New Nano-structured Electrode Materials with Niobium for Energy Storage Applications

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The Use of "**Niobium**" Ions for Battery Materials

N. Yabuuchi *et al.*,

Nb-Mn, *PNAS*, **112**, 7650 (2015).

Nb-Mn, *Nature Communications*, **7**, 13814 (2016).

Nb-V, *Chemical Communications*. **52**, 2051 (2016).

Nb-V, *Chemistry of Materials*, **29**, 6927 (2017).

Nb-Mn-Na, *Chemistry of Materials*, **29**, 5043 (2017).

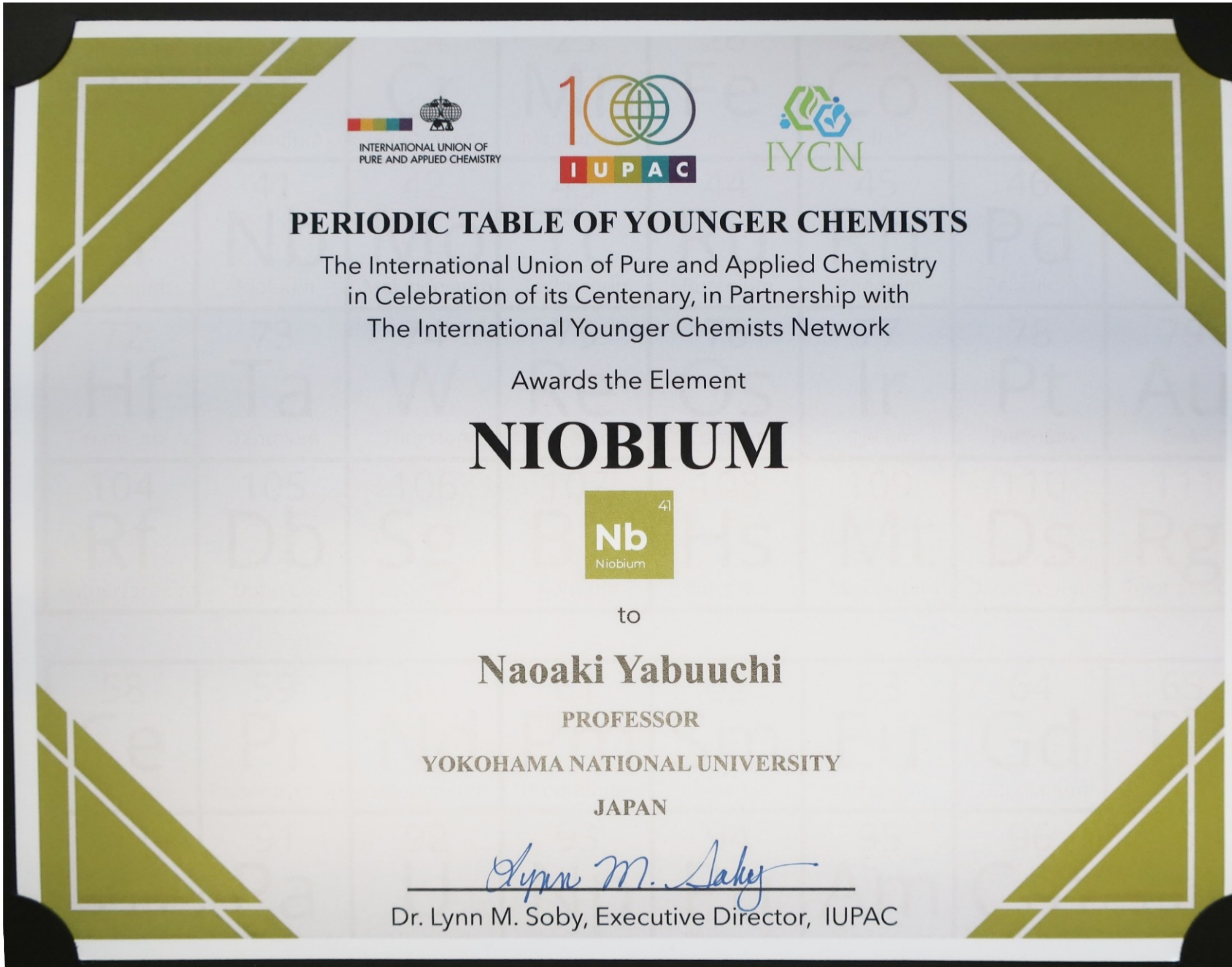
Nb-Mo, *ACS Energy Letters*, **2**, 733 (2017).

Nb-Mo for aqueous batteries, *PNAS*, in-press

Carbon coated **Nb**-V system, *submitted*

Nb-Ni and **Nb**-Co system, *submitted*

Research Award from IUPAC (2019)



Growing Demand for Li-ion Batteries

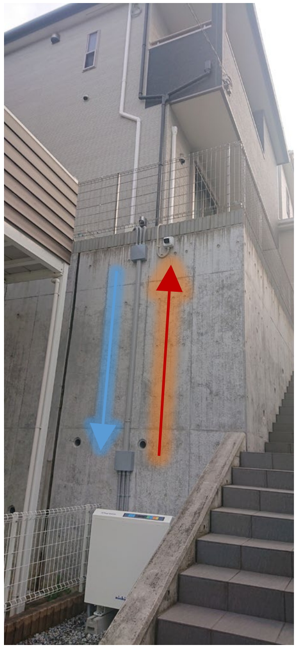
Global market for Li-ion batteries

2020 40.5 Billion USD

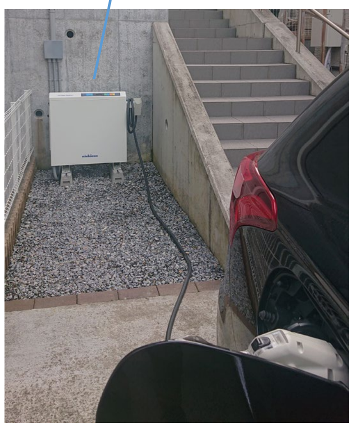
2026 91.9 Billion USD (expectation)

https://www.researchandmarkets.com/reports/5308805/

V2H; Electric vehicles in my home



V2H device
(**V**ehicle **to** **H**ome)

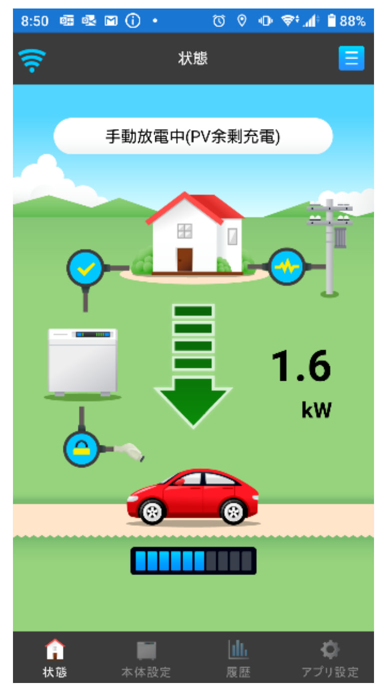


Solar panel
(4.4 kW)

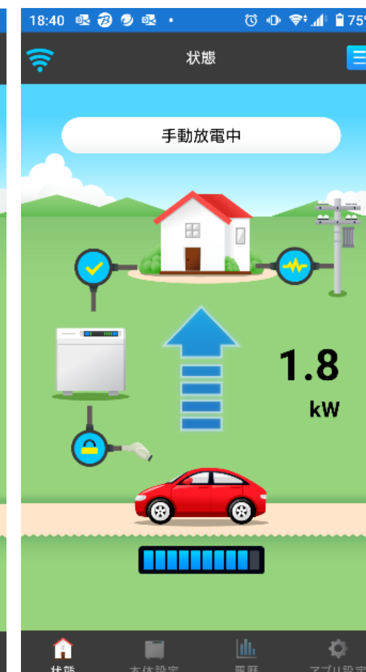
You can monitor your electric vehicle from your smart phone.

Plug-in electric vehicles
(Capacity; 13.8 kWh)

Electric vehicles with Li-ion batteries are important for the effective utilization of renewable energy recourses.



Daytime



Nighttime

Why Nb ions? Advantage of 4d transition metals

scandium 21 **Sc** 44.956	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.942	chromium 24 **Cr** 51.996	manganese 25 **Mn** 54.938	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.933	nickel 28 **Ni** 58.693	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.39
yttrium 39 **Y** 88.906	zirconium 40 **Zr** 91.224	niobium 41 **Nb** 92.906	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.91	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.87	cadmium 48 **Cd** 112.41
lutetium 71 **Lu** 174.97	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.95	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.21	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.22	platinum 78 **Pt** 195.08	gold 79 **Au** 196.97	mercury 80 **Hg** 200.59

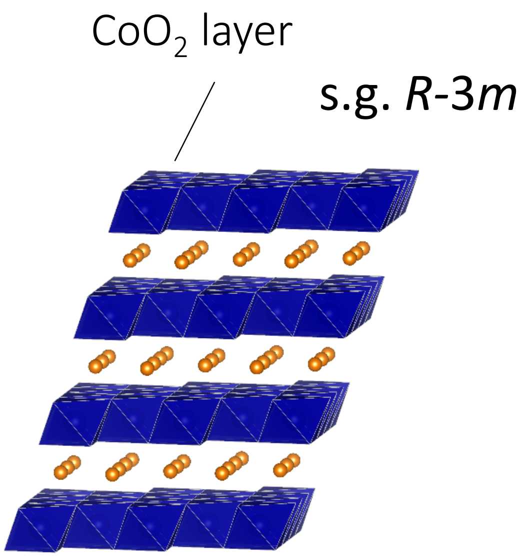
Ions with higher oxidation states are chemically stable.

