マグネシウム循環社会推進協議会
「Mg-Day in SENDAI　Ⅲ」
（於：　東北大学片平さくらホール）

講演４

「マグネシウム蓄電池（正極材料）の開発の経緯と現状迄の進展」

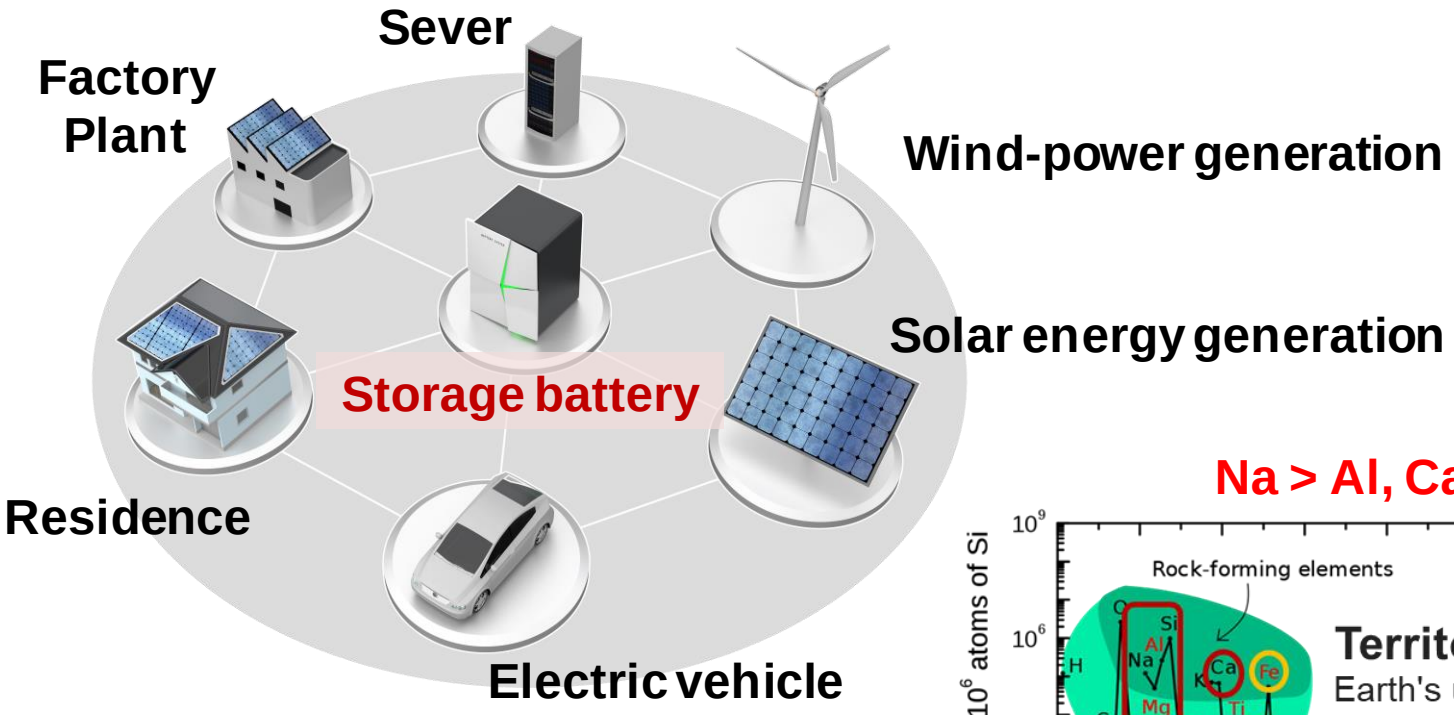
15：10～15：30

東北大学金属材料研究所構造制御機能材料学研究部門
教授　市坪　哲

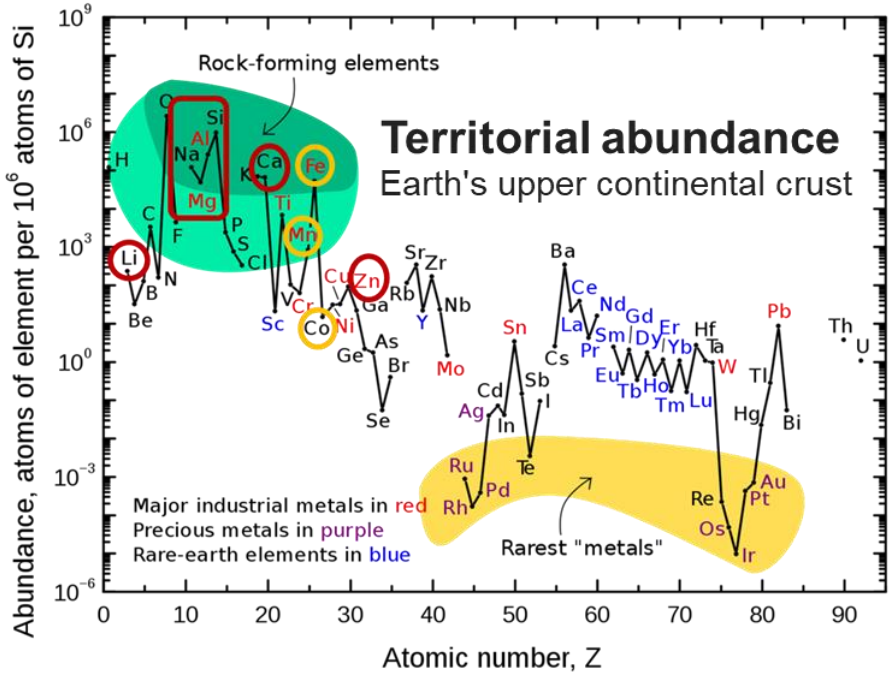
2006 Mg蓄電池研究開始
研究補助金：
ALCA（逢坂蓄電デバイス）2011-2013
ALCA-SPRING移籍（金村TL）2013-2023　正極開発GLなど任務

How to utilize the sustainable energy?

