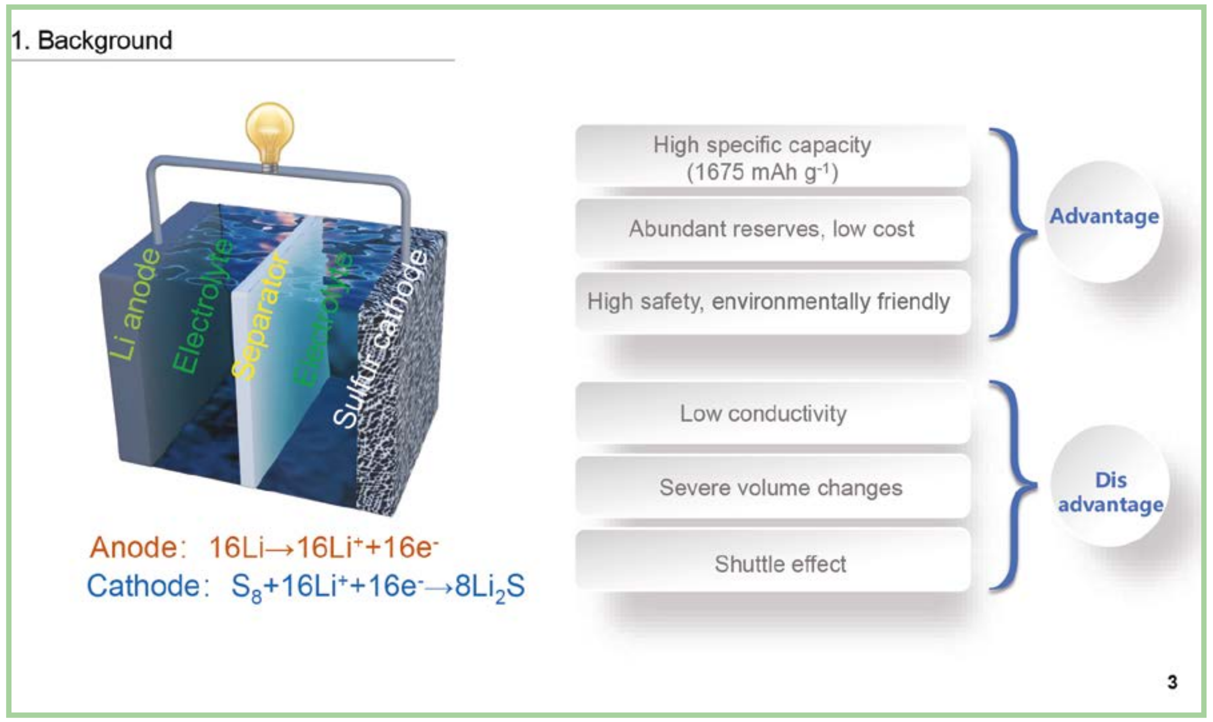
- Jiayi Wang
- Gaoran Li
- Dan Luo
- Yongguang Zhang
- Yan Zhao
- Guofu Zhou
- Lingling Shui
- Xin Wang
- Zhongwei Chen

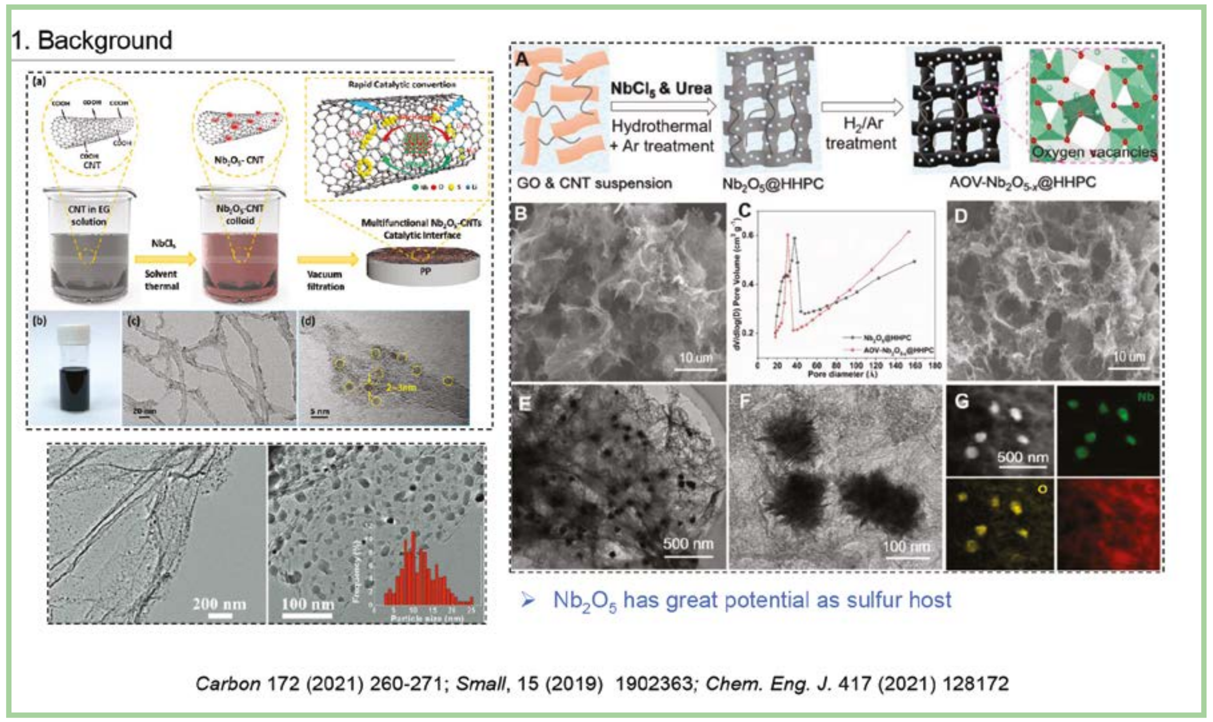
2022 International Conference on Niobium Based Batteries