V_2O_5: Chemically less stable compound

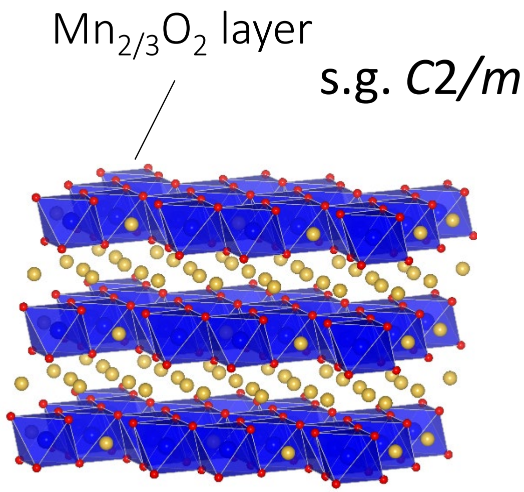
Nb_2O_5: Chemically extremely stable compound

→ The use of "Niobium ions" as 4d-transition metals

Why Nb ions? Design of Li-enriched Materials

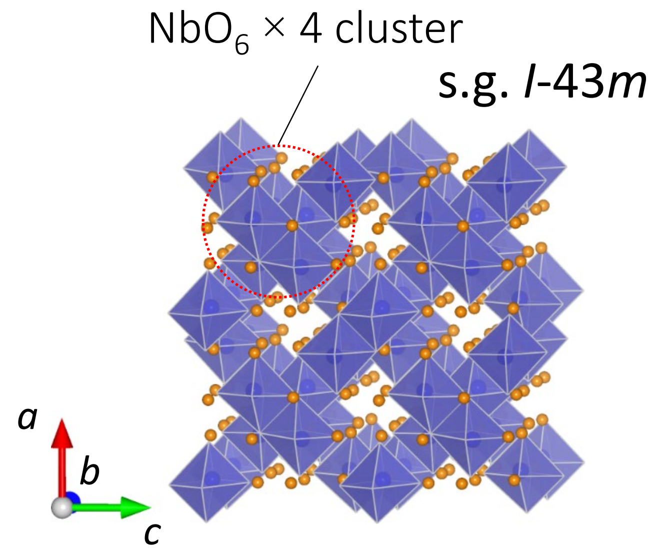


$LiCo^{3+}O_2$



$Li_2Mn^{4+}O_3$

$(Li_{1.33}Mn_{0.67}O_2)$



$Li_3Nb^{5+}O_4$

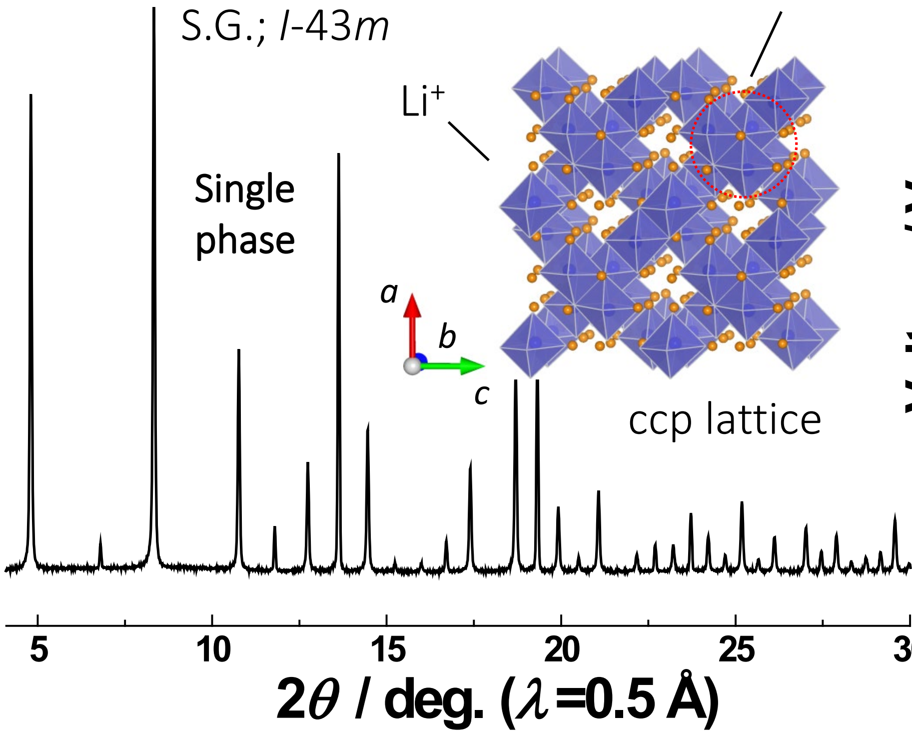
$(Li_{1.5}Nb_{0.5}O_2)$

Increase in the oxidation states of metal ions results in the enrichment of lithium contents in host structures (and thus higher theoretical capacities).

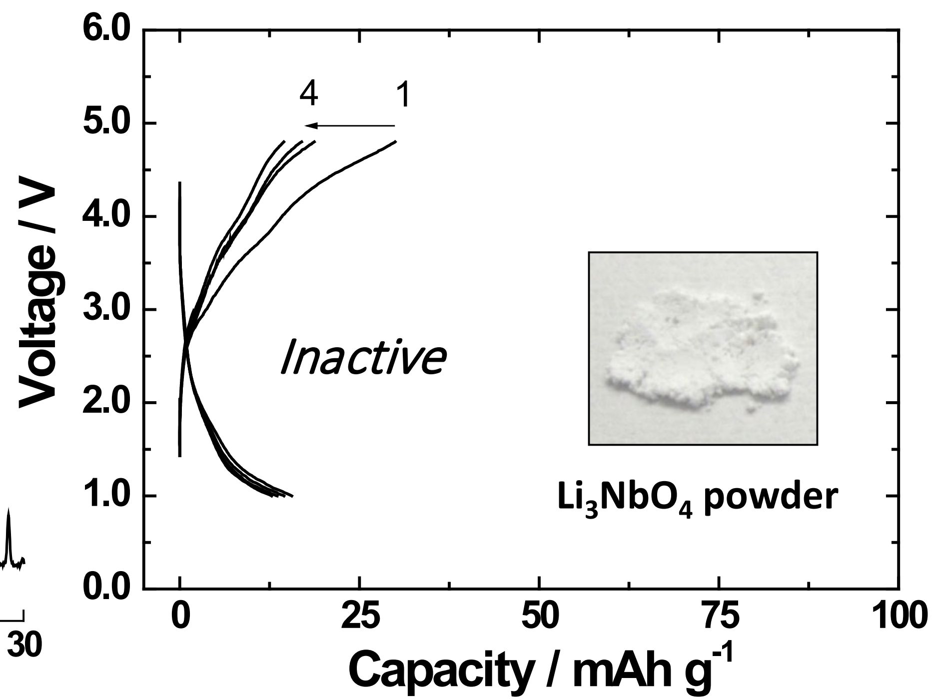
➔ Potential new host materials for Li battery materials