Smart-grid system for energy sustainability



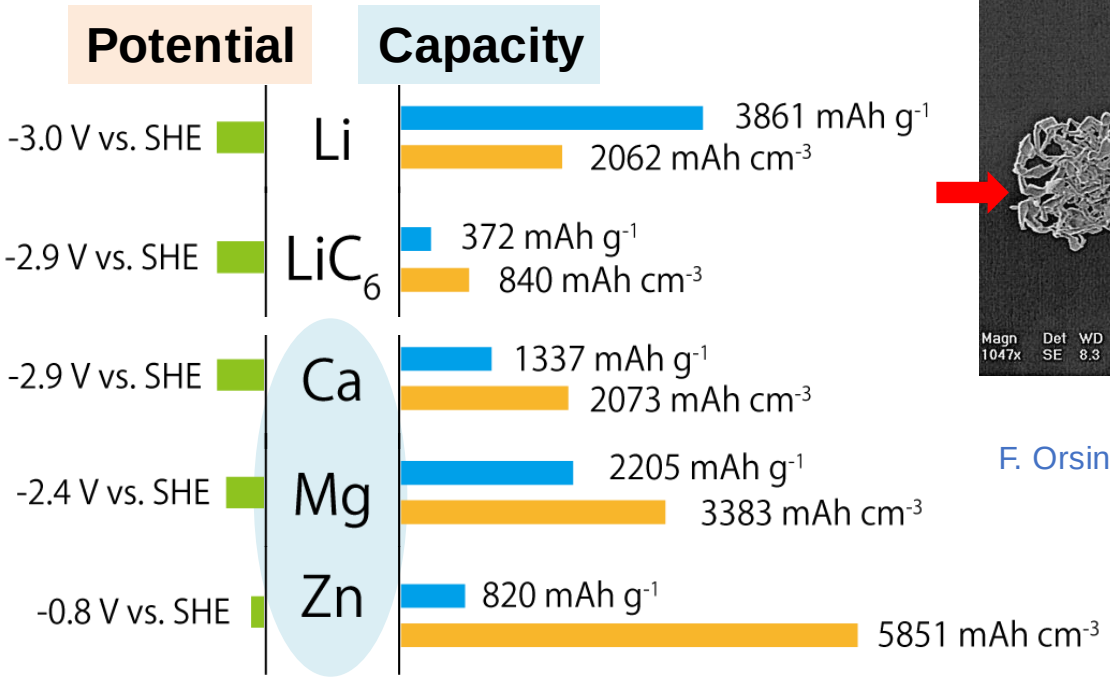
Na > Al, Ca, Mg >> Li

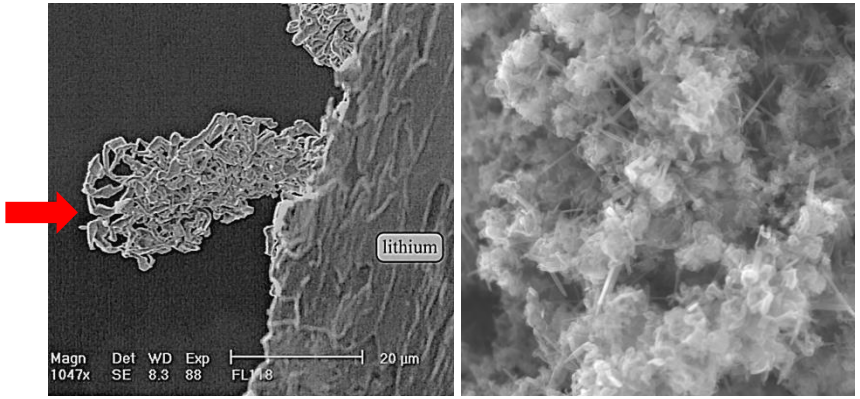


Necessary conditions for scaling-up

1. **Resources must be abundant!**
2. **The most important thing is that rechargeable battery must be safe!!**

Various metal anodes and deposited morphology





Dangerous Li dendrites

F. Orsini et al, *J. Power Sources* **76**, 19 (1998).

Multivalent metals hardly form dendrite morphology upon charge.

O. Mizrahi et al, *J. Electrochem. Soc.*, **155**, A103 (2008).

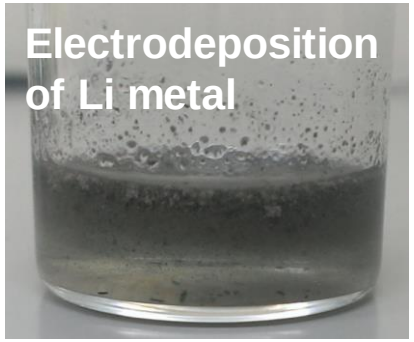
A. Ponrouch et al, *Nat. Mater.* **15**, 169 (2015).

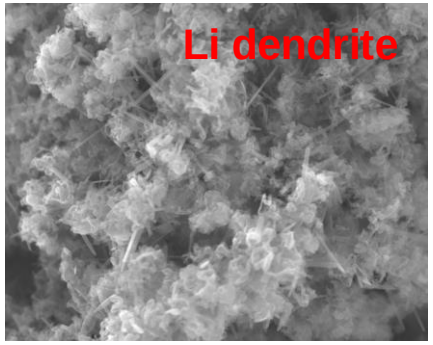
F. Wang et al, *Nat. Mater.* **17**, 543 (2018).

Why magnesium rechargeable battery (MRB) ?

Lithium ion battery (LIB)

Li metal cannot be used as anode material due to a fatal problem, i.e., dendrite electrodeposition of Li metal.

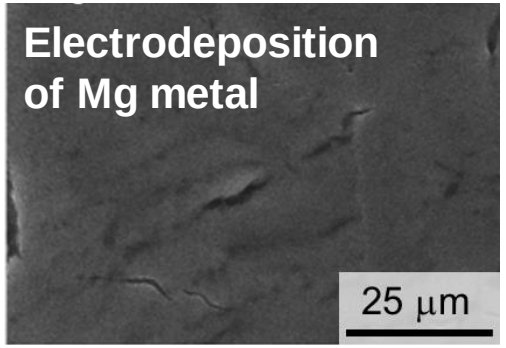




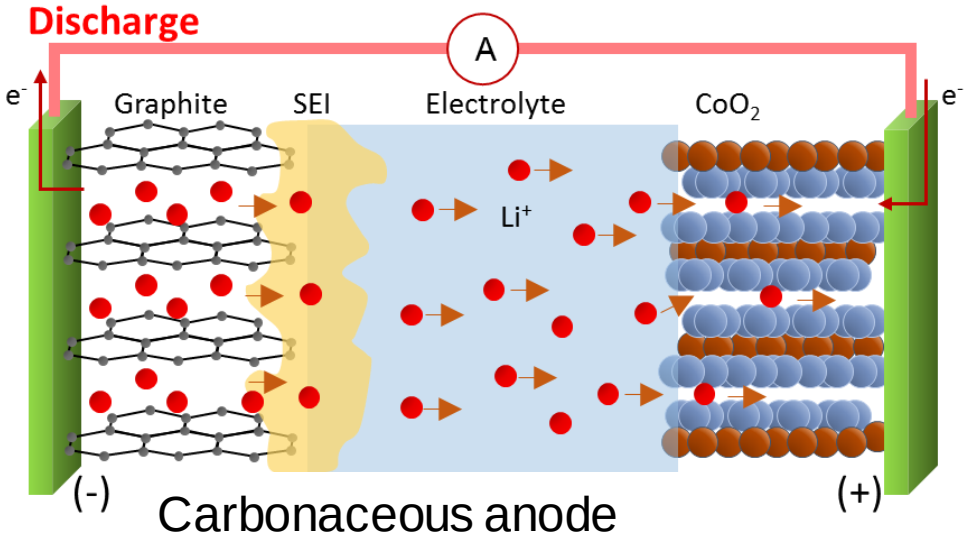
LiC_6 : 72g-carbon per 1mol-electron.
(3.7V-140Ah/kg |EC/DMC| Graphite)
→ 370 Wh/kg