5TH EDITION

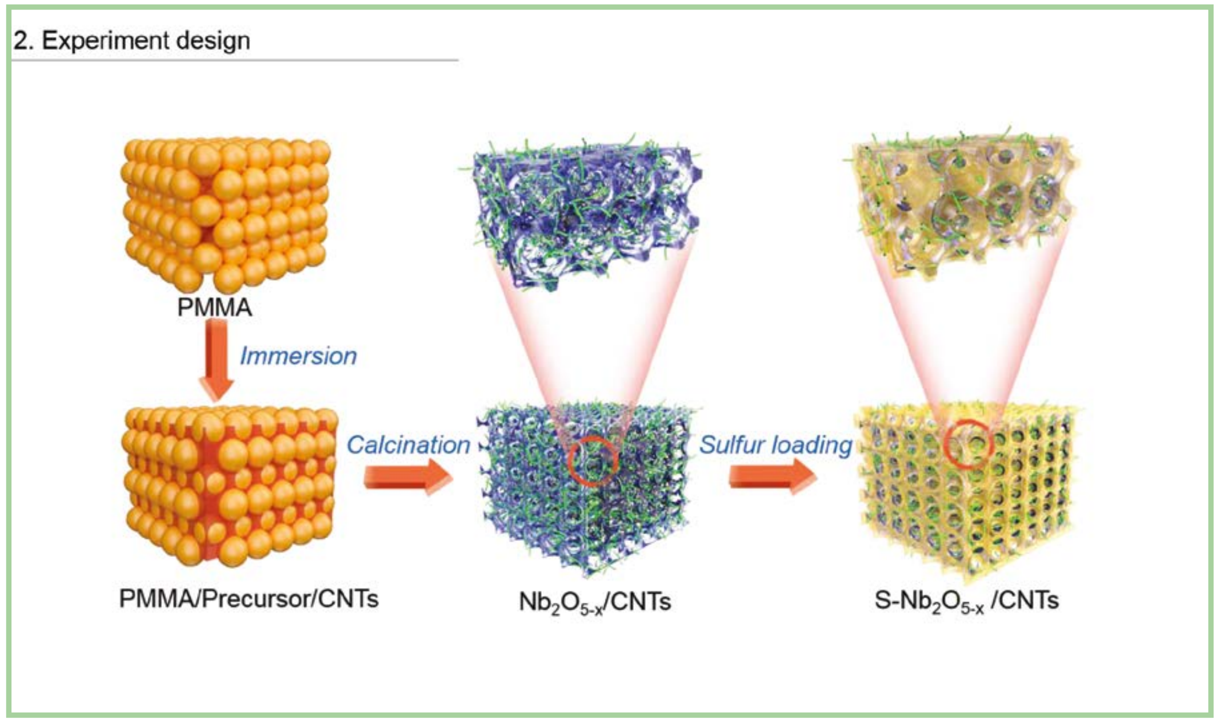


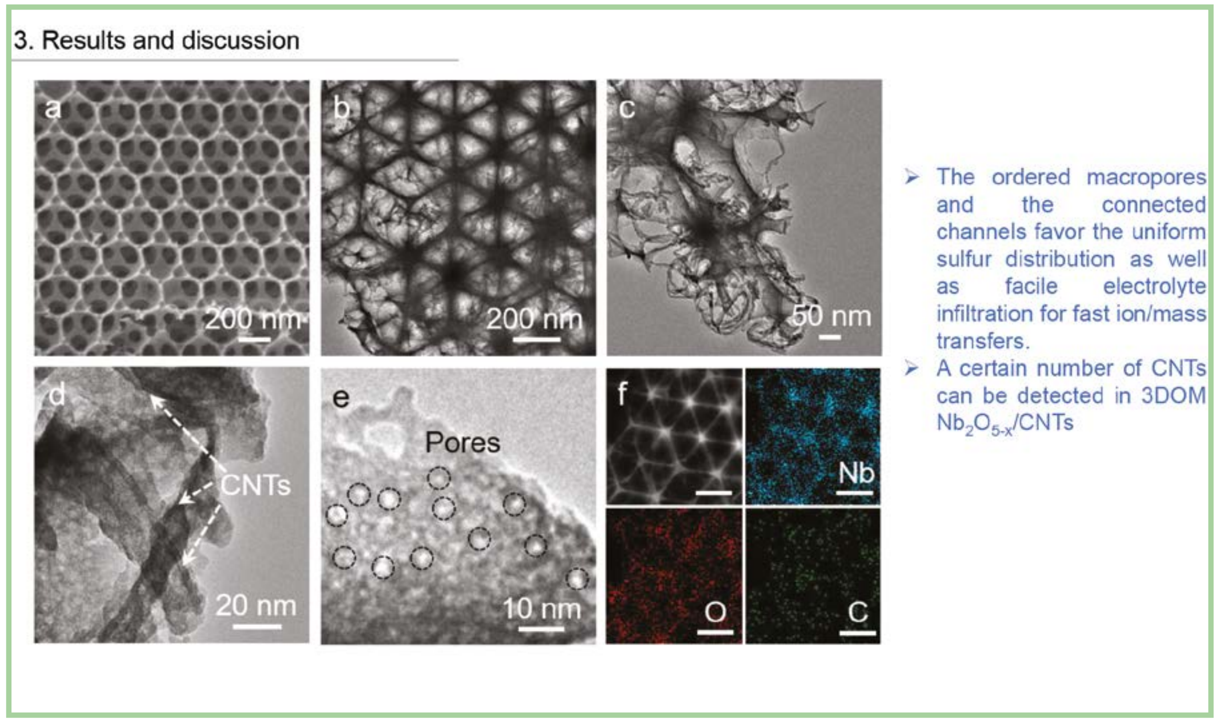




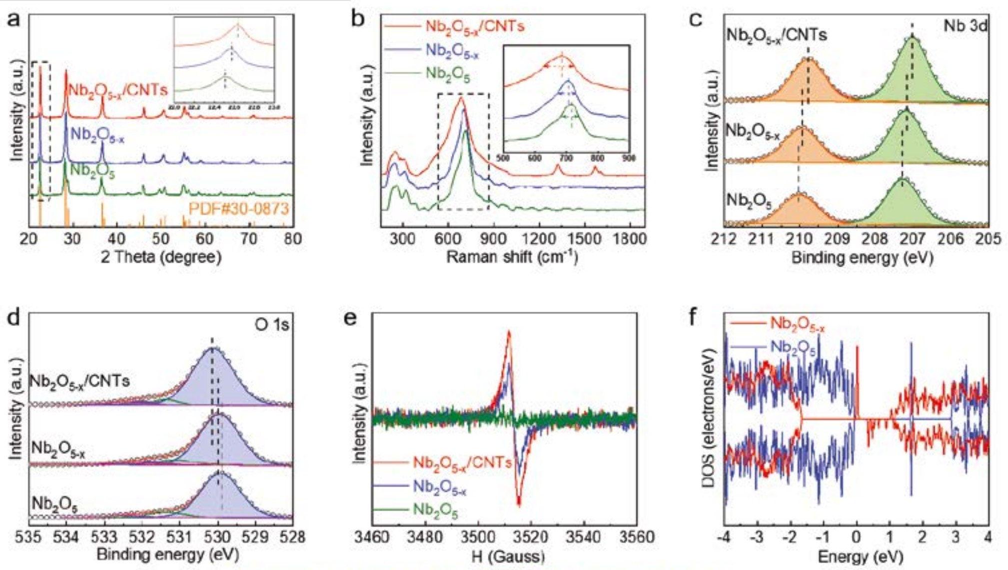


2022 International Conference on Niobium Based Batteries
5TH EDITION



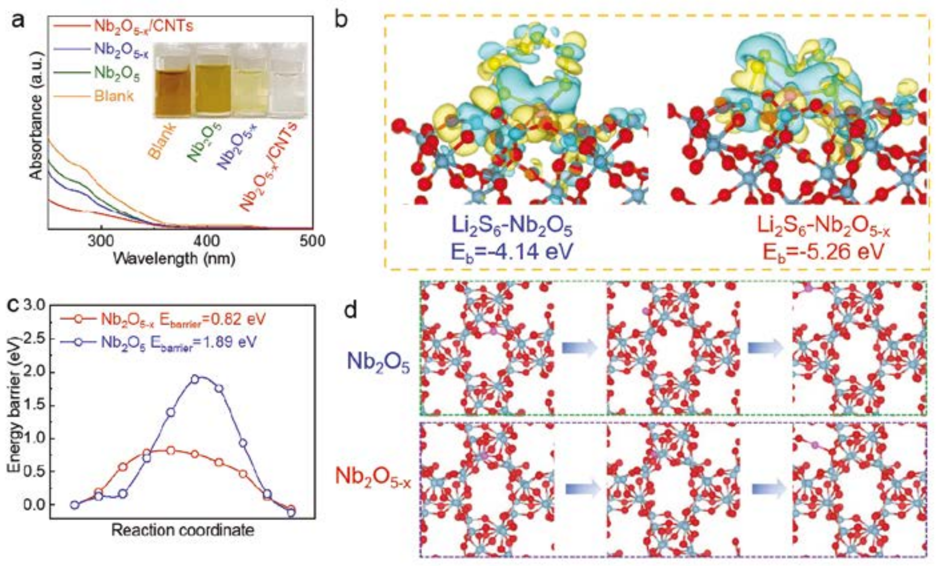


3. Results and discussion



- Oxygen vacancies are introduced simultaneously
- Nb_2O_{5-x} displays a narrowed band gap than that of Nb_2O_5

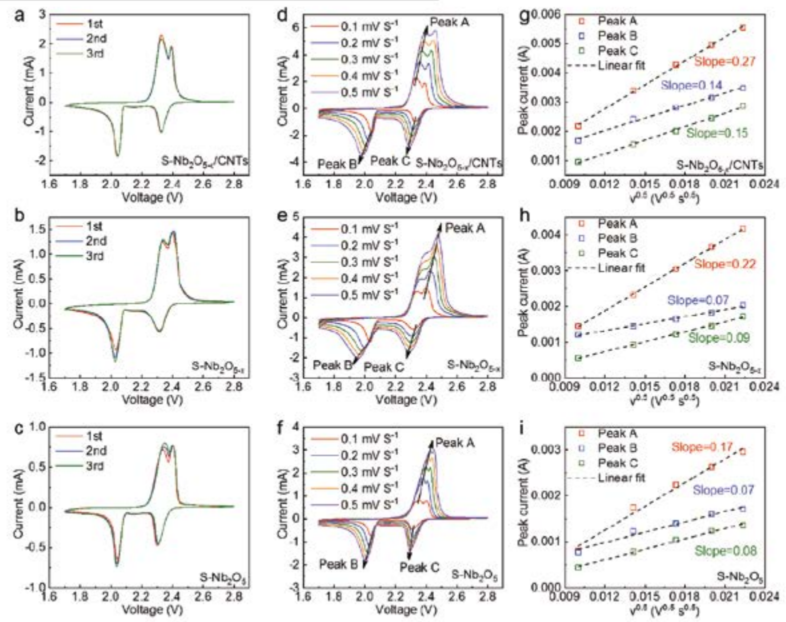
3. Results and discussion



- Strong polysulfide immobilization and fast Li ion transport

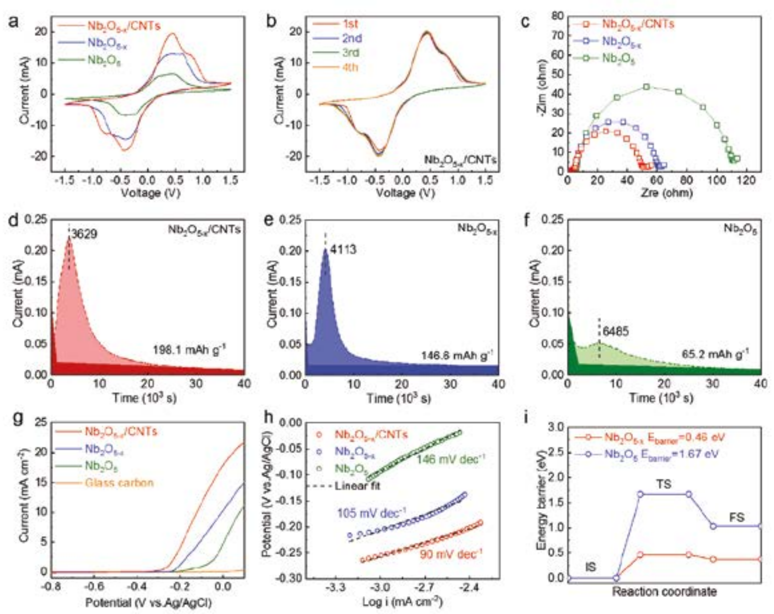
2022 International Conference on Niobium Based Batteries
5TH EDITION