Li_3NbO_4 as electrode materials for LIBs

▪XRD pattern of Li_3NbO_4



▪Electrochemical Performance in Li cells

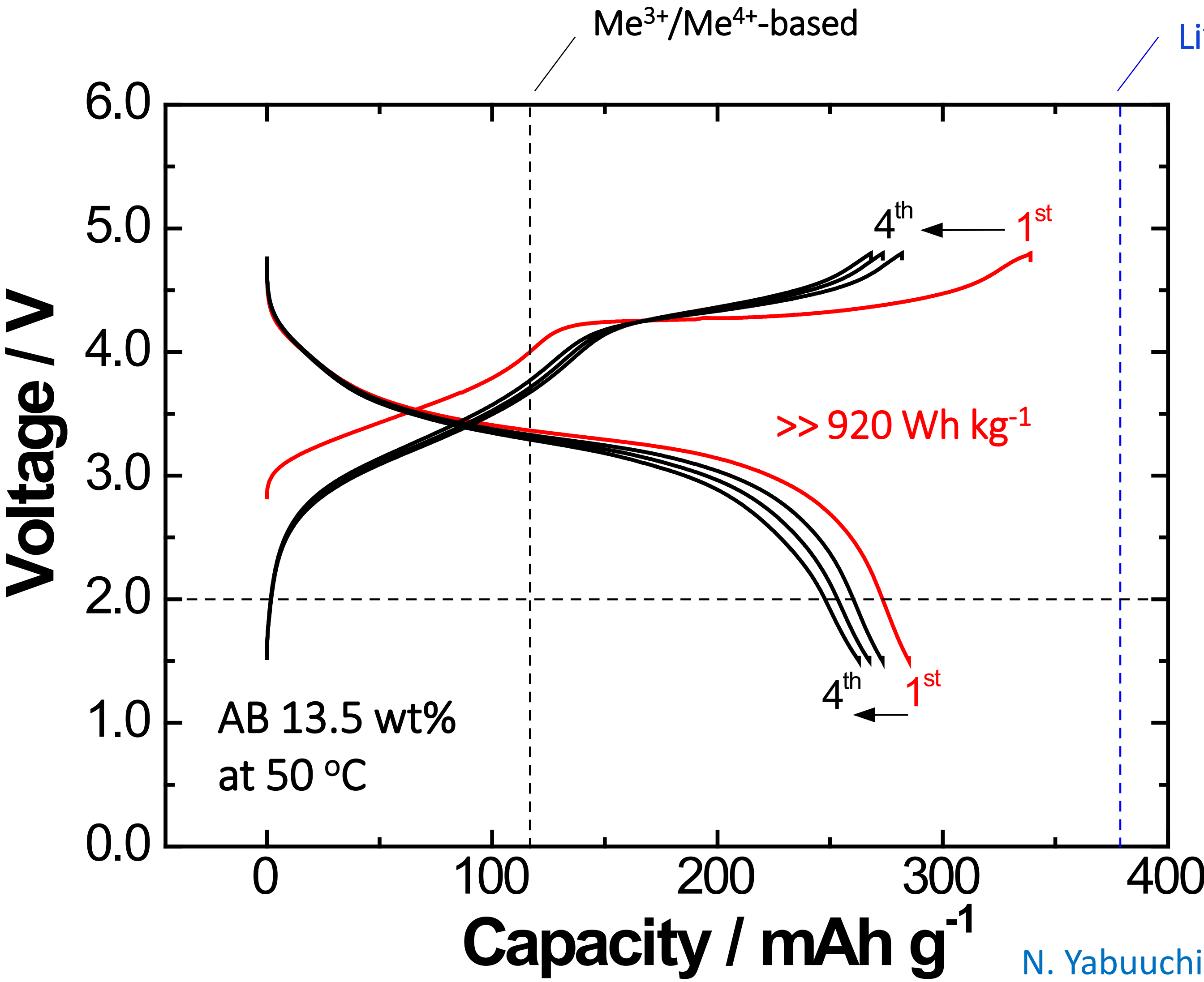


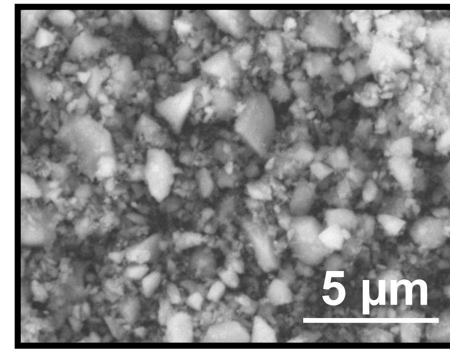
$Nb^{5+}(4d^0)$ ➔ low electron conductivity and thus small capacity

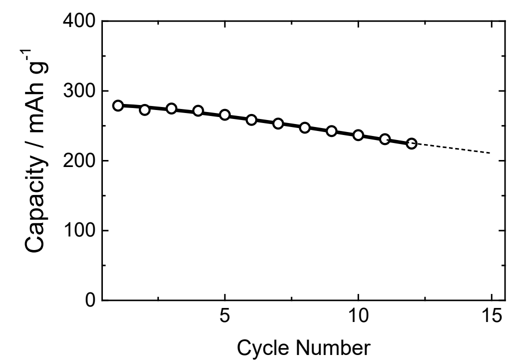
Can we activate oxide ions in Li_3NbO_4?

➔ Synthesis of "Li_3NbO_4 – $LiMnO_2$" binary system.

Electrochemical Properties of $Li_{1.3}Nb_{0.30}Mn_{0.40}O_2$





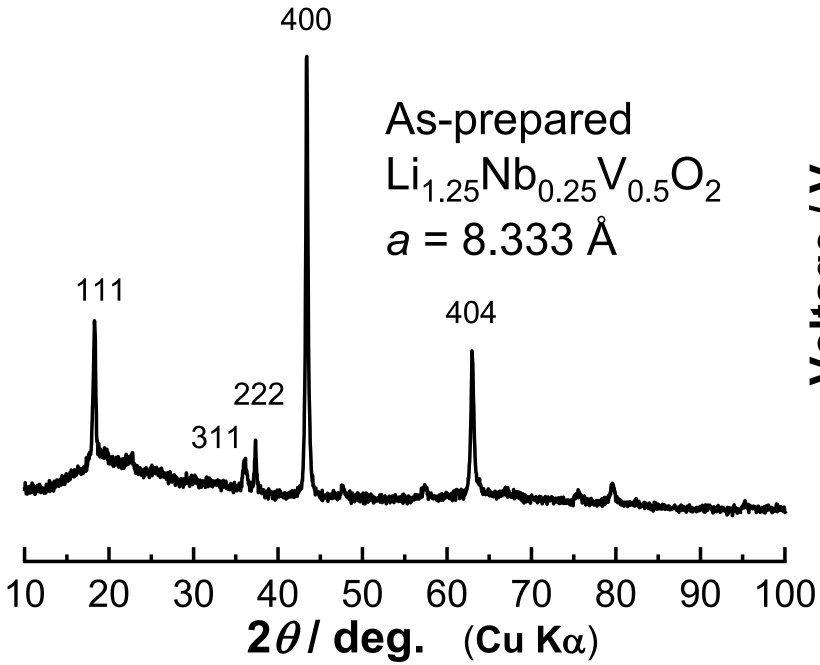


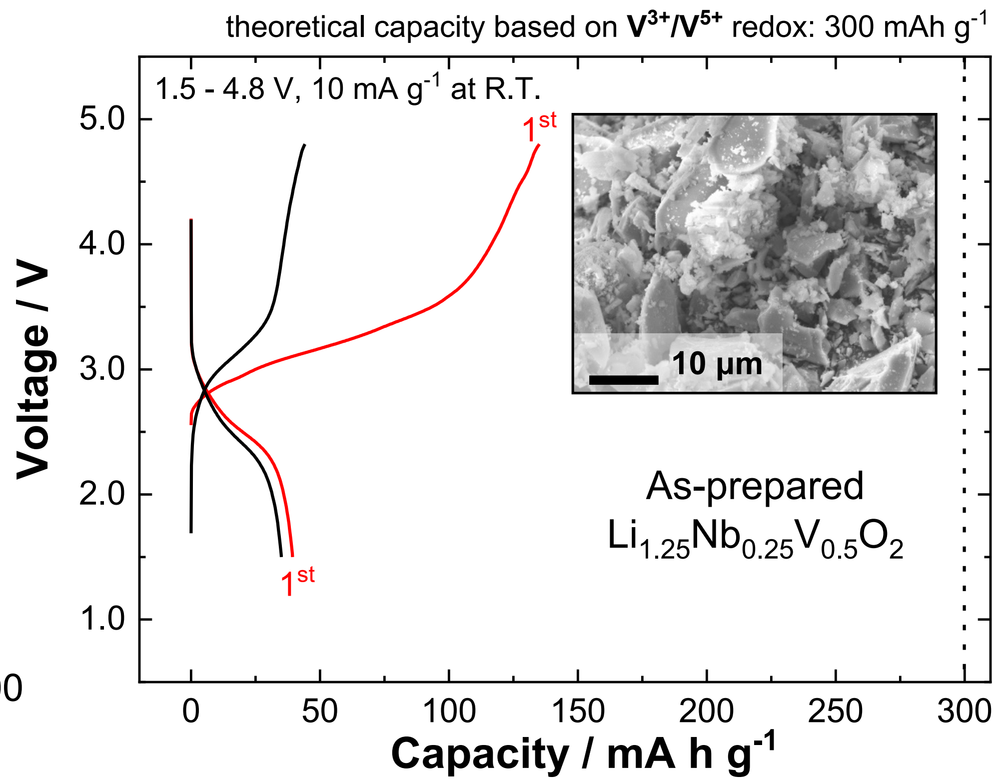
Capacity retention is needed to be improved.

N. Yabuuchi *et al.*, *PNAS*, **112**, 7650 (2015).

A new 300 mAh g^{-1} class positive electrode material for LIB.