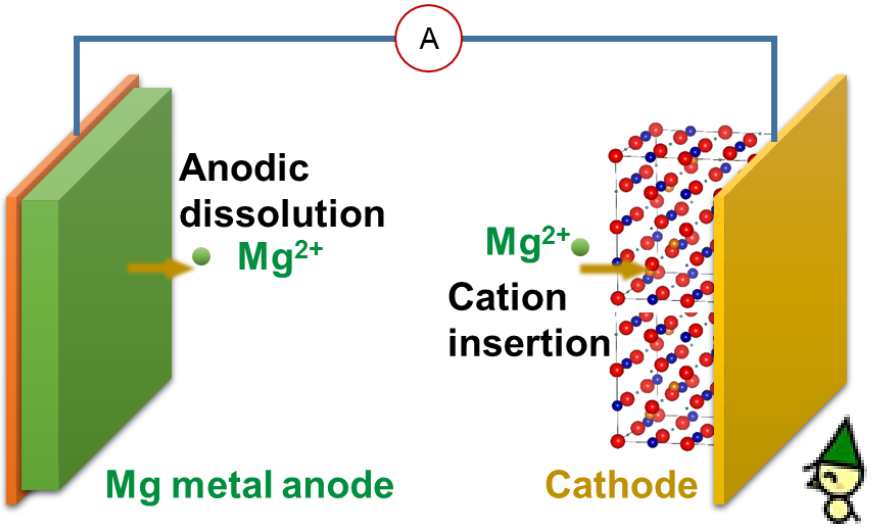
Magnesium rechargeable battery (MRB)

Mg metal can be used as anode material, because Mg metal is electrodeposited smoothly on current collector surface.

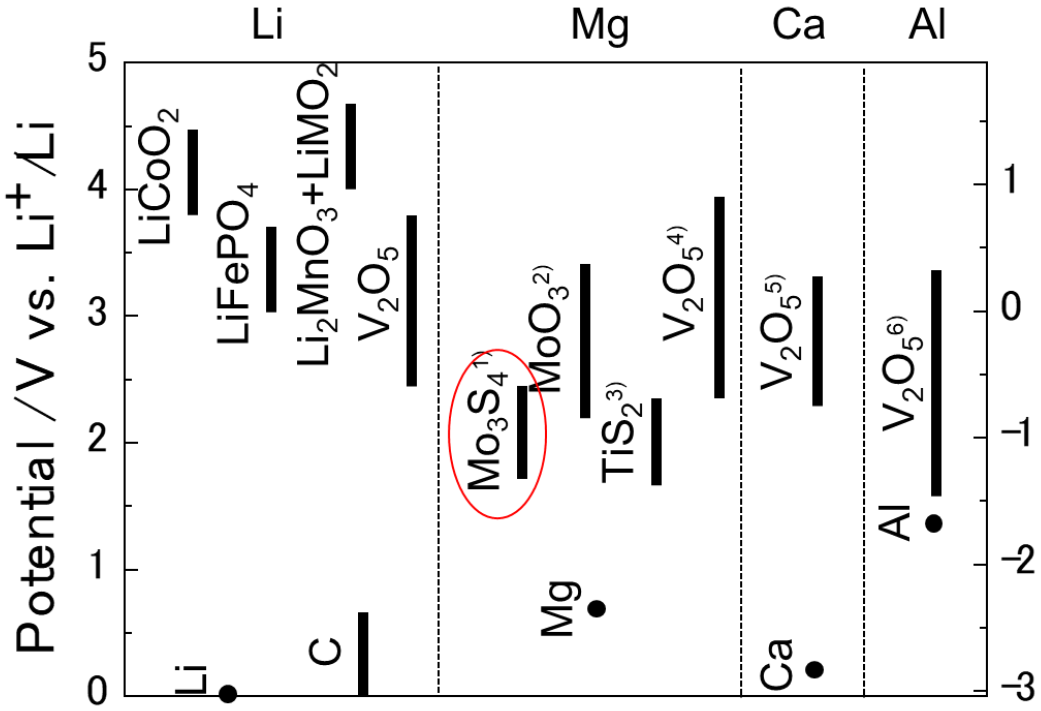


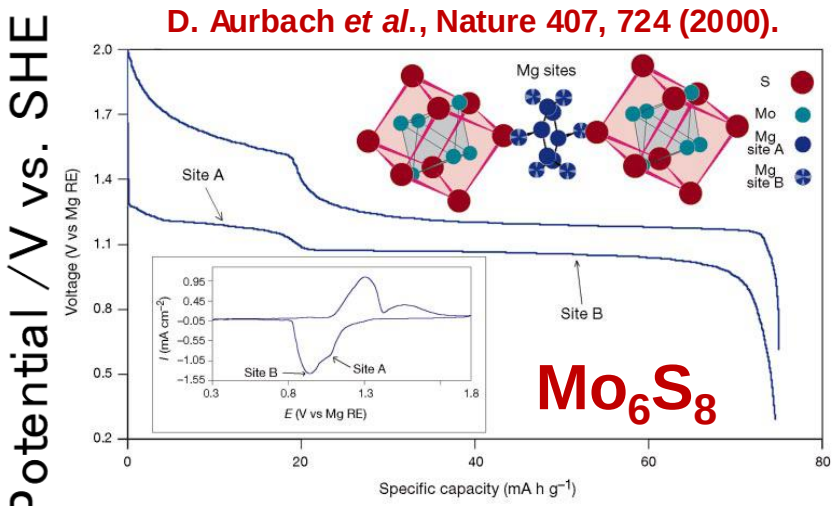
Only 12g-Mg for 1mol-electron
(2.8V-200Ah/kg |Electrolyte| Mg-metal)
→ 510 Wh/kg





§ 2. Cathode material candidates for rechargeable batteries





Only 1V vs Mg → low voltage

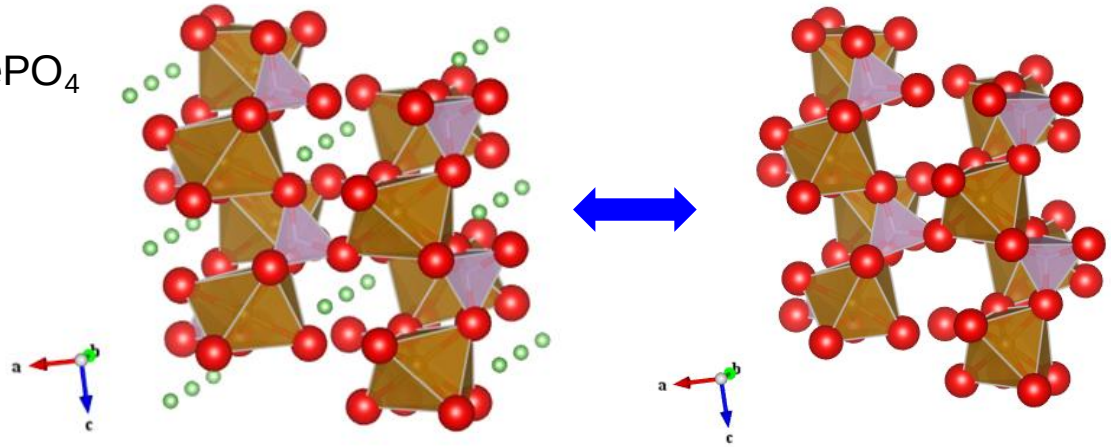
Many cathode candidates for LIB,
but few materials for multivalent cations!