3. Results and discussion



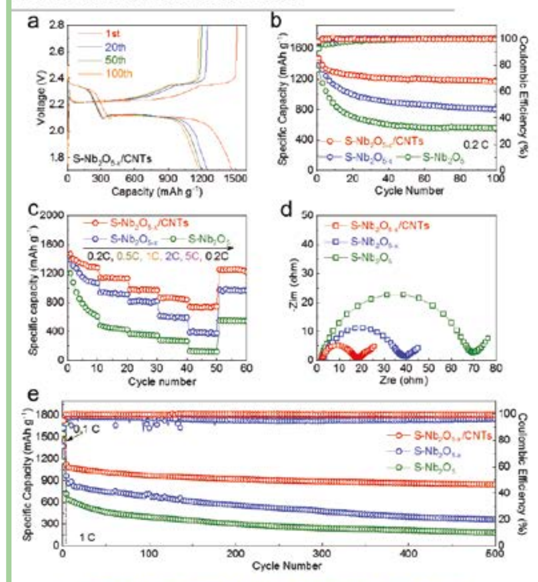
- According to the Randles-Sevick equation, the slope of the fitting line corresponds to the D_{Li+}, which positively reflects the mobility of Li^+ within the electrode. Obviously, the S-Nb_2O_{5-x}/CNTs electrode delivers highest D_{Li+} at all the redox states (peak A, B, and C), strongly confirming the significantly facilitated Li^+ diffusion behaviors by the defect engineering.

3. Results and discussion

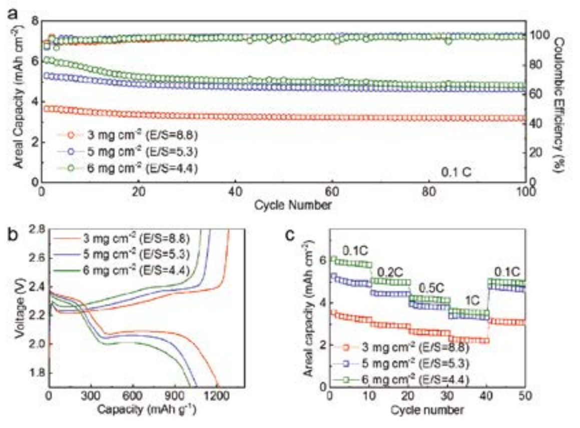


- Symmetric cell test manifest its fastest polysulfide conversion kinetics.
- Li_2S deposition behaviors suggest the reduced energy barrier for the nucleation and growth of Li_2S on Nb_2O_{5-x}/CNTs surface
- The Li_2S oxidization profiles indicate the lower energy barrier to initiate the Li_2S decomposition

3. Results and discussion



➢ Excellent cyclability and rate capability



➢ Great promise in the practical Li-S batteries

4. Conclusions

- ➢ We have developed a unique long-range consecutive and oxygen deficient 3DOM Nb_2O_{5-x}/CNT as advanced sulfur host material in Li-S batteries.
- ➢ The successful implement of defect engineering and CNT embedment renders enhanced conductivity as well as strengthened sulfur adsorpability and catalytic activity, contributing to potent sulfur immobilization and fast reaction kinetics.
- ➢ The construction of the open and 3DOM architecture benefits the facile ion/mass transfer as well as further intensifying the host-guest interactions due to the sufficiently exposed active interfaces.
- ➢ Sulfur electrodes based on Nb_2O_{5-x}/CNTs realized outstanding cyclability over 500 cycles and superb rate performance up to 5 C, as well as impressive areal capacities under raised sulfur loading and limited electrolyte.

2022 International Conference on Niobium Based Batteries
5TH EDITION

華南師範大學
SOUTH CHINA NORMAL UNIVERSITY

Thank you

Excellent Paper Award Recognition for Research on Niobium Based Batteries

3rd Place Paper Presentation

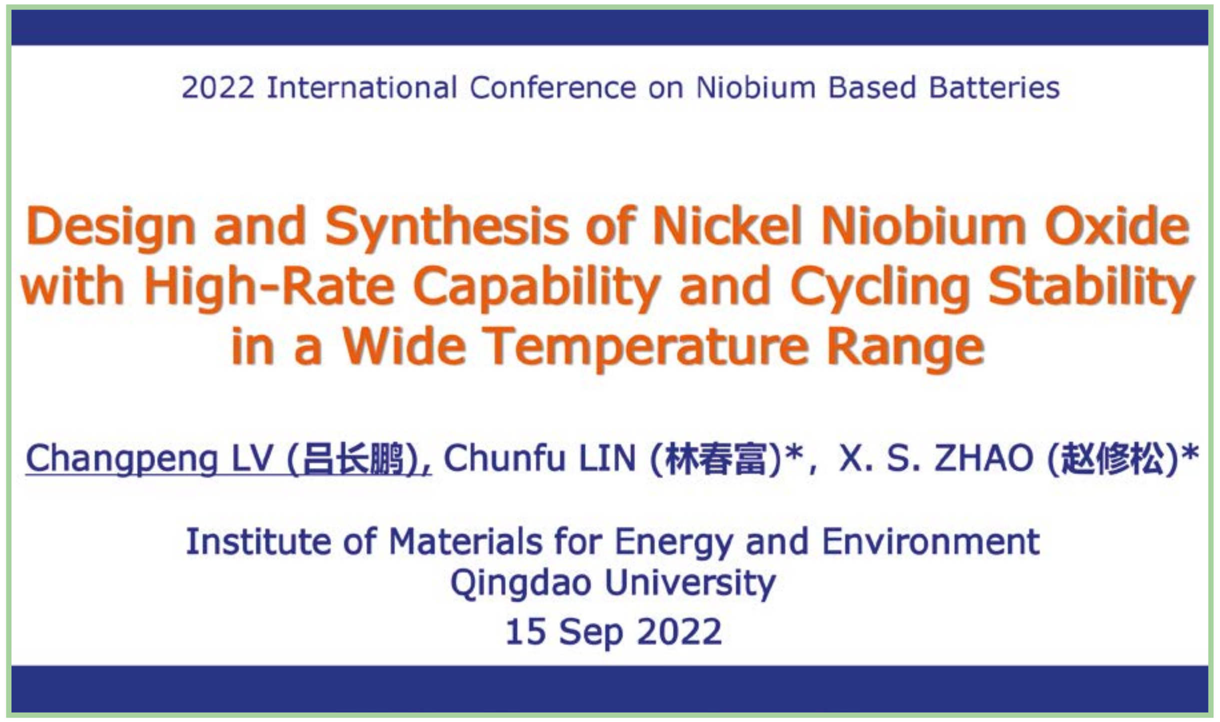
Design and Synthesis of Nickel Niobium Oxide with High-Rate Capability and Cycling Stability in a Wide Temperature Range

Advanced Energy Materials, 2022,12(3): e2102550.
https://doi.org/10.1002/aenm.202102550

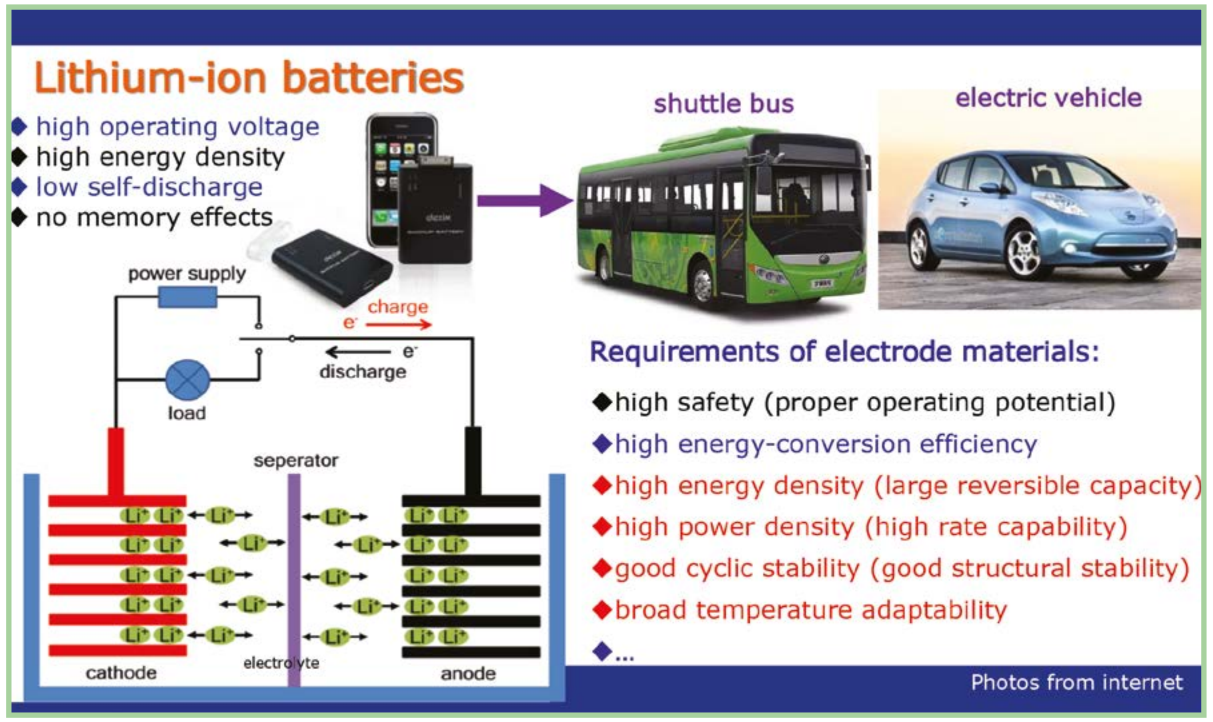
- Changpeng Lv
- Chunfu Lin
- X. S. Zhao