Li-excess Compounds with "vanadium" ions



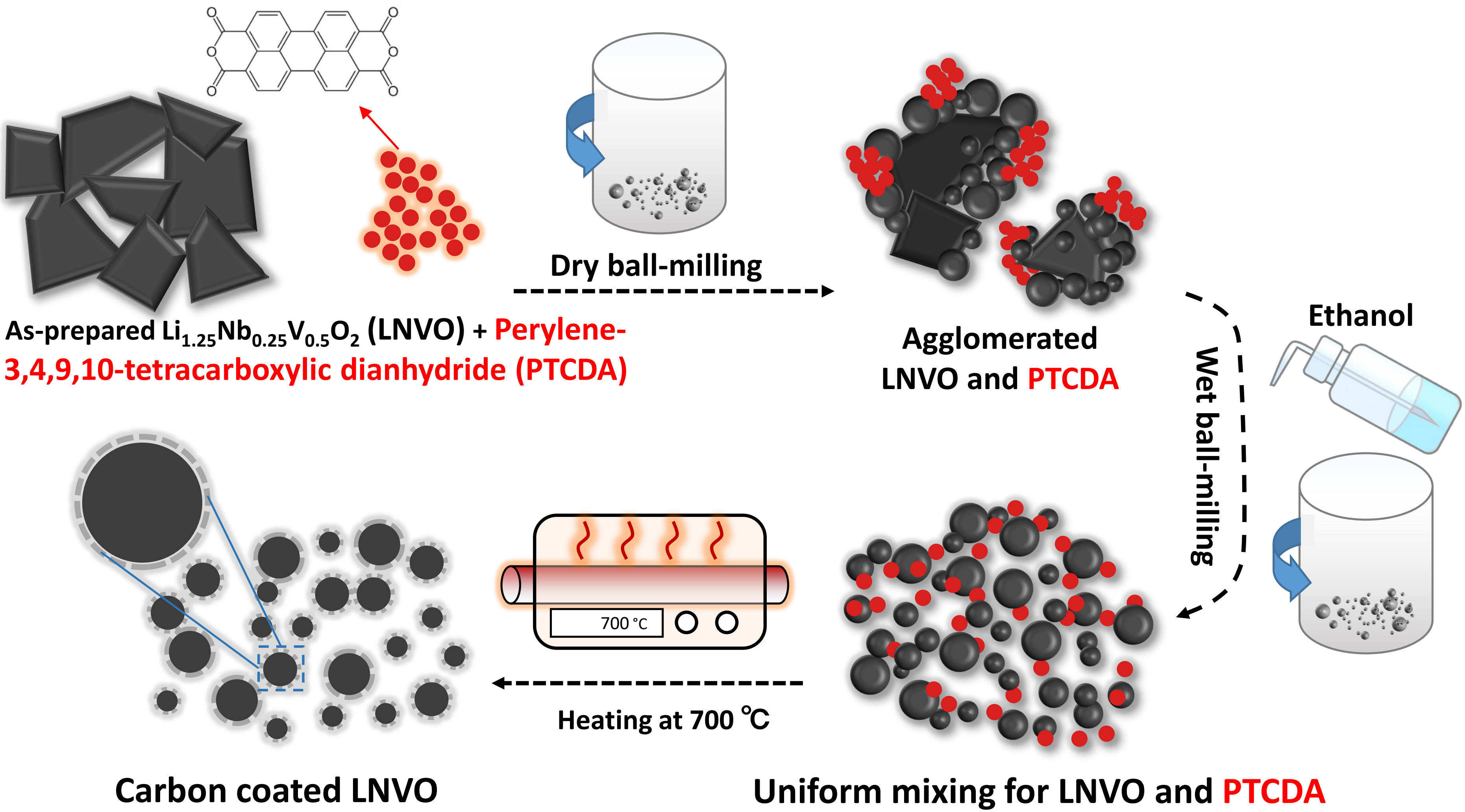


Electrode reversibility of $Li_{1.25}Nb_{0.25}V_{0.5}O_2$ is not high enough

for the micrometer-sized sample.

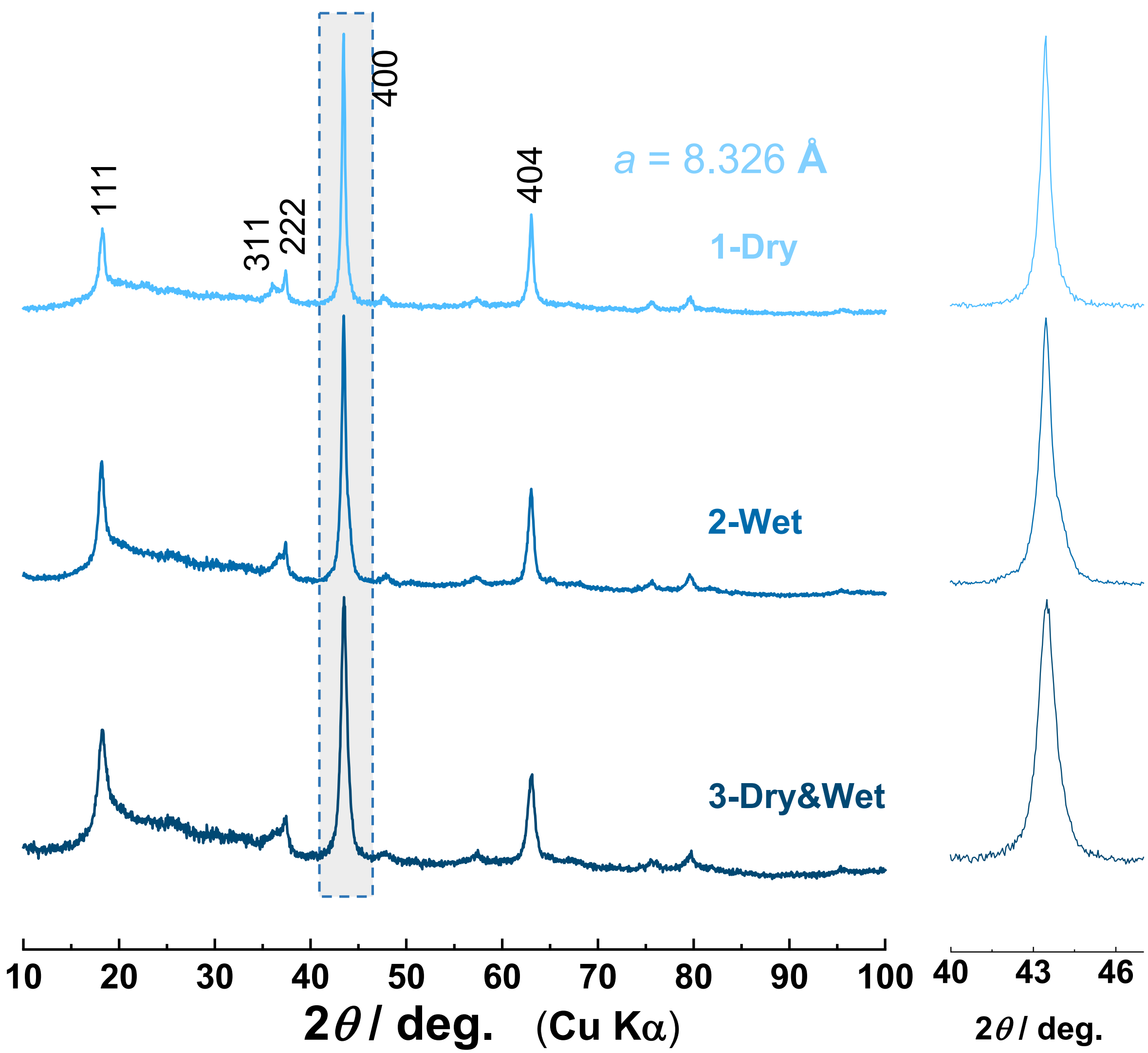
M. Nakajima and N. Yabuuchi, *Chemistry of Materials*, **29**, 6927 (2017).