1) D. Aurbach *et al.*, Nature **407**, 724 (2000).
2) M. E. Spahr *et al.*, J. Power Sources **54**, 346 (1995).
3) Z. Tao *et al.*, Chem. Commun. **40**, 2080 (2004).
4) P. Novak *et al.*, J. Electrochem. Soc. **140**, 140 (1993).
5) M. Hayashi *et al.*, J. Power Sources **119**, 617 (2003).
6) N. Jayaprakash *et al.*, Chem. Commun. **47**, 12610 (2012).

§ 2. Activation energy movement: Divalent ions vs Li ion

Olivine : $LiFePO_4$

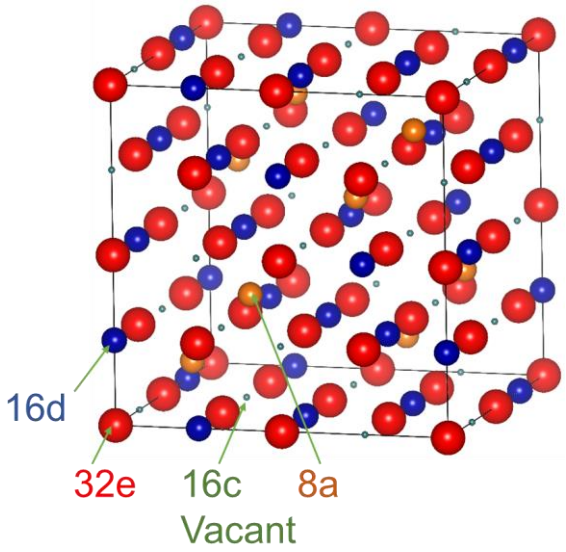
$LiFePO_4$



$FePO_4$

Very fast transition
ΔE(diffusion) ~ 200 meV
Ceder et al.

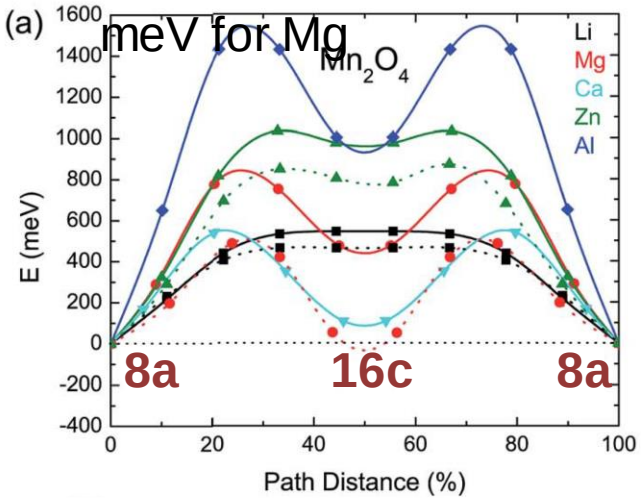
Spinel : AB_2O_4

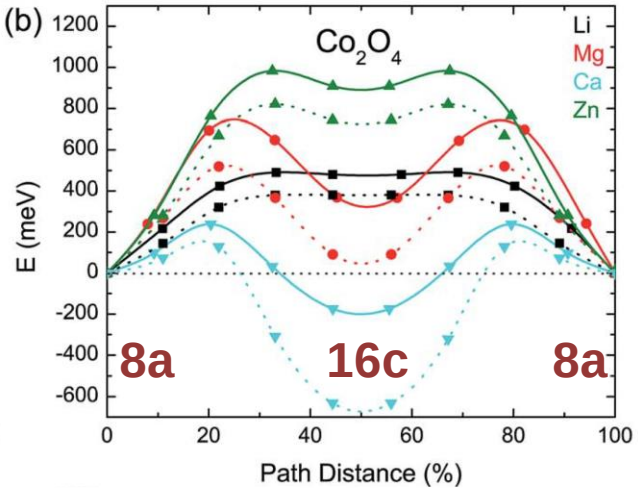


ab-initio calculation by Ceder et al.