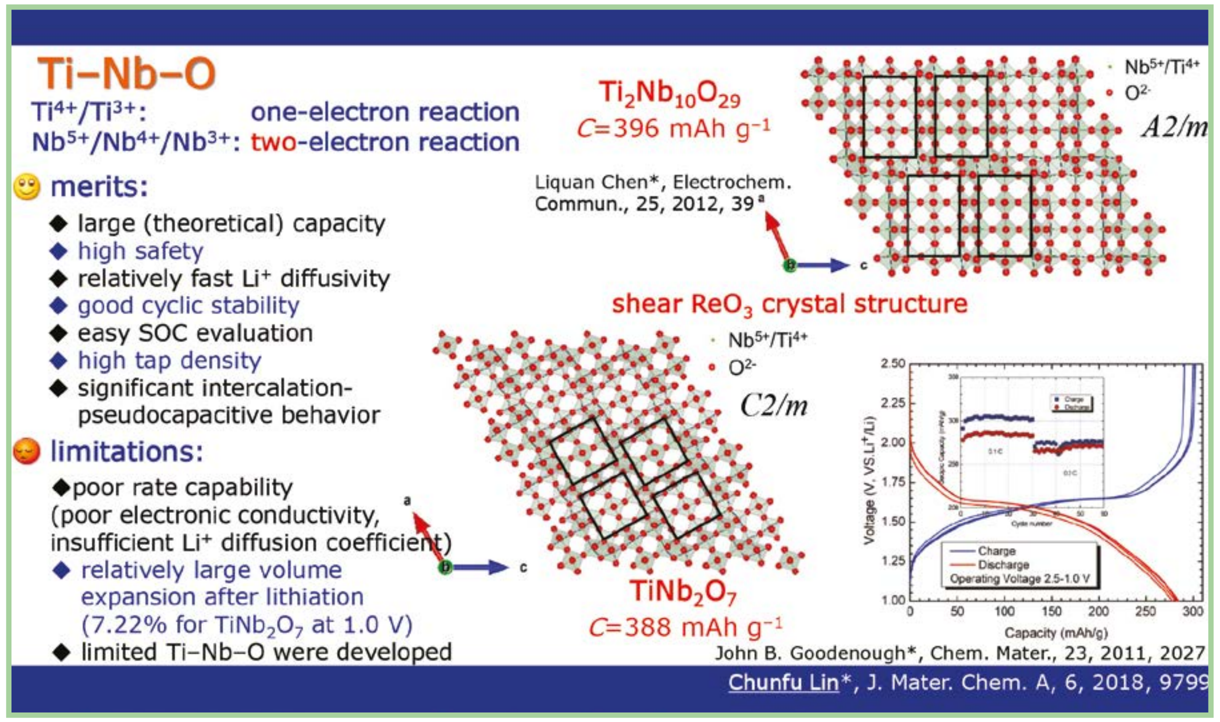
2022 International Conference on Niobium Based Batteries