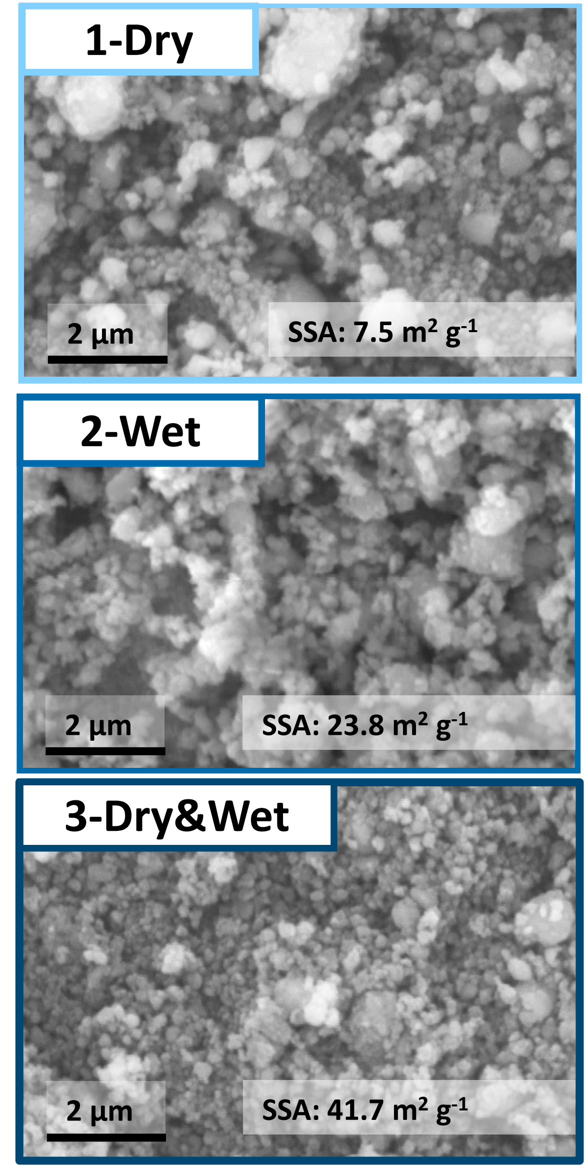
Synthesis of Nanostructured Oxides



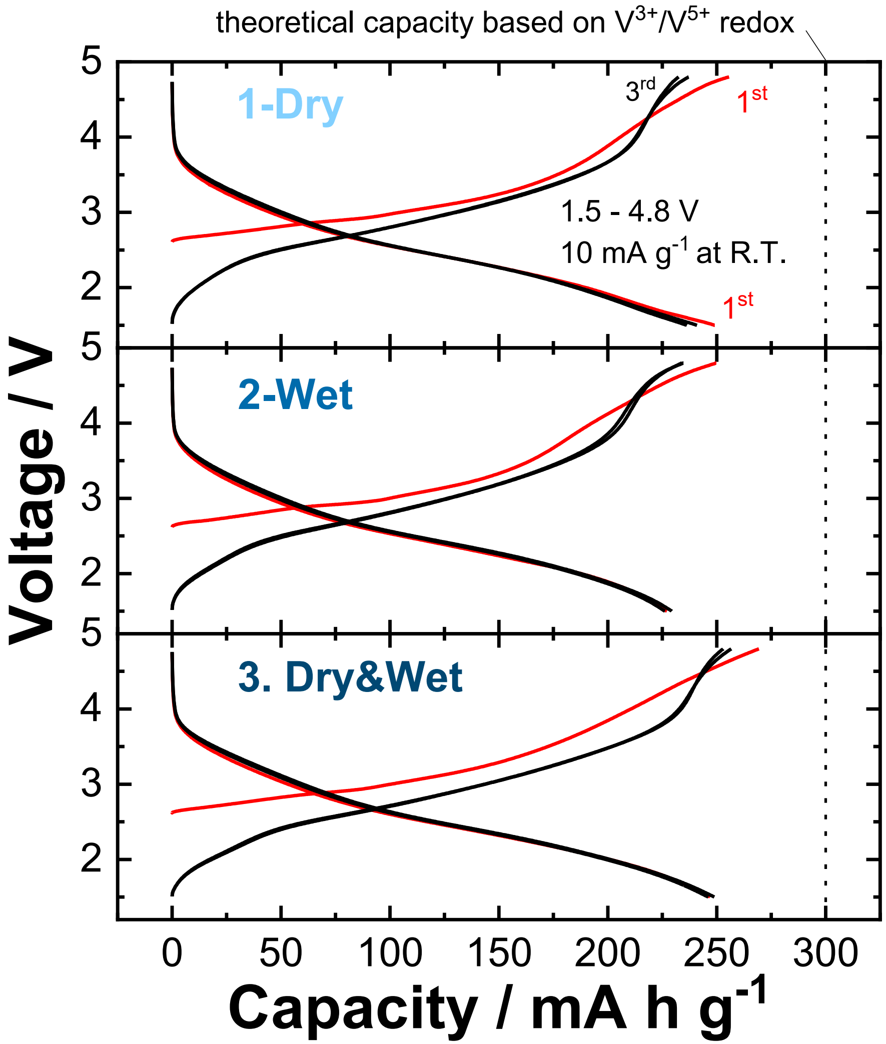
R. Qi *et al.*, and N. Yabuuchi, *submitted*