ΔE ~ 400 meV for Li

ΔE ~ 600-800 meV for Mg

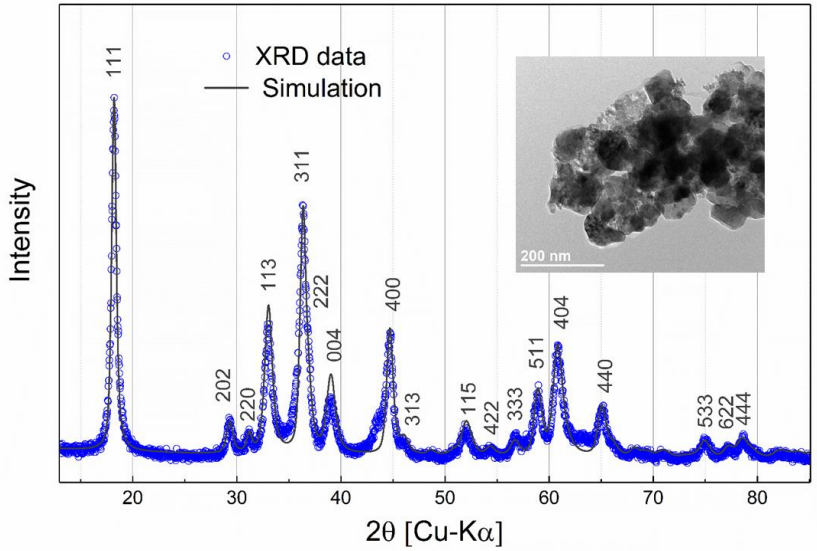


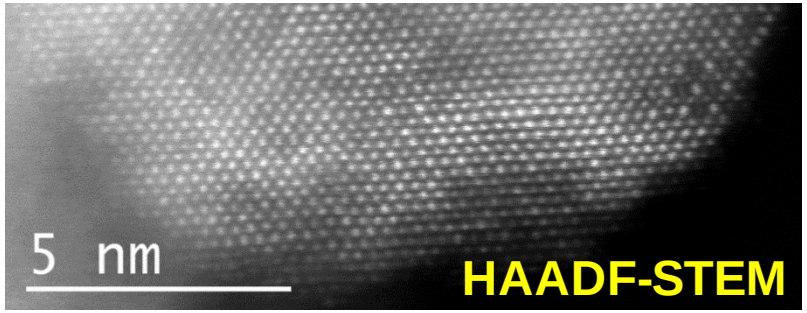


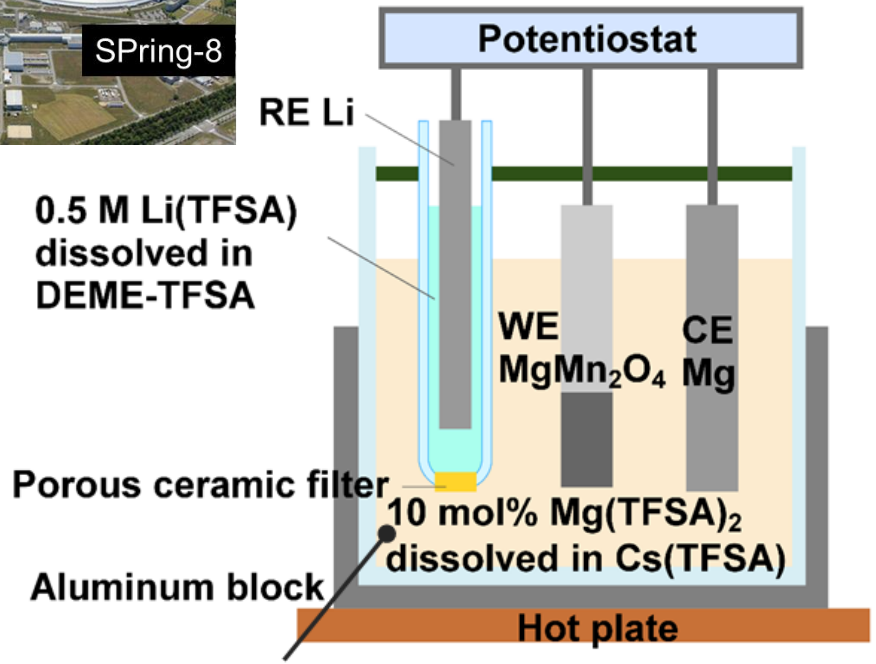
M. Liu, G. Ceder, K.A. Persson et al., Energy Environ. Sci., 2015, 8, 964

Sample preparation and electrochemical method

1. Electrochemical measurement at moderate temperatures
   → using Mg/Cs-TFSA ionic liquid (~150ºC)
2. Inverse co-precipitation method
   → Very fine (primary) particles of about 5-10 nm
3. Sample characterization
   → Synchrotron XRD, XAFS, XPS, STEM, ICP







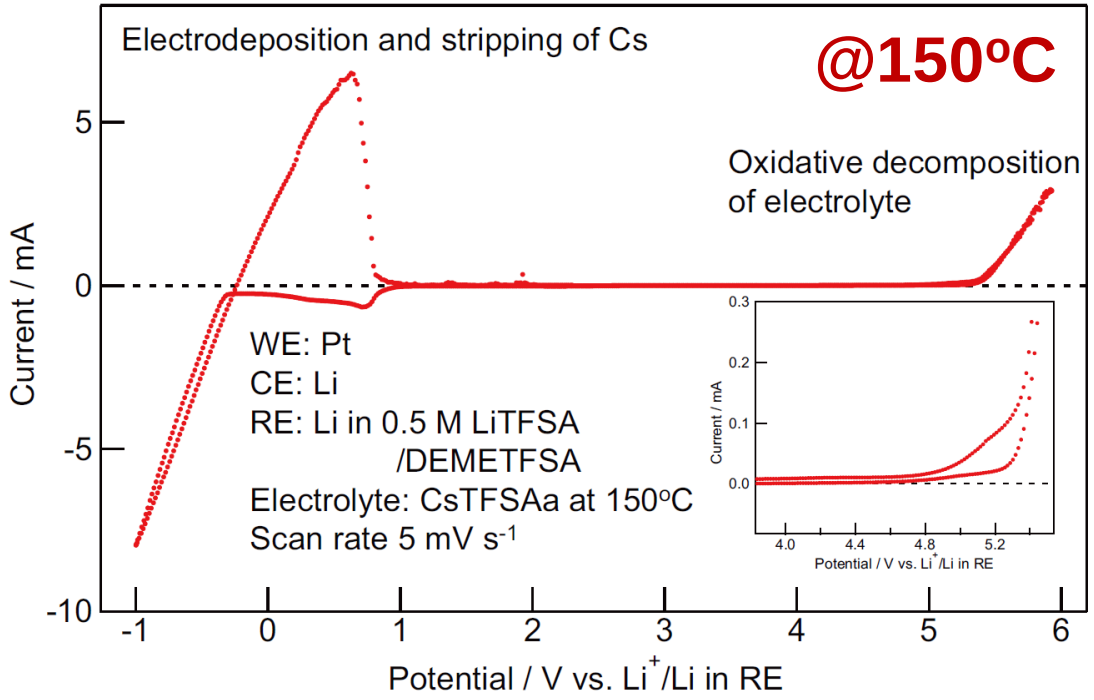
Heated up to 150 °C to enhance Mg diffusion

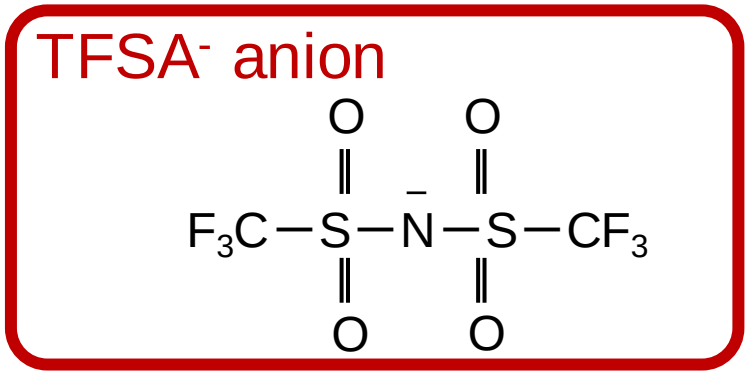
Moderate-temperature ionic liquid

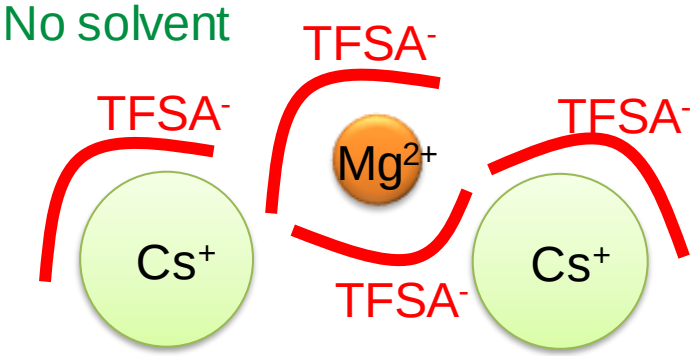
Cs-TFSA based ionic liquid
by Prof. Hagiwara et al.