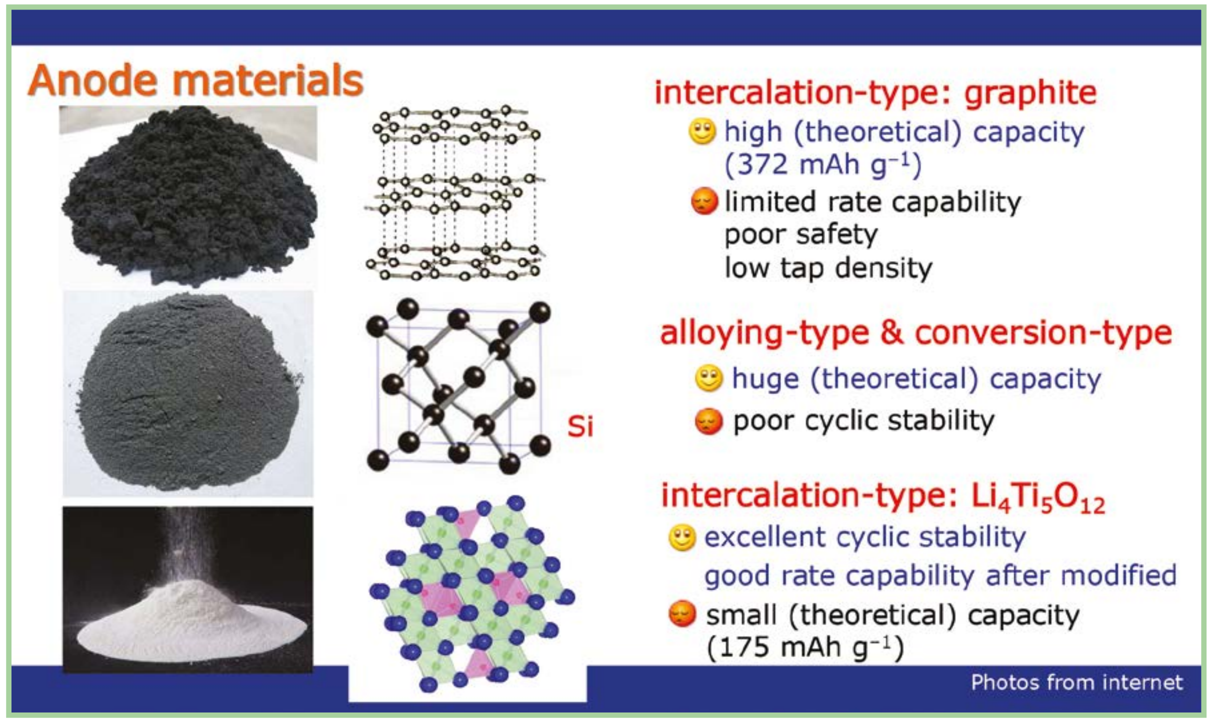
5TH EDITION

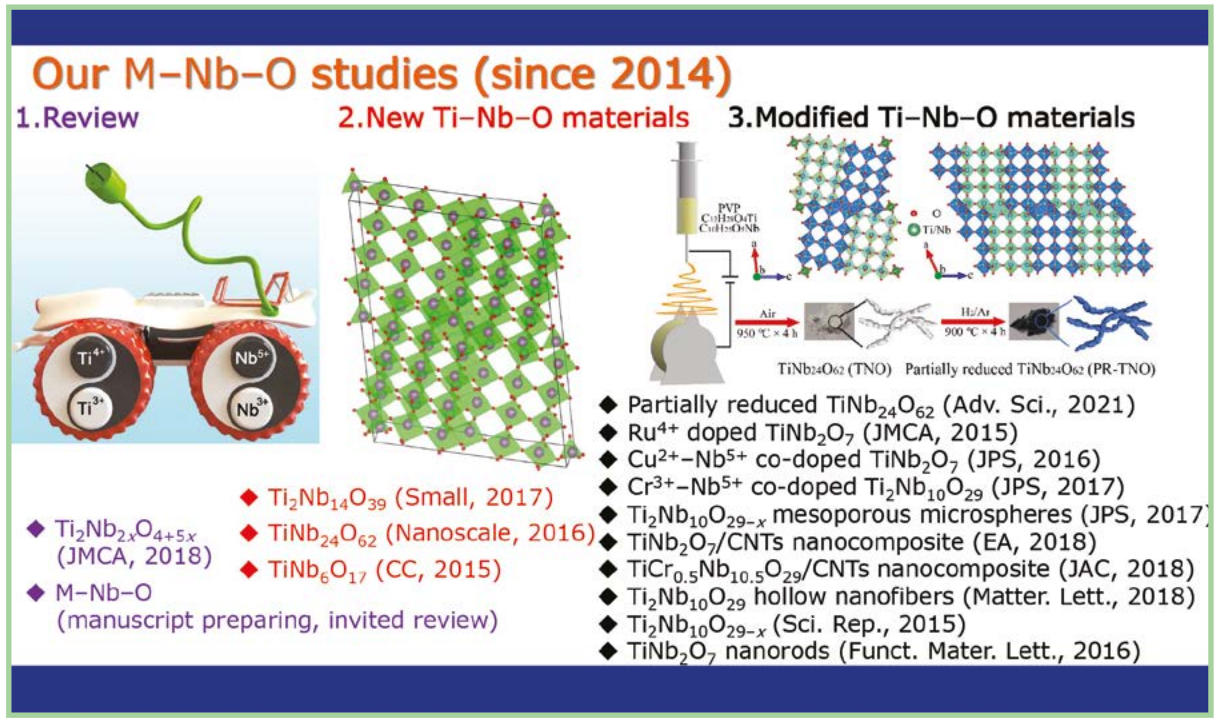


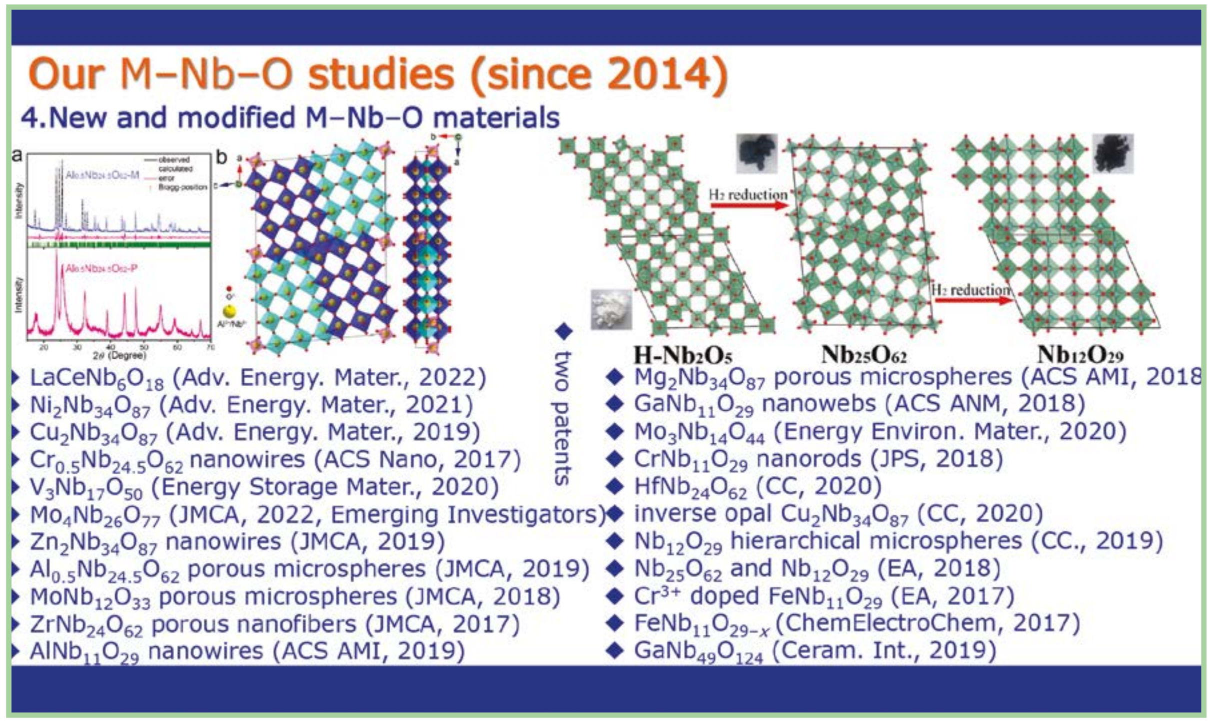
2022 International Conference on Niobium Based Batteries