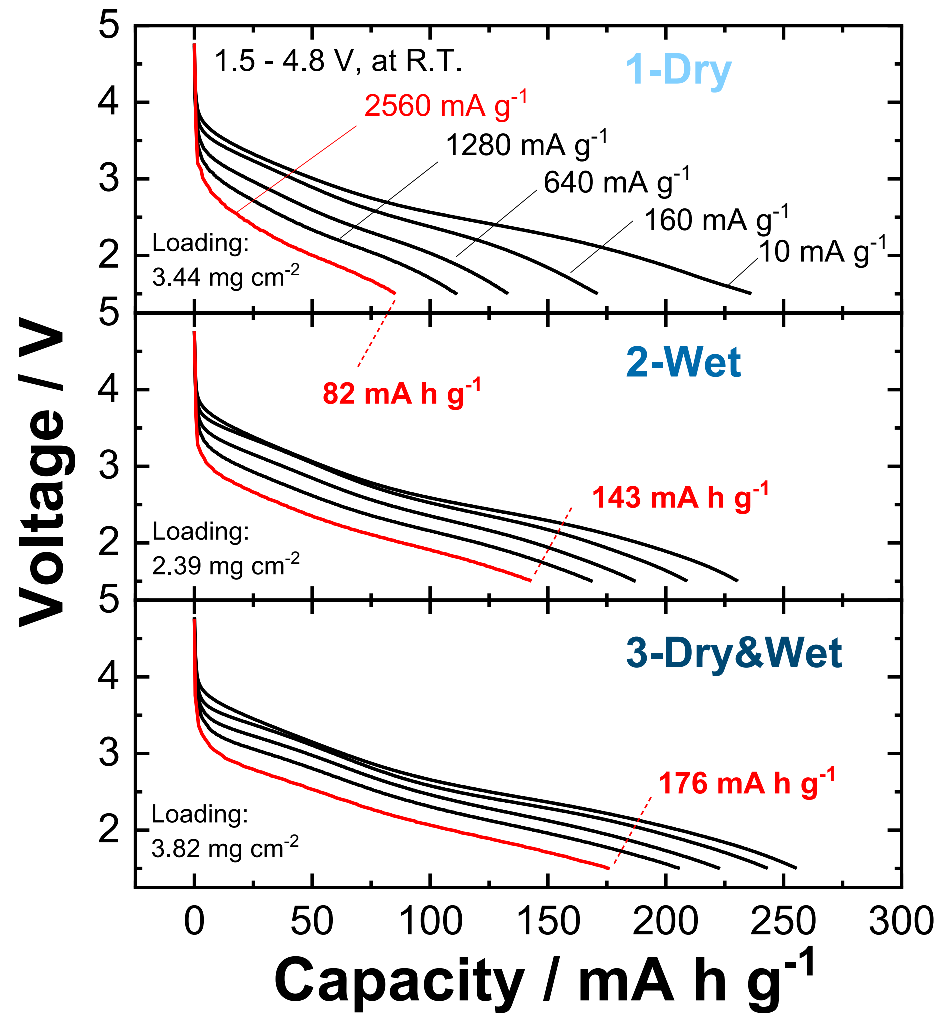
Synthesis of Nanostructured Oxides



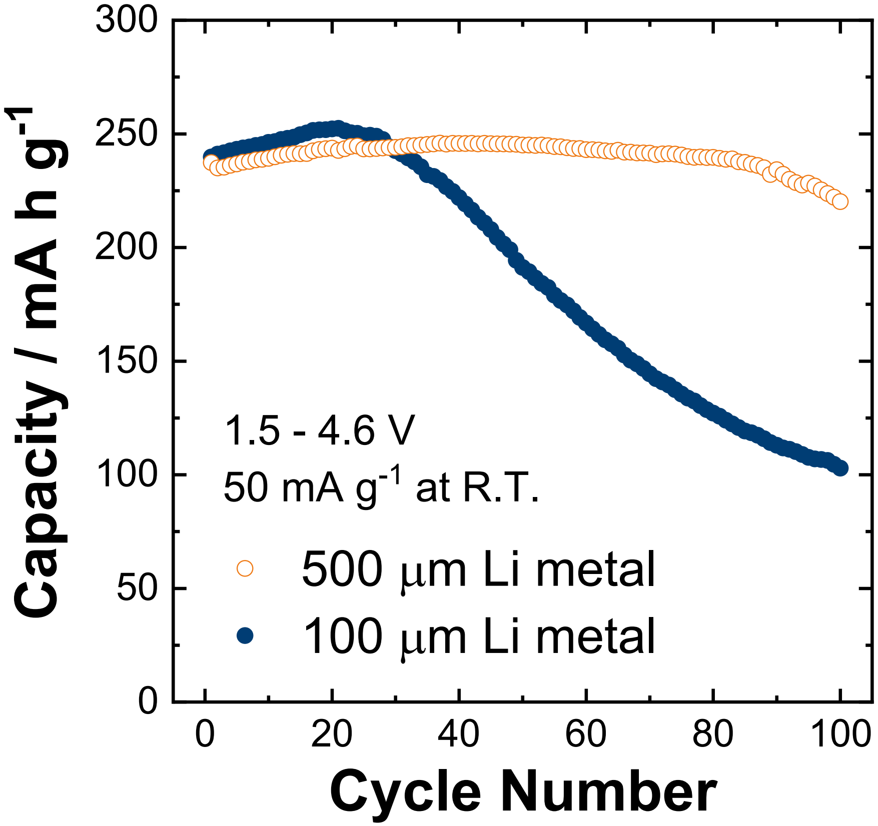


Electrode Performance of Nanostructured Oxides

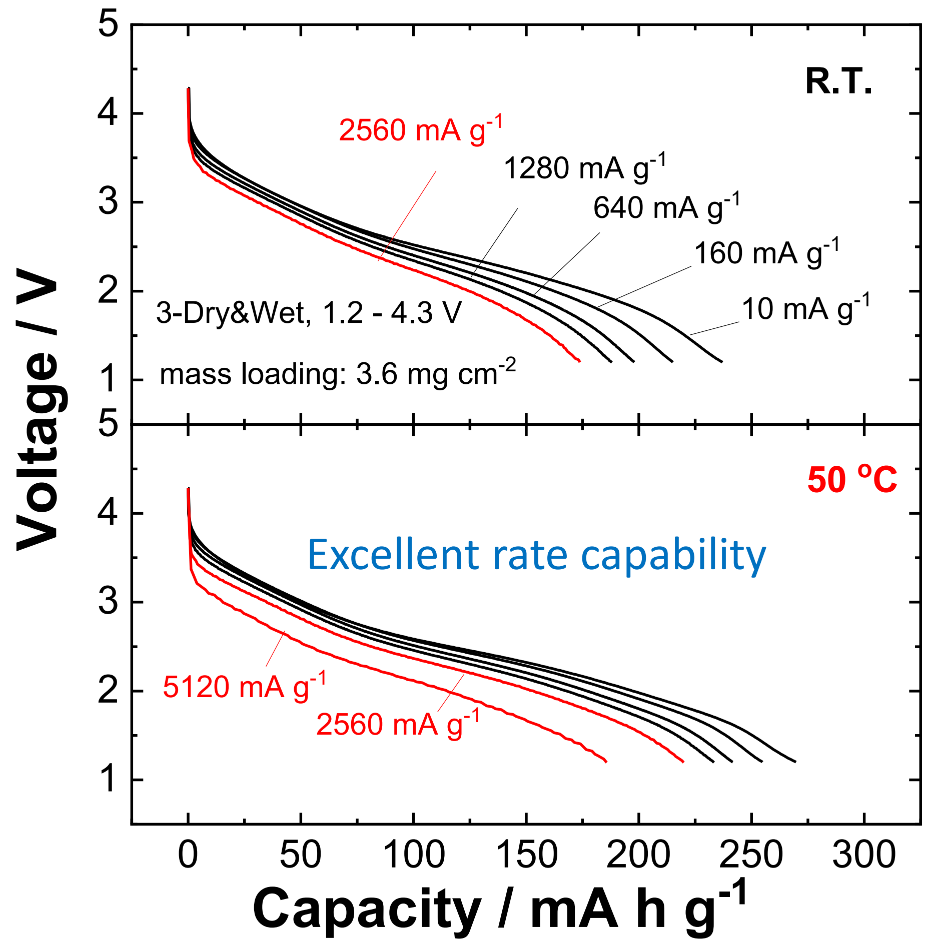




Electrode Performance of Nanostructured Oxides



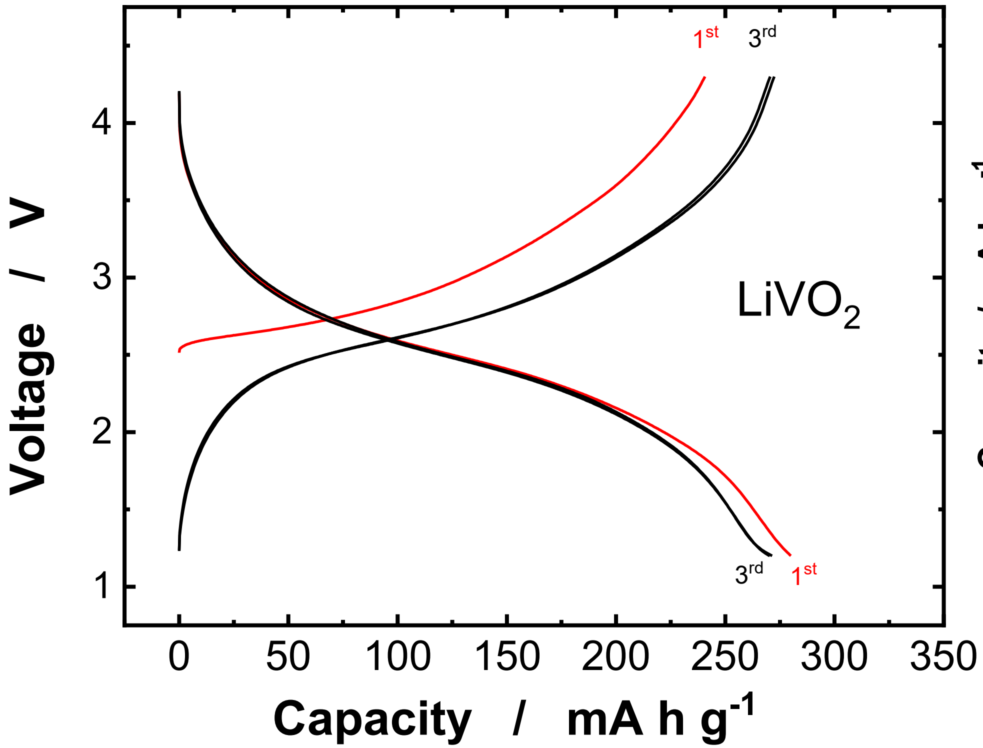
Excellent capacity retention

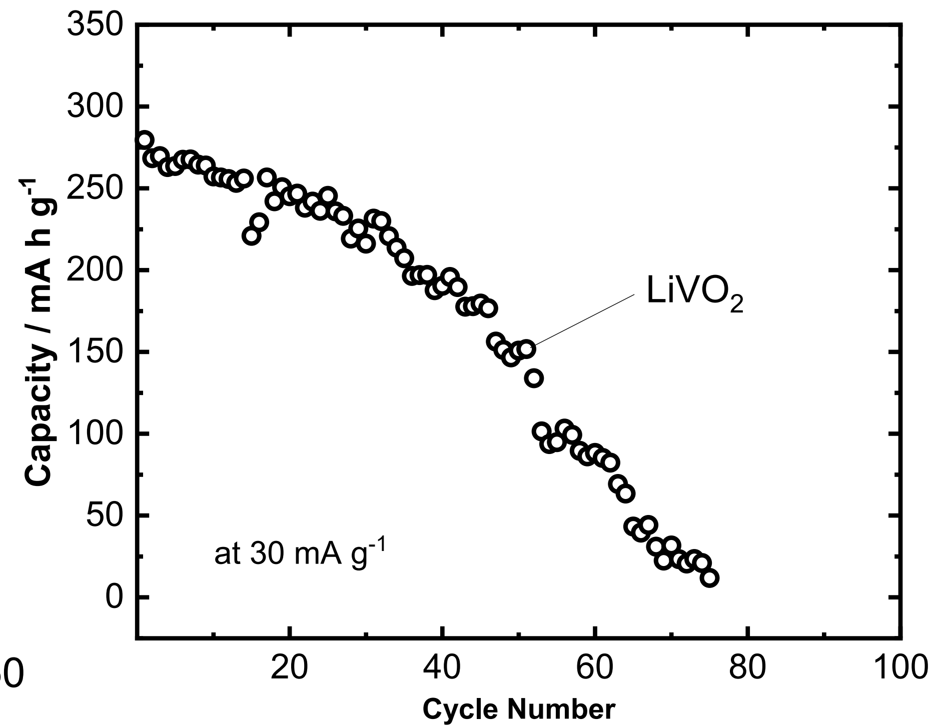


70% of capacity is obtained within "**3 min**".

R. Qi *et al.*, and N. Yabuuchi, *submitted*

Capacity retention of V-based oxide “without” Nb ions





I. Konuma, *et al.* and N. Yabuuchi, submitted

✓Capacity retention of V system with the rocksalt structure is effectively improved by the presence of chemically stable Nb ions.

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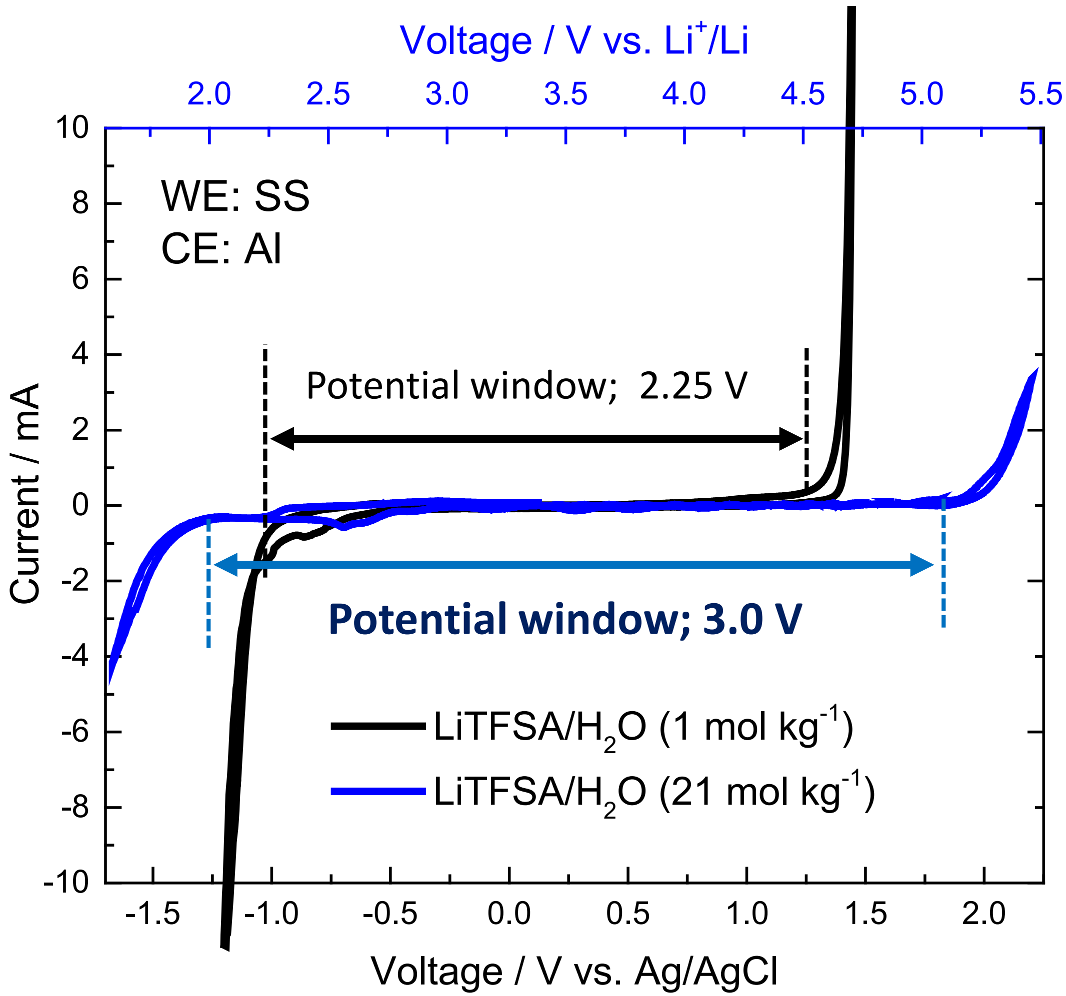
Development of "**Safe**" Li-ion Batteries

with **Nanosized Nb-Mo Oxides** and

Water-based Electrolyte

N. Yabuuchi *et al.*, *PNAS* in-press

Cyclic voltammograms; LiTFSA aqueous electrolyte



LiTFSA	H_2O
6.0 g	1.0 g
(21 mmol)	(56 mmol)