Molten Salts Chemistry and Technology, M. Gaune-Escard and G. M. Haarberg eds., John Wiley & Sons, Ltd. Chapt. 5.4 (2014).

Melting temperature of Cs-TFSA: 120°C







Advantageous points:

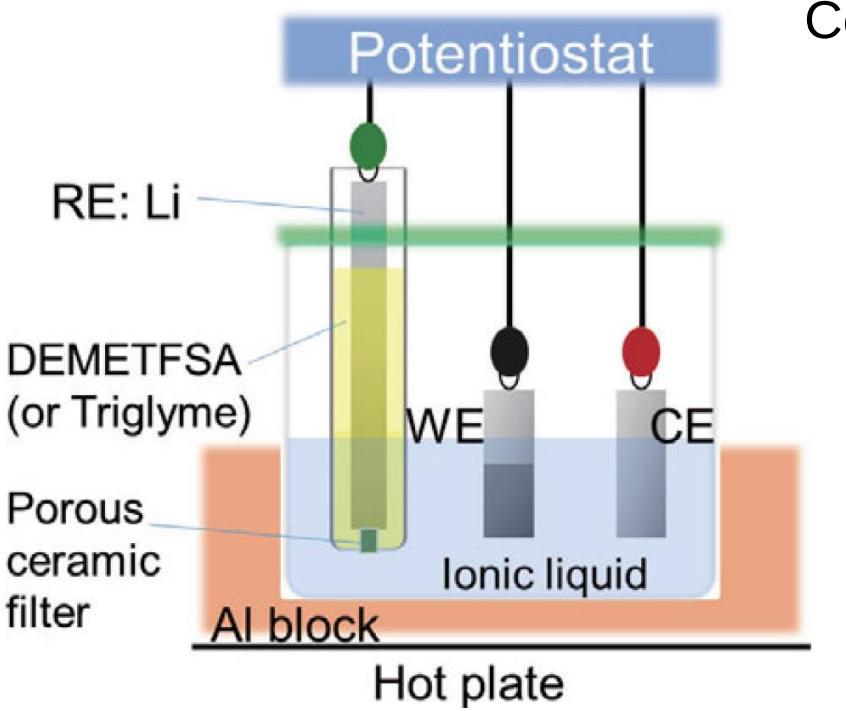
1. Possible to operate at moderate temperatures (120-200 °C)
2. Wide electrochemical window: High oxidation limit (~5V vs Li)

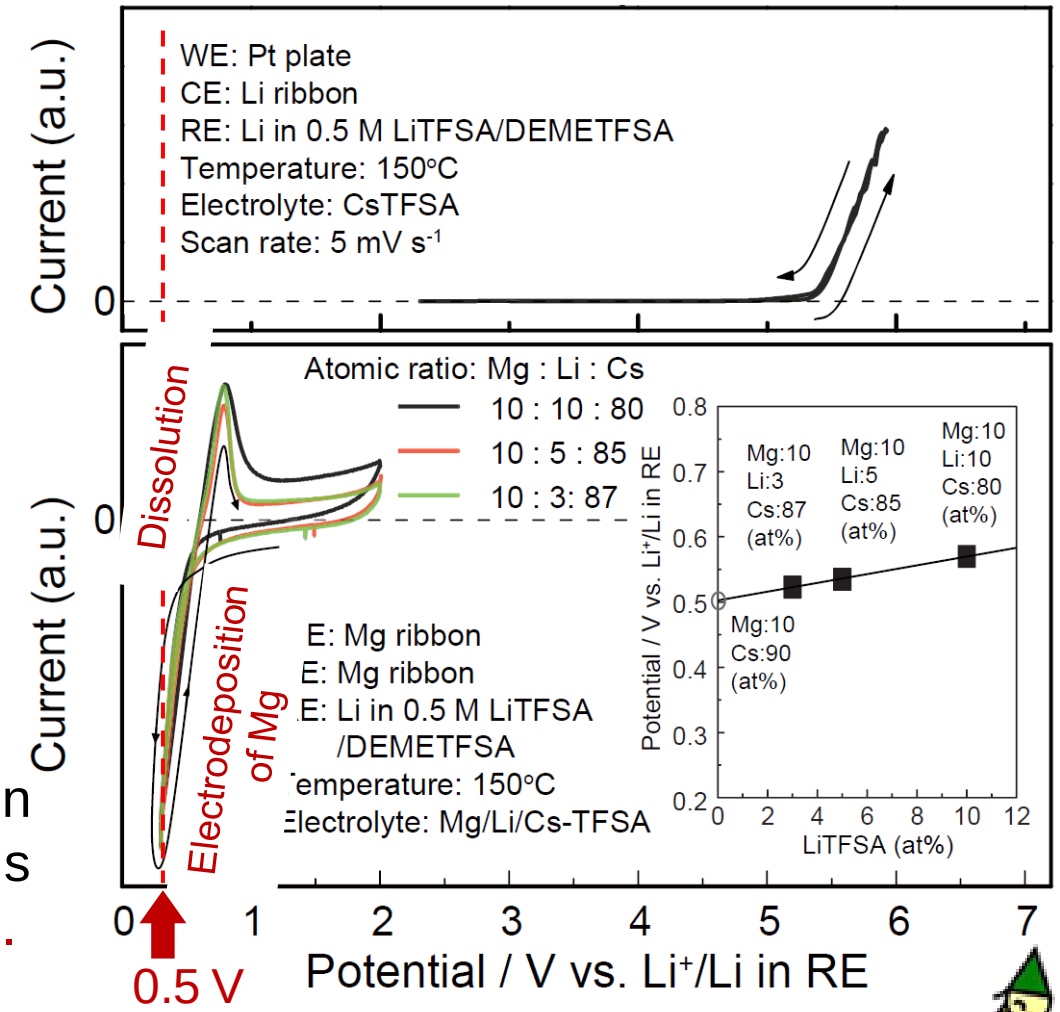
Estimating Redox Potential of Mg in (Mg10/Cs90)-TFSA liquid

$Mg(TFSA)_2$ / CsTFSA = 10 / 90

Ar atmosphere
Dew point: -70 ~ -80 ºC

Reference electrode (RE): Li in 0.5M LiTFSA / DEME-TFSA solution
Counter electrode (CE): Mg ribbon





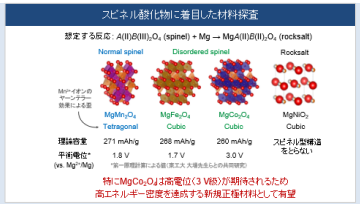
Redox potential conversion rule

The redox potential of Mg/Mg^{2+} in (Mg10/Cs90)-TFSA ionic liquid is estimated to be **0.5 V vs Li (in RE)**.