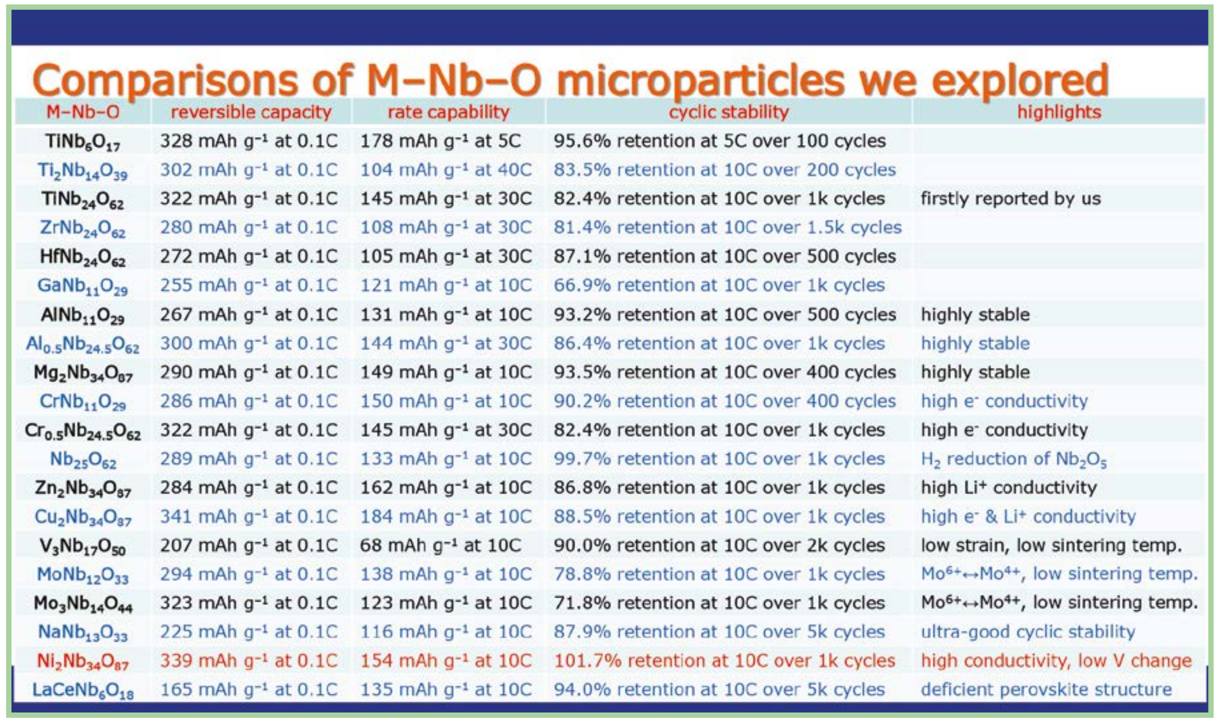






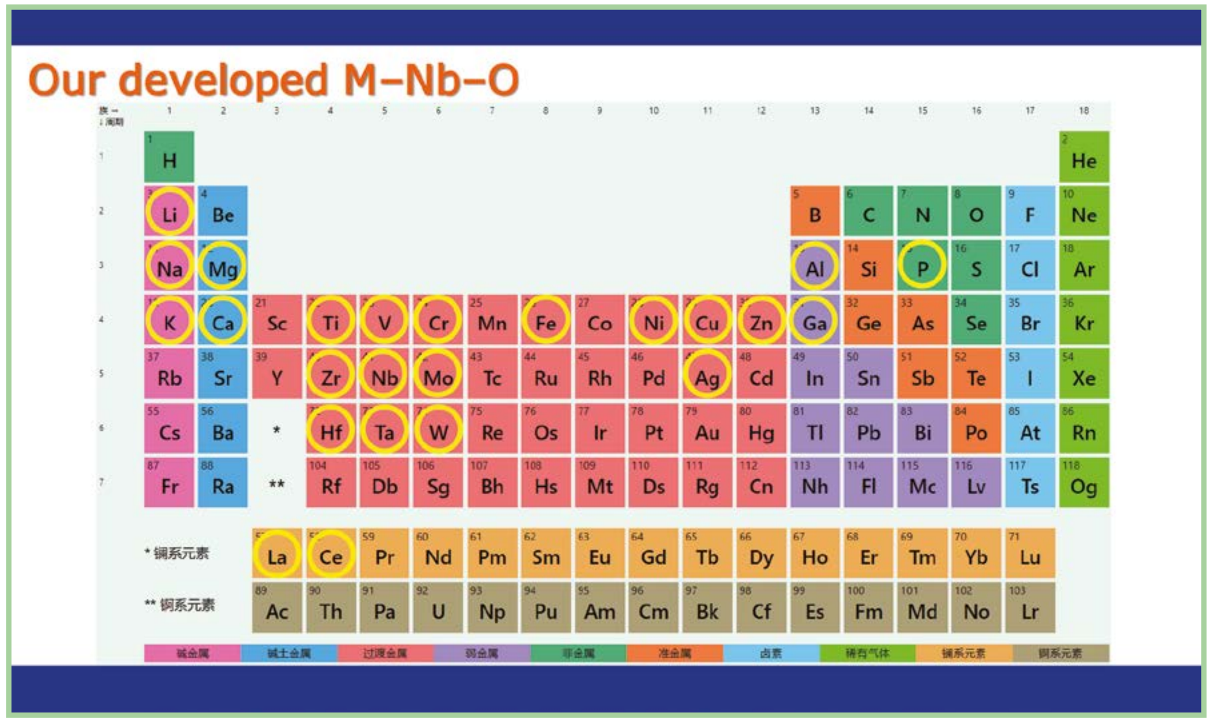


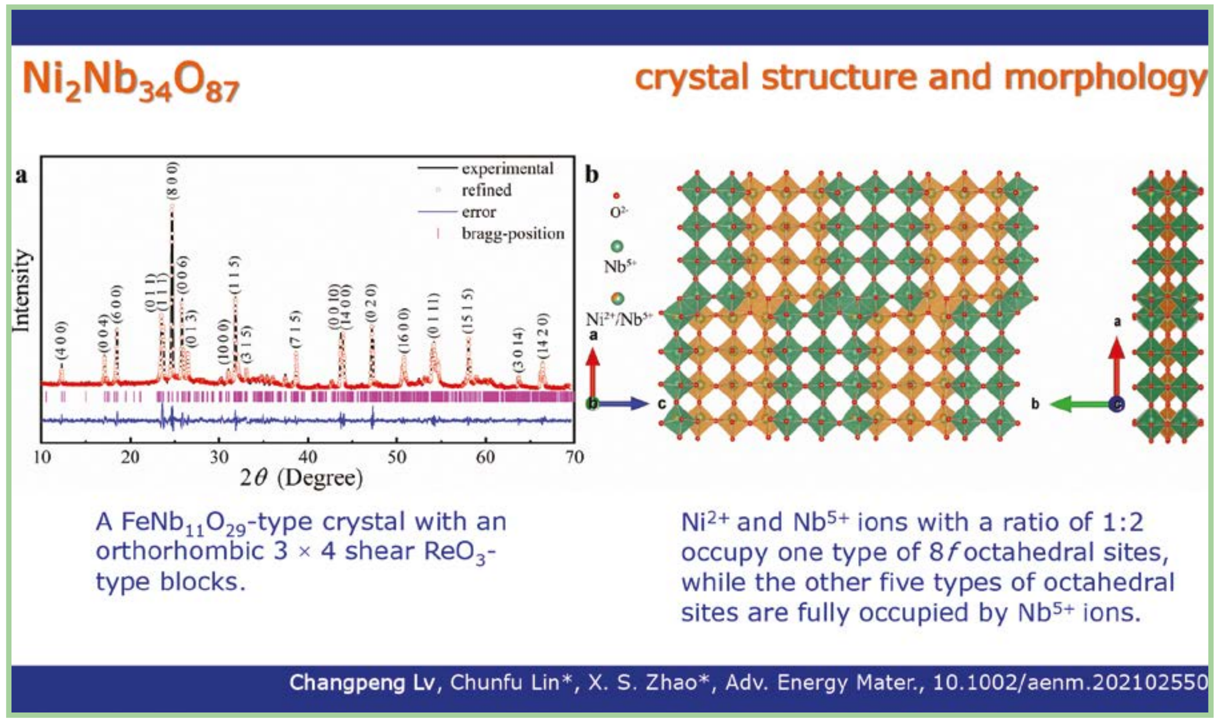




Comparisons of M-Nb-O microparticles we explored

M-Nb-O	reversible capacity	rate capability	cyclic stability	highlights
$TiNb_6O_{17}$	328 mAh g^{-1} at 0.1C	178 mAh g^{-1} at 5C	95.6% retention at 5C over 100 cycles	
$Ti_2Nb_{14}O_{39}$	302 mAh g^{-1} at 0.1C	104 mAh g^{-1} at 40C	83.5% retention at 10C over 200 cycles	
$TiNb_{24}O_{62}$	322 mAh g^{-1} at 0.1C	145 mAh g^{-1} at 30C	82.4% retention at 10C over 1k cycles	firstly reported by us
$ZrNb_{24}O_{62}$	280 mAh g^{-1} at 0.1C	108 mAh g^{-1} at 30C	81.4% retention at 10C over 1.5k cycles	
$HfNb_{24}O_{62}$	272 mAh g^{-1} at 0.1C	105 mAh g^{-1} at 30C	87.1% retention at 10C over 500 cycles	
$GaNb_{11}O_{29}$	255 mAh g^{-1} at 0.1C	121 mAh g^{-1} at 10C	66.9% retention at 10C over 1k cycles	
$AlNb_{11}O_{29}$	267 mAh g^{-1} at 0.1C	131 mAh g^{-1} at 10C	93.2% retention at 10C over 500 cycles	highly stable
$Al_{0.5}Nb_{24.5}O_{62}$	300 mAh g^{-1} at 0.1C	144 mAh g^{-1} at 30C	86.4% retention at 10C over 1k cycles	highly stable
$Mg_2Nb_{34}O_{87}$	290 mAh g^{-1} at 0.1C	149 mAh g^{-1} at 10C	93.5% retention at 10C over 400 cycles	highly stable
$CrNb_{11}O_{29}$	286 mAh g^{-1} at 0.1C	150 mAh g^{-1} at 10C	90.2% retention at 10C over 400 cycles	high e^- conductivity
$Cr_{0.5}Nb_{24.5}O_{62}$	322 mAh g^{-1} at 0.1C	145 mAh g^{-1} at 30C	82.4% retention at 10C over 1k cycles	high e^- conductivity
$Nb_{25}O_{62}$	289 mAh g^{-1} at 0.1C	133 mAh g^{-1} at 10C	99.7% retention at 10C over 1k cycles	H_2 reduction of Nb_2O_5
$Zn_2Nb_{34}O_{87}$	284 mAh g^{-1} at 0.1C	162 mAh g^{-1} at 10C	86.8% retention at 10C over 1k cycles	high Li^+ conductivity
$Cu_2Nb_{34}O_{87}$	341 mAh g^{-1} at 0.1C	184 mAh g^{-1} at 10C	88.5% retention at 10C over 1k cycles	high e^- & Li^+ conductivity
$V_3Nb_{17}O_{50}$	207 mAh g^{-1} at 0.1C	68 mAh g^{-1} at 10C	90.0% retention at 10C over 2k cycles	low strain, low sintering temp.
$MoNb_{12}O_{33}$	294 mAh g^{-1} at 0.1C	138 mAh g^{-1} at 10C	78.8% retention at 10C over 1k cycles	$Mo^{6+} \leftrightarrow Mo^{4+}$, low sintering temp.
$Mo_3Nb_{14}O_{44}$	323 mAh g^{-1} at 0.1C	123 mAh g^{-1} at 10C	71.8% retention at 10C over 1k cycles	$Mo^{6+} \leftrightarrow Mo^{4+}$, low sintering temp.
$NaNb_{13}O_{33}$	225 mAh g^{-1} at 0.1C	116 mAh g^{-1} at 10C	87.9% retention at 10C over 5k cycles	ultra-good cyclic stability
$Ni_2Nb_{34}O_{87}$	339 mAh g^{-1} at 0.1C	154 mAh g^{-1} at 10C	101.7% retention at 10C over 1k cycles	high conductivity, low V change
$LaCeNb_6O_{18}$	165 mAh g^{-1} at 0.1C	135 mAh g^{-1} at 10C	94.0% retention at 10C over 5k cycles	deficient perovskite structure



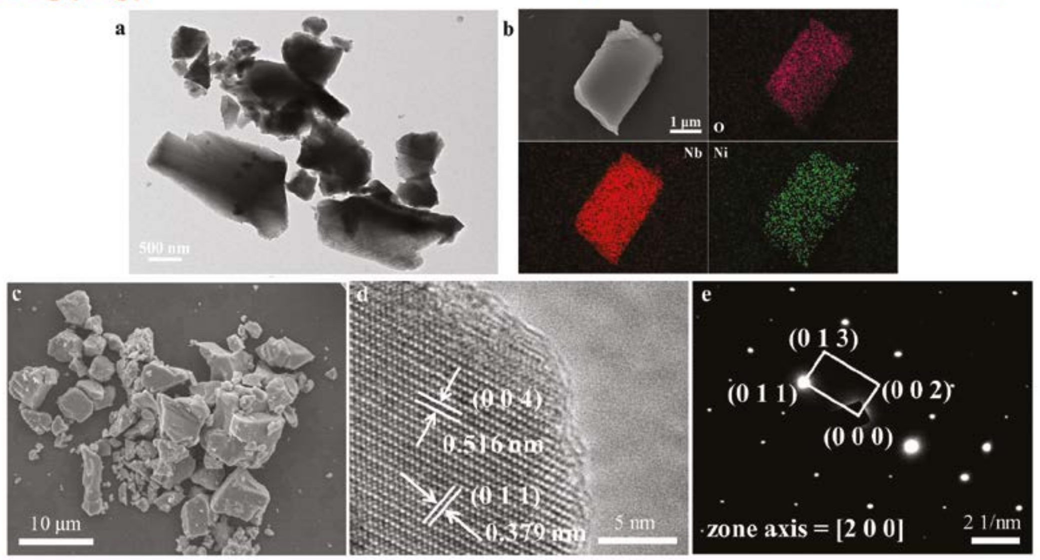


$Ni_2Nb_{34}O_{87}$ crystal structure and morphology

sample	a (Å)	b (Å)	c (Å)	β (°)	V (Å³)
$Ni_2Nb_{34}O_{87}$	28.69691	3.84015	20.66244	90	2277.011
$Cu_2Nb_{34}O_{87}$	15.59868	3.83115	20.64336	113.063	1135.059
$Zn_2Nb_{34}O_{87}$-N	15.61179	3.83217	20.66574	113.089	1137.327
$Mg_2Nb_{34}O_{87}$	15.60459	3.83071	20.64403	113.096	1135.119
$Ti_2Nb_{10}O_{29}$	15.52369	3.81104	20.54769	113.058	1118.512
$CrNb_{11}O_{29}$	15.6085	3.8335	20.6481	113.067	1136.69
$AlNb_{11}O_{29}$	15.55789	3.81126	20.53599	113.303	1118.354
$Zn_2Nb_{34}O_{87}$-B	28.71489	3.82780	20.65497	90	2270.295
$GaNb_{11}O_{29}$	28.63126	3.80931	20.57555	90	2244.078
$FeNb_{11}O_{29}$	28.6862	3.82465	20.6120	90	2261.43
$TiNb_{24}O_{62}$	29.79212	3.81751	21.09986	95.018	2390.526
$ZrNb_{24}O_{62}$	29.87123	3.82209	21.16379	95.078	2406.798
$HfNb_{24}O_{62}$	29.92508	3.82525	21.21133	95.068	2418.588
$Cr_{0.5}Nb_{24.5}O_{62}$	29.91514	3.82628	21.15166	94.944	2412.092
$Al_{0.5}Nb_{24.5}O_{62}$	29.9005	3.8228	21.1950	95.079	2413.20
$TiNb_2O_7$	20.36708	3.79885	11.89108	127.227	794.945
$W_5Nb_{16}O_{55}$	29.657	3.8225	23.106	126.50	550.8
$WNb_{12}O_{33}$	22.2474	3.8201	17.7290	unrevealed	unrevealed
$MoNb_{12}O_{33}$	2.27931	3.82094	17.72972	123.3	1261.021

Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.20210255C

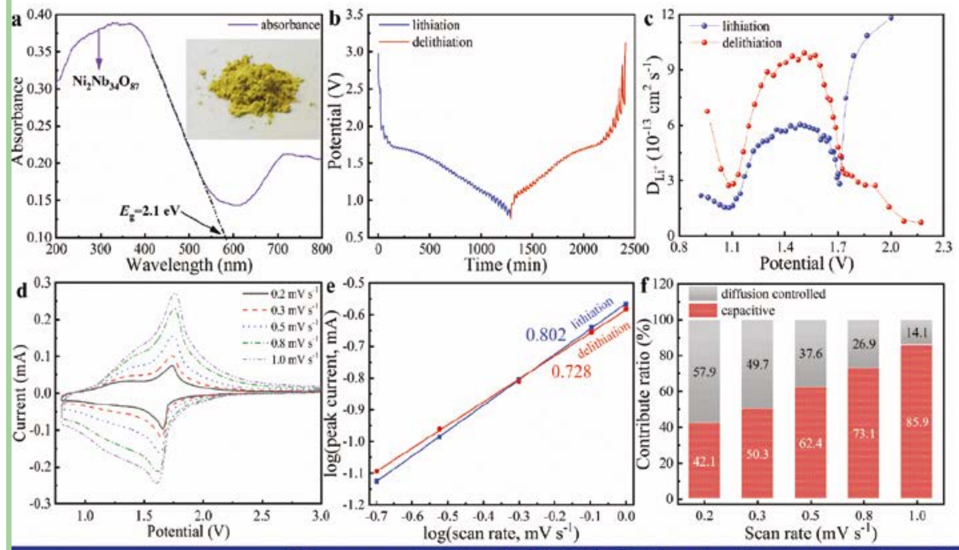
$Ni_2Nb_{34}O_{87}$ crystal structure and morphology



Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.20210255C

2022 International Conference on Niobium Based Batteries
5TH EDITION

$Ni_2Nb_{34}O_{87}$ charge transport kinetics



high electronic conductivity: 5.0×10^{-6} S cm^{-1}.

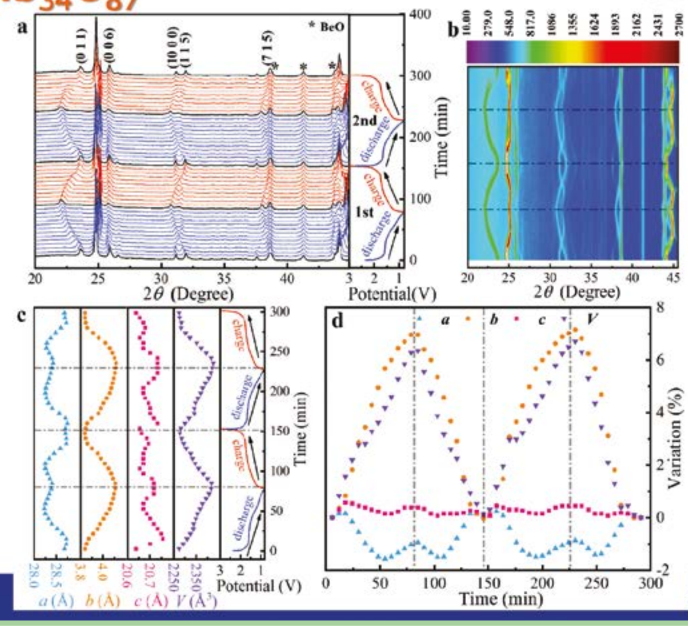
large Li$^+$ diffusion coefficients: 4.8×10^{-13} cm^2 s^{-1} (lithiation, GITT); 5.8×10^{-13} cm^2 s^{-1} (delithiation, GITT)

small electrode polarization

significant intercalation-pseudocapacitive behavior

Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.20210255C

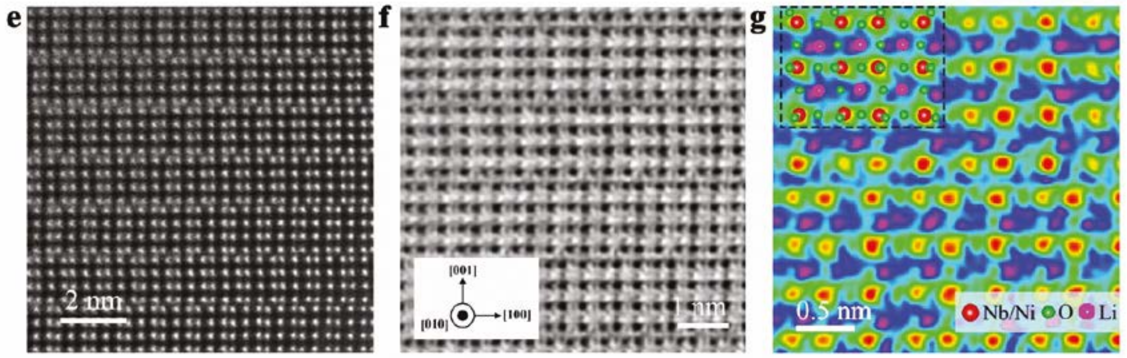
$Ni_2Nb_{34}O_{87}$ unit-cell-volume expansion



Unit-cell volume expansion after lithiation (at 0.8 V): 6.71%

nergy Mater., 10.1002/aenm.20210255C

$Ni_2Nb_{34}O_{87}$ — Li^+-storage sites

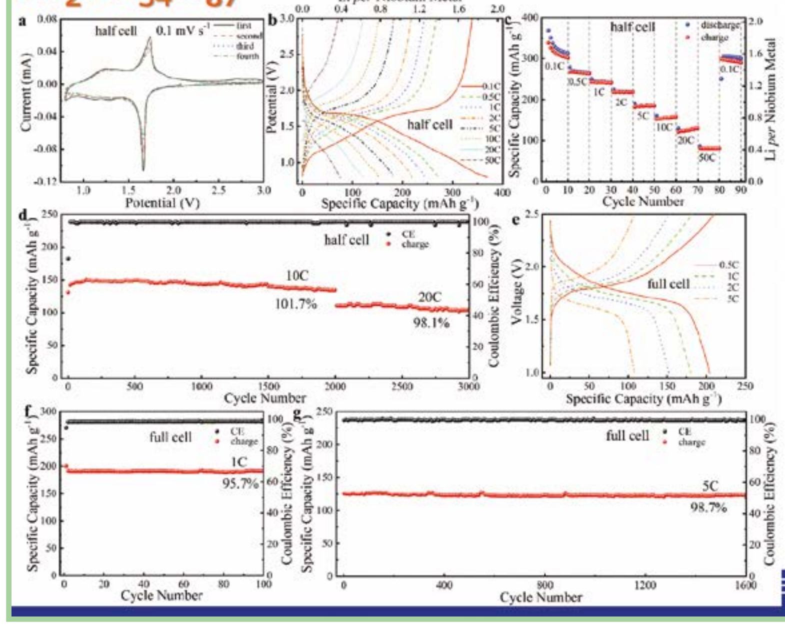


The majority of Li^+ ions repeatedly insert into/extracts from the (010) crystallographic planes of the $Ni_2Nb_{34}O_{87}$ lattices.

Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.202102550

$Ni_2Nb_{34}O_{87}$ — half and full cells

small $Ni_2Nb_{34}O_{87}$ loading: 1.1 mg cm^{-2}, A:B:C=7:2:1



high reversible capacity: 339 mAh g^{-1} (0.1C)

high initial Coulombic efficiency: 91.9%

safe operating potential: ~1.69 V

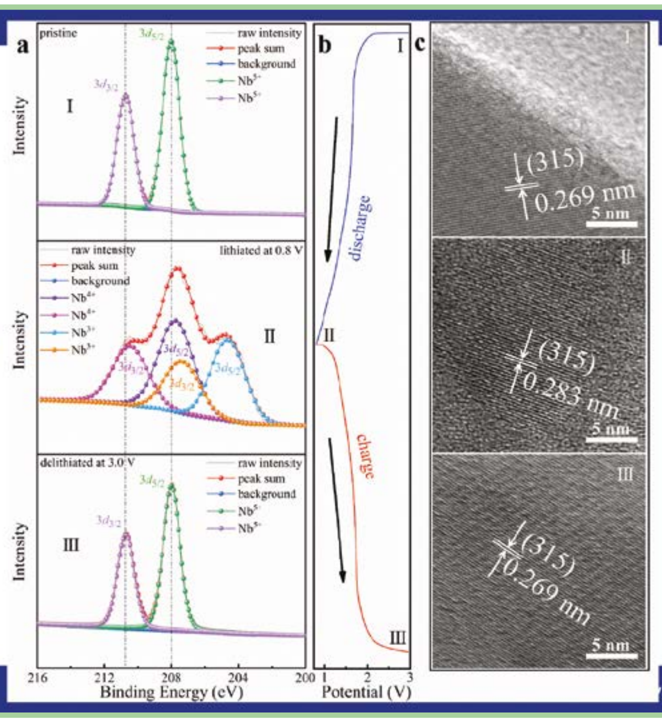
high rate capability: 154 mAh g^{-1} (10C)

excellent cyclic stability: 101.7% capacity retention after 2000 cycles at 10C and 98.1% capacity retention after 1000 cycles at 20C

Energy Mater., 10.1002/aenm.202102550

$Ni_2Nb_{34}O_{87}$ — XPS and HRTEM

Two-electron transfer *per* Nb is confirmed.