21 mol kg^{-1}

LiTFSA/H_2O

Molar ratio (LiTFSA : H_2O = 1 : 2.6)

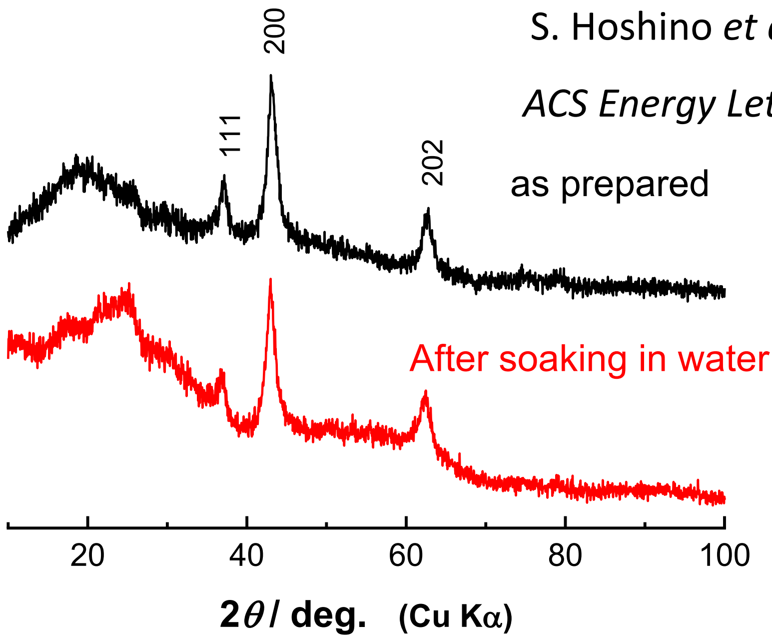
L. Suo *et al.*, *Science*, **350**, 938 (2015).

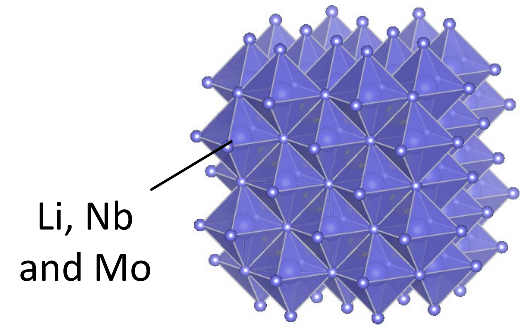
Anomalously wide electrochemical potential window is realized for concentrated LiTFSA aqueous electrolyte.

Lithium Extraction from $Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$ by Chemical Oxidation by Water

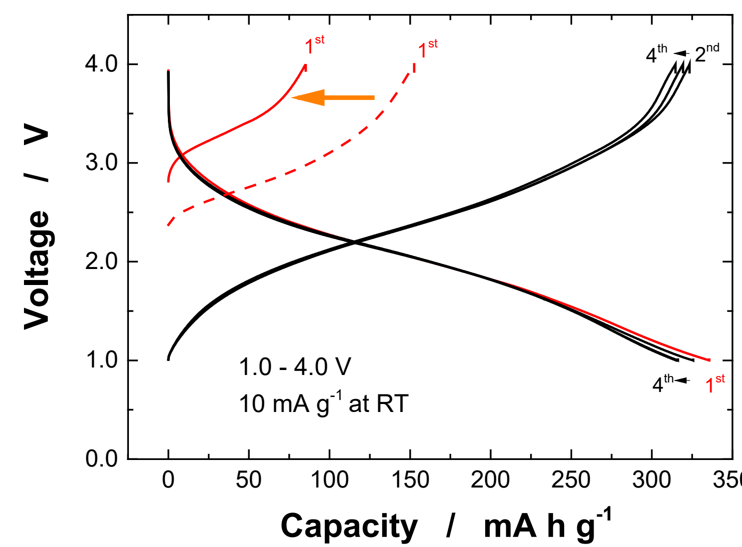
Cation-disordered rocksalt oxide; $Li_{9/7}Nb_{2/7}Mo_{3/7}O_2$

S. Hoshino *et al.*, N. Yabuuchi,
ACS Energy Lett. **2**, 733 (2017).





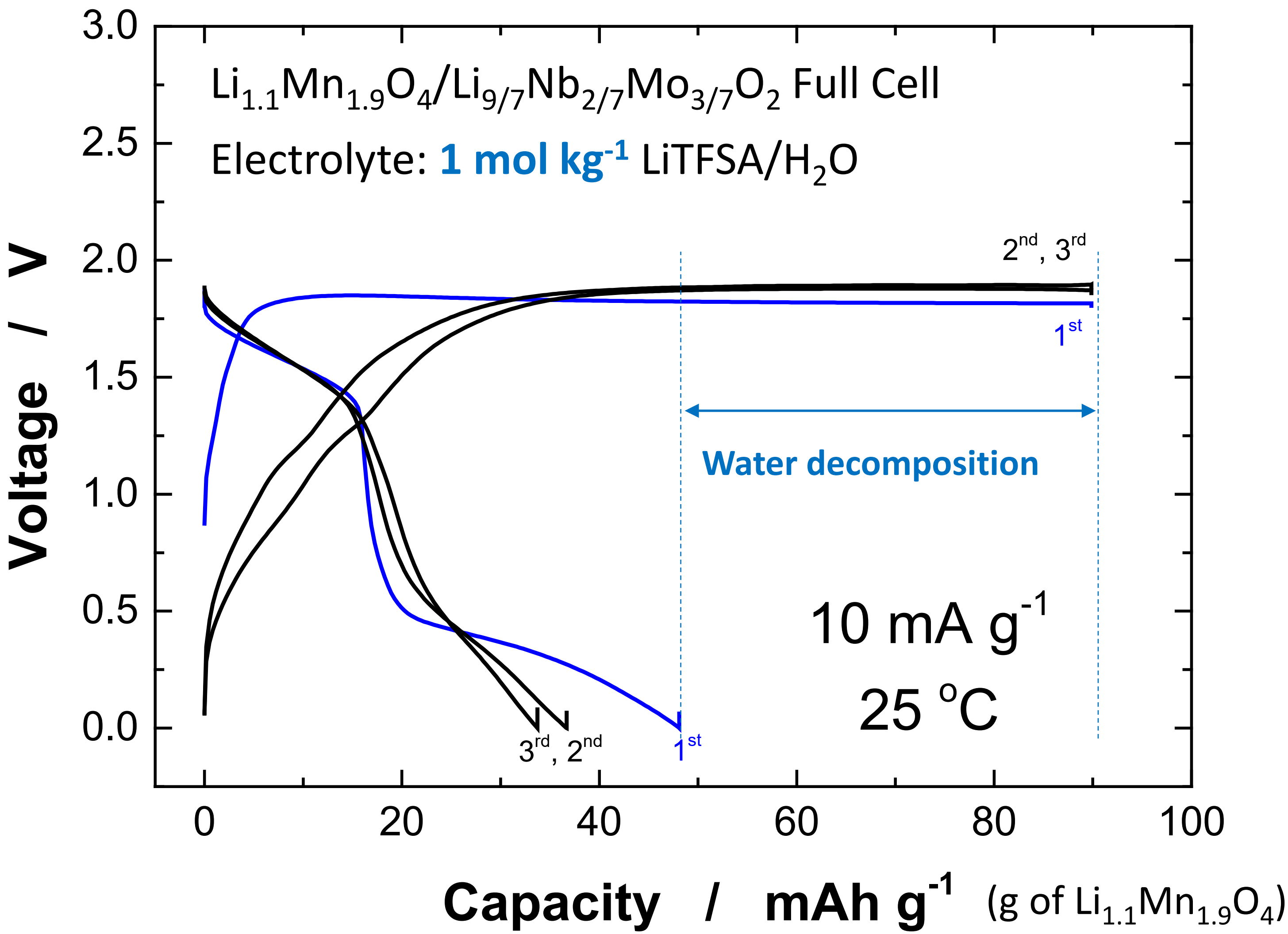
$Li/Li_xNb_{2/7}Mo_{3/7}O_2$ Cell



No change in the crystal structure after oxidation by water.