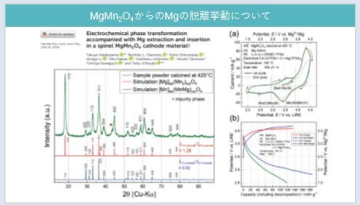
Mg蓄電池用正極材料の新しい設計指針の確立

東北大金研　市坪　哲，下川 航平，畠山 拓也，岡本 範彦

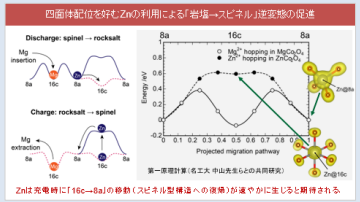
1. スピネル酸化物に着目した材料探査：スピネル-岩塩相転移の発見



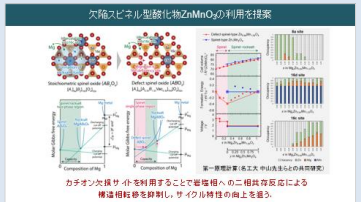
2. スピネル酸化物$MgMn_2O_4$からのMg脱離の実行可能性



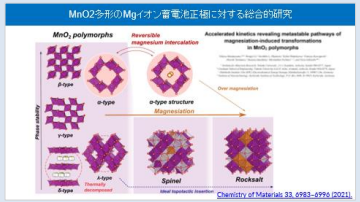
3. Zn基スピネル酸化物：可逆性の向上



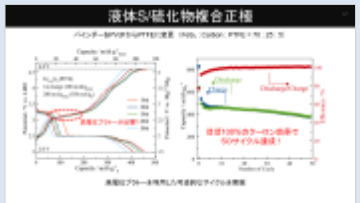
4. 欠陥スピネル酸化物$ZnMnO_3$の高サイクル特性



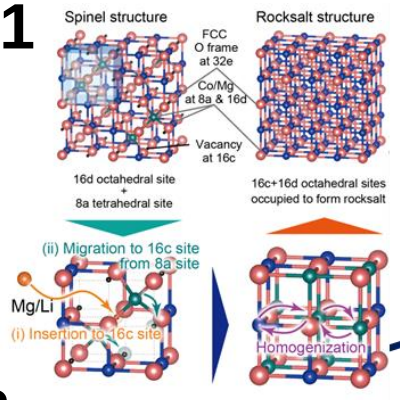
5. MnO_2多形に対するMg挿入相変態の研究



6. TMS_2からのTM脱離によるS正極の開発



1



酸化物
高電位低容量低レート

VS

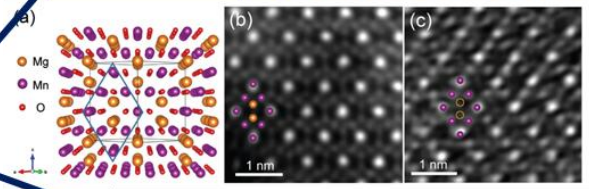
硫化物
低電位高容量高レート

Spinel → Rocksalt

$MgCo_2O_4$　スピネル･岩塩間相転移
Mgの確かな脱挿入を実証

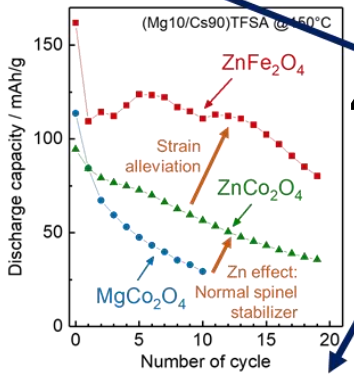
2

$MgMn_2O_4$　スピネル･8a欠陥スピネル
Mgの部分的な脱離も可能



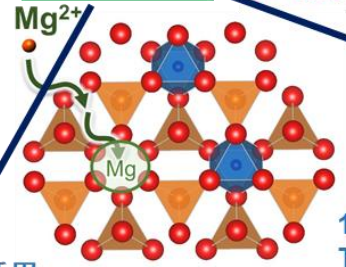
3

$ZnFe_2O_4$　スピネル･岩塩間相転移
可逆性が向上



4

$ZnMnO_3$

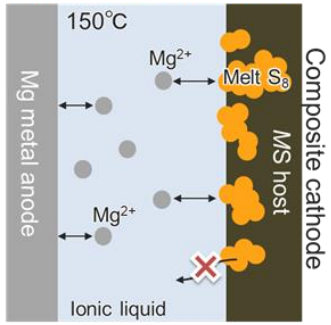


XO_2 +AO
MnO_2へのAO添加によりさらなる多形構造へ展開
山中G，小林Gらと共同検討

16d欠陥スピネル･スピネル間相転移
Topotacticな領域の活用で可逆性がさらに向上

6　FeS_2･CoS_2
溶解性が高い硫黄Sを
FeS_2ポーラス組織中に保持

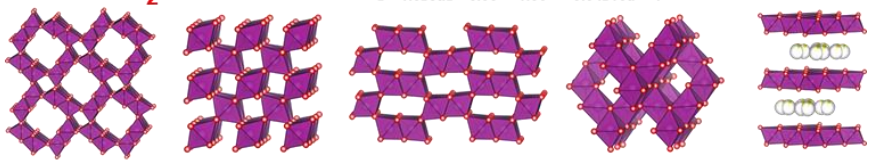
イオン液体との組み合わせで
液体硫黄の使用も可能に



5

XO_2　多形構造の活用
X = Cr, V, Ti, Mn
MnO_2

欠陥スピネル型構造
$A(II)B(IV)O_3$
$[A_{1.0}]_{8a}[A_{0.33}B_{1.33}\square_{0.34}]_{16d}O_4$