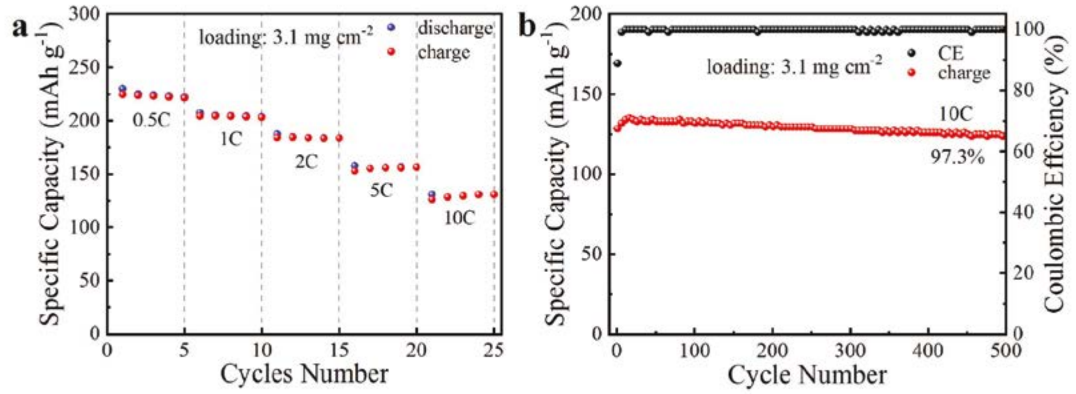


High structural stability against cycling is verified.

10.1002/aenm.202102550

$Ni_2Nb_{34}O_{87}$ — half cell (large loading)

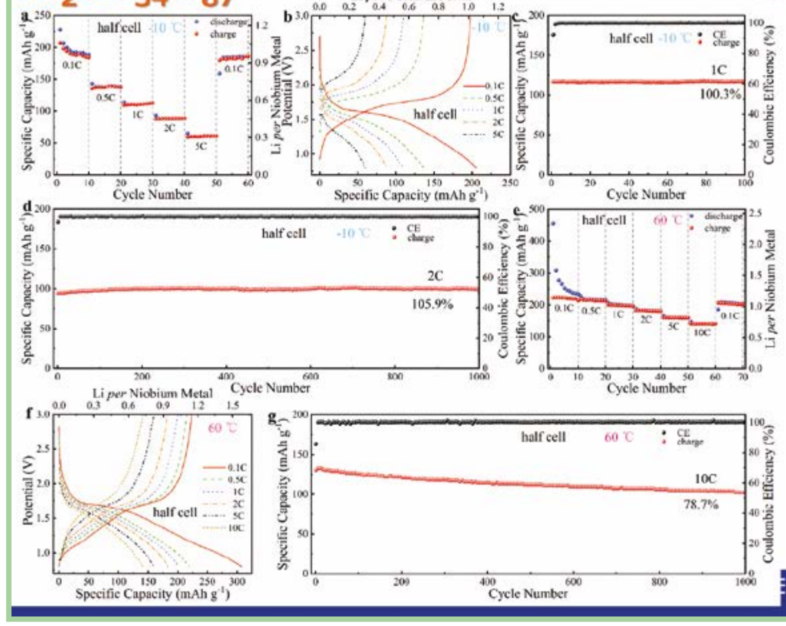
large $Ni_2Nb_{34}O_{87}$ loading: 3.1 mg cm^{-2}



The thicker electrode still maintains high rate capability with 57.8% capacity retention when the current rate was increased from 0.5C to 10C, and good cyclic stability with 97.3% capacity retention over 500 cycles at 10C.

Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.202102550

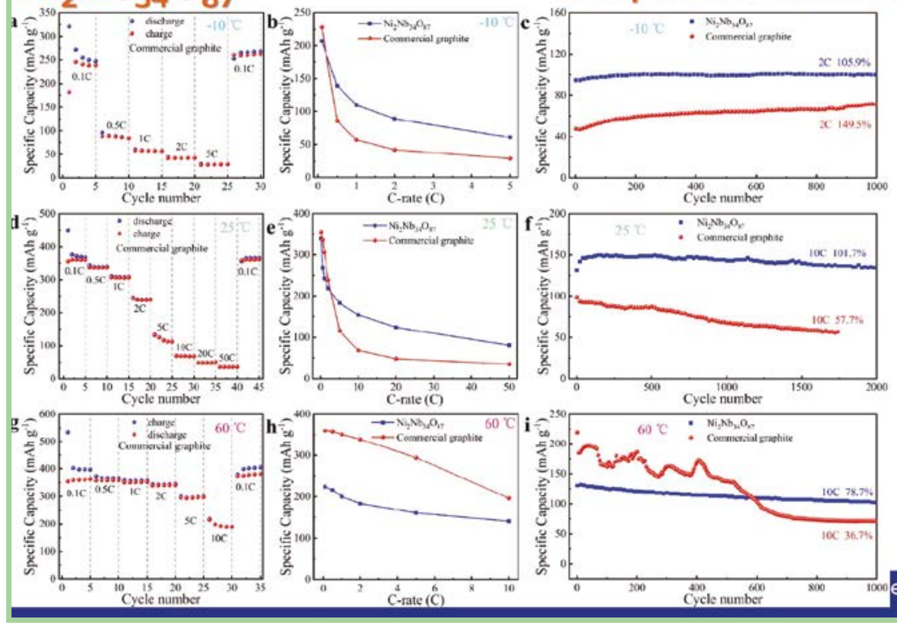
$Ni_2Nb_{34}O_{87}$ half cells at -10 and 60 °C



- acceptable reversible capacity: 207 mAh g^{-1} (0.1C)
- high initial Coulombic efficiency: 91.2%
- excellent cyclic stability: 105.9% capacity retention after 1000 cycles (2C)
- acceptable reversible capacity: 224 mAh g^{-1} (0.1C)
- enhanced rate capability: 141 mAh g^{-1} (10C)
- good cyclic stability: 78.7% capacity retention after 1000 cycles (10C)

Energy Mater., 10.1002/aenm.202102550

$Ni_2Nb_{34}O_{87}$ Comparison with commercial graphite



Commercial graphite only performs well at room temperature and low current rates.

At low temperature, commercial graphite suffers from poor electrochemical kinetics.

At high temperature, commercial graphite cannot be stably charged/discharged.

er., 10.1002/aenm.202102550

2022 International Conference on Niobium Based Batteries
5TH EDITION

Conclusion

◆$Ni_2Nb_{34}O_{87}$ microparticles, prepared through conventional solid-state reaction, show an orthorhombic 3×4 shear ReO_3 crystal structure with a large A–B–A interlayer spacing of 3.84 Å, which is among the largest values in shear ReO_3 crystal structures. Therefore, $Ni_2Nb_{34}O_{87}$ exhibits fast Li^+ diffusivity and small unit-cell-volume expansion of only 6.71% after lithiation (at 0.8 V).

◆The 3*d* electrons in Ni^{2+} enables a high electronic conductivity of $Ni_2Nb_{34}O_{87}$.

◆$Ni_2Nb_{34}O_{87}$ exhibits comprehensively good electrochemical properties, including a high reversible capacity, high initial Coulombic efficiency, safe operating potential, high rate capability, and excellent cyclic stability, even when the $Ni_2Nb_{34}O_{87}$ is large and the $Ni_2Nb_{34}O_{87}$ particle sizes are on the order of micrometers.

◆The low- and high-temperature electrochemical properties of $Ni_2Nb_{34}O_{87}$ are still good, demonstrating that $Ni_2Nb_{34}O_{87}$ is an all-climate anode materials.

◆The material design strategy demonstrated in this work opens a new approach to the exploration of high-performance electrode materials.

Changpeng Lv, Chunfu Lin*, X. S. Zhao*, Adv. Energy Mater., 10.1002/aenm.202102550

Acknowledgements

Team members:

◆Prof. Hongliang Li
◆Dr. Hongbin Feng
◆Dr. Kuikui Wang
◆Dr. Xuehua Liu
◆Mr. Changpeng Lv
◆Mr. Cihui Huang
◆Mr. Jiazhe Gao
◆Mr. Tian Jiang
◆Mr. Wenze Wang
◆Mr. Songjie Li
◆Mr. Yi Lei
◆Mr. Yan Zhao
◆Mr. Qiangyuan
◆Miss Xingxing Jin

Fundings: NSFC, CITIC Metal (CBMM)

2018-2021 铌在电池中应用国际研讨会

技术商务联系人

技术：刘中柱　博士 / 教授级高工

中信金属股份有限公司铌产品业务部

010-5966 1994，18510074397（可加微信），liuzz3@citic.com

商务：李慧超　副总经理

中信金属股份有限公司铌产品业务部

010-5966 1907，13911416051（可加微信），lihc@citic.com

2022 | International Conference on Niobium Based Batteries

中信金属股份有限公司
CITIC Metal Co., Ltd

CBMM | Niobium Nb

了解更多铌科技领域前沿资讯请扫描下方二维码

微信公众号

微信小程序

https://niobium.tech/cn