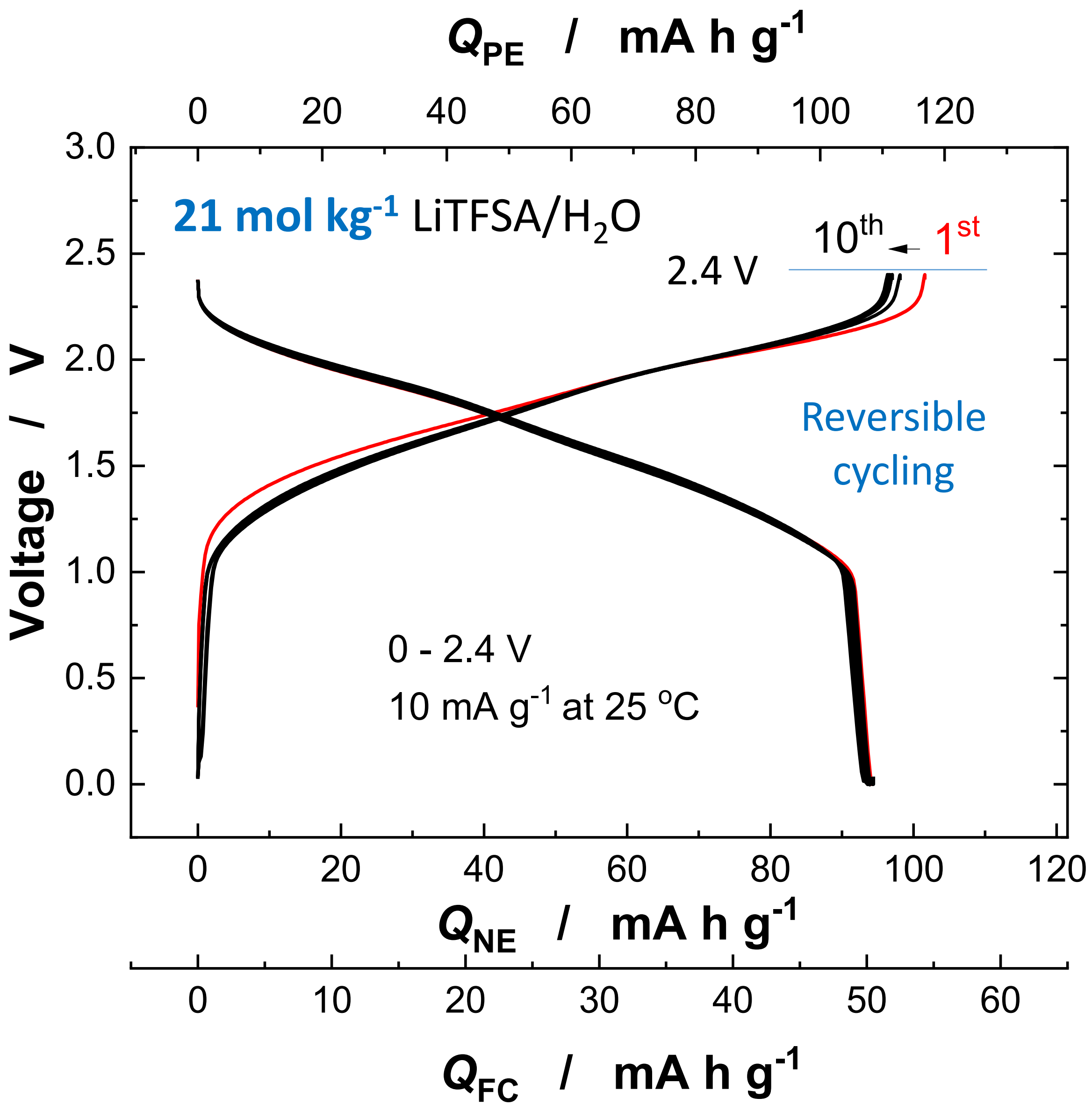
✓ A Li deficient phase, $Li_xNb_{2/7}Mo_{3/7}O_2$, was successfully obtained by water oxidation, and possibly used for negative electrode materials for aqueous Li batteries.

$Li_{1.1}Mn_{1.9}O_4/Li_xNb_{2/7}Mo_{3/7}O_2$ Full Cell in 1 mol kg^{-1} LiTFSA/H_2O

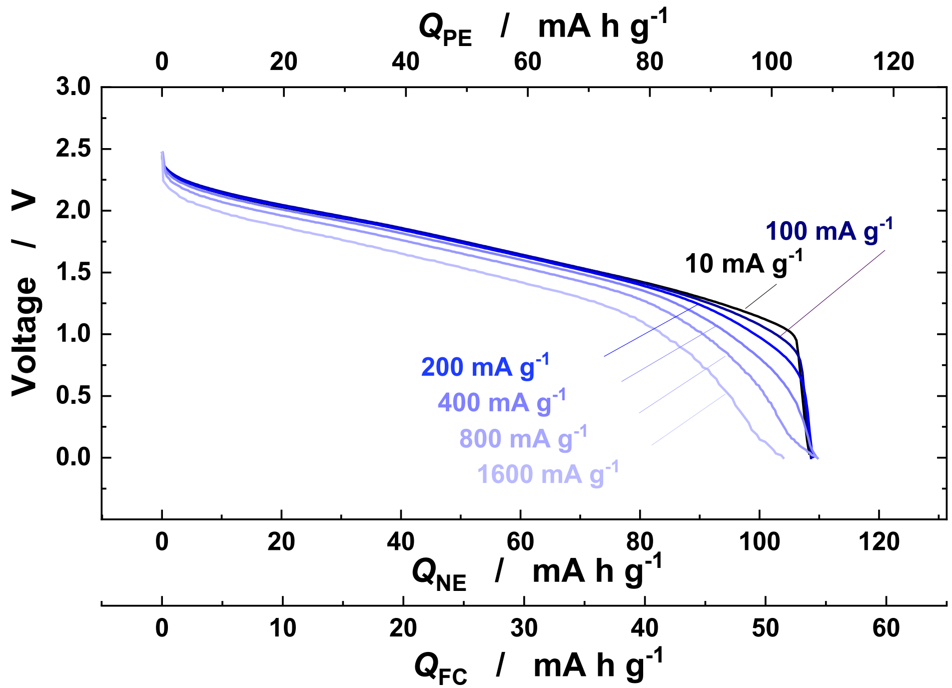


A full cell with $Li_xNb_{2/7}Mo_{3/7}O_2$ does not work because of decomposition of water.

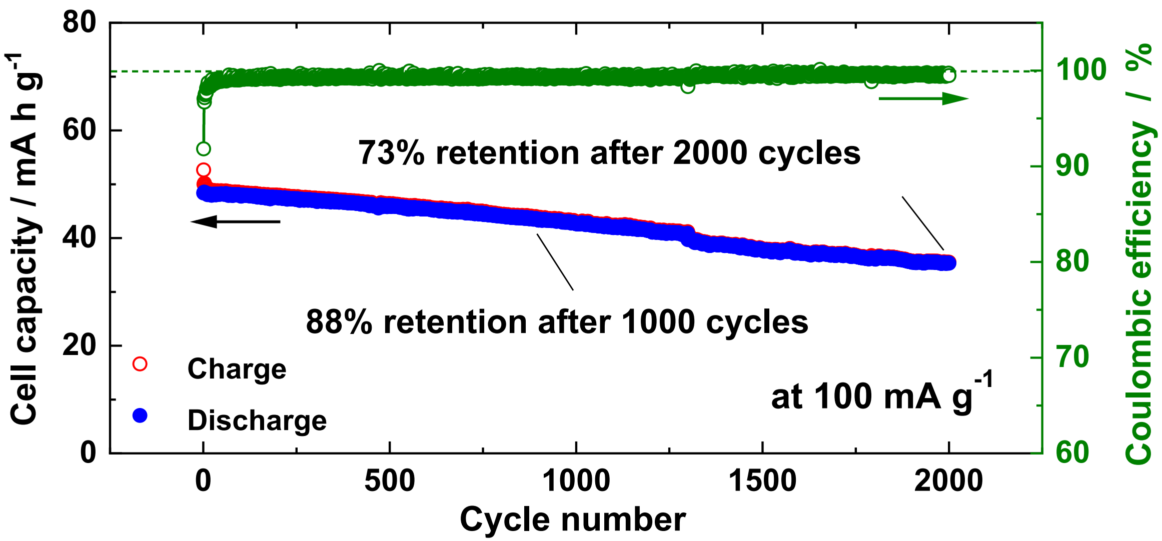
$Li_{1.1}Mn_{1.9}O_4/Li_xNb_{2/7}Mo_{3/7}O_2$ Full Cell in 21 mol kg^{-1} LiTFSA/H_2O



$Li_{1.1}Mn_{1.9}O_4/Li_xNb_{2/7}Mo_{3/7}O_2$ Full Cell in 21 mol kg^{-1} LiTFSA/H_2O



Excellent rate performance even at a very fast charge rate (1600 mA g^{-1}) with Nb-based oxide and aqueous electrolytes.



Good capacity retention; 2000 cycles with aqueous electrolyte **because of superior chemical stability of Nb ions**

Conclusions

▪ Niobium is the important element, associated with higher oxidation states with excellent chemical stability, to design high-performance battery materials.

▪ Further exploring of battery materials containing niobium ions is encouraged, potentially resulting in the development of advanced lithium batteries with high energy density and high safety in the future.

Acknowledgments

Collaborators

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Prof. M. Nakayama

Ritsumeikan University (SR center)

Prof. T. Ohta, Mr. K. Yamanaka

University of New South Walls

Prof. Neeraj Sharma

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Interface IONICS

ESICB