新しい化合物候補群を生み出す
演繹的な考え方の創出
↓
室温可動正極・設計指針の確立

今後の進展へ向けて

- 容量の増大化 100 → 200 or 300 Ah/kg
  MnO_2ベースで開発促進

- Mg脱挿入の低温度化（できれば室温）

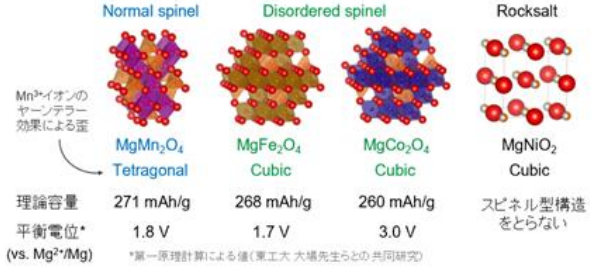
- HFIP系電解液での可逆的な脱挿入の実現

- デュアルカチオンの検討

説明用の詳細スライド

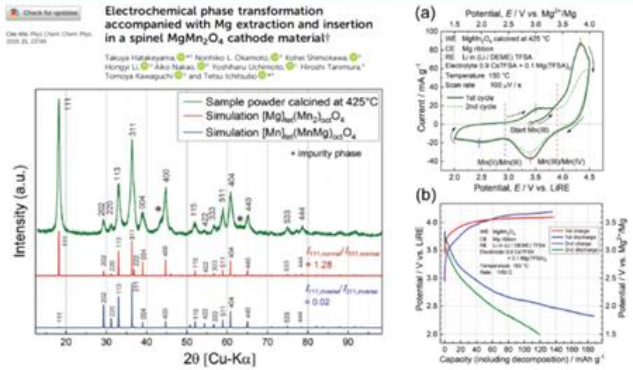
スピネル酸化物に着目した材料探査

想定する反応: $A(II)B(III)_2O_4$ (spinel) + Mg → $MgA(II)B(II)_2O_4$ (rocksalt)

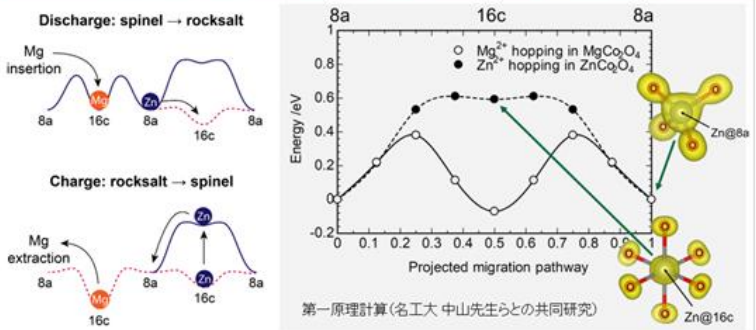


特に$MgCo_2O_4$は高電位(3 V級)が期待されるため
高エネルギー密度を達成する新規正極材料として有望

$MgMn_2O_4$からのMgの脱離挙動について

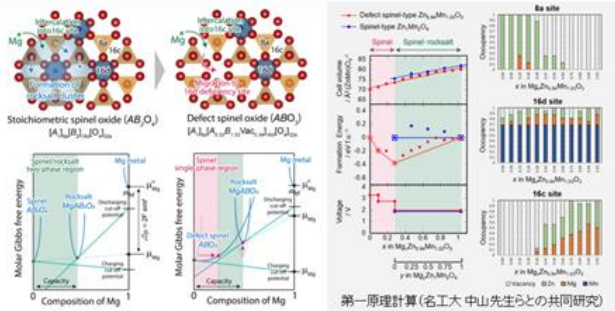


四面体配位を好むZnの利用による「岩塩→スピネル」逆変態の促進



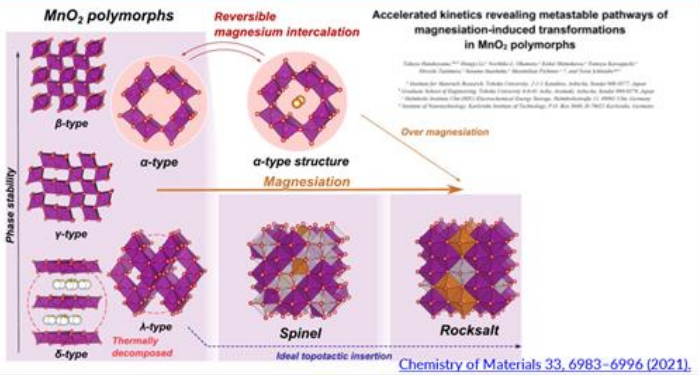
Znは充電時に「16c→8a」の移動(スピネル型構造への復帰)が速やかに生じると期待される.

欠陥スピネル型酸化物$ZnMnO_3$の利用を提案



カチオン欠損サイトを利用することで岩塩相への二相共存反応による
構造相転移を抑制し, サイクル特性の向上を狙う.

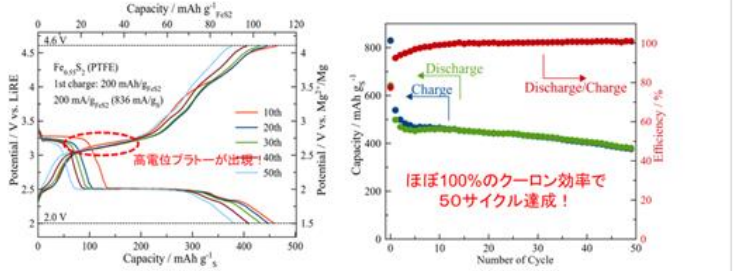
MnO2多形のMgイオン蓄電池正極に対する総合的研究



Chemistry of Materials 33, 6983–6996 (2021).

液体S/硫化物複合正極

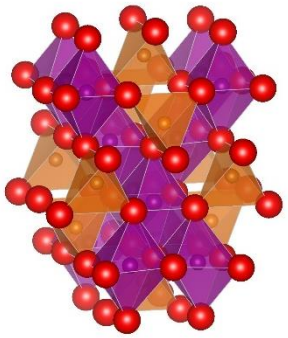
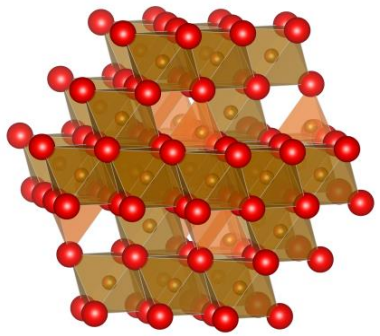
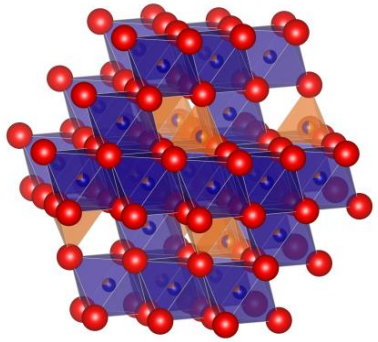
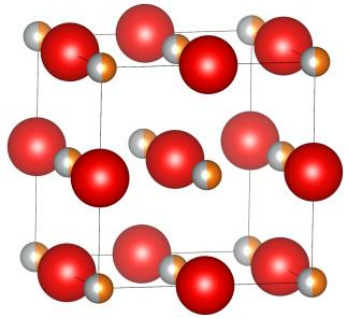
バインダーをPVdFからPTFEに変更 (FeS_2 : Carbon : PTFE = 70 : 25 : 5)



高電位プラトーを利用した可逆的なサイクルを実現

スピネル酸化物に着目した材料探査

想定する反応: $A(\mathrm{II})B(\mathrm{III})_2O_4$ (spinel) + Mg → $\mathrm{Mg}A(\mathrm{II})B(\mathrm{II})_2O_4$ (rocksalt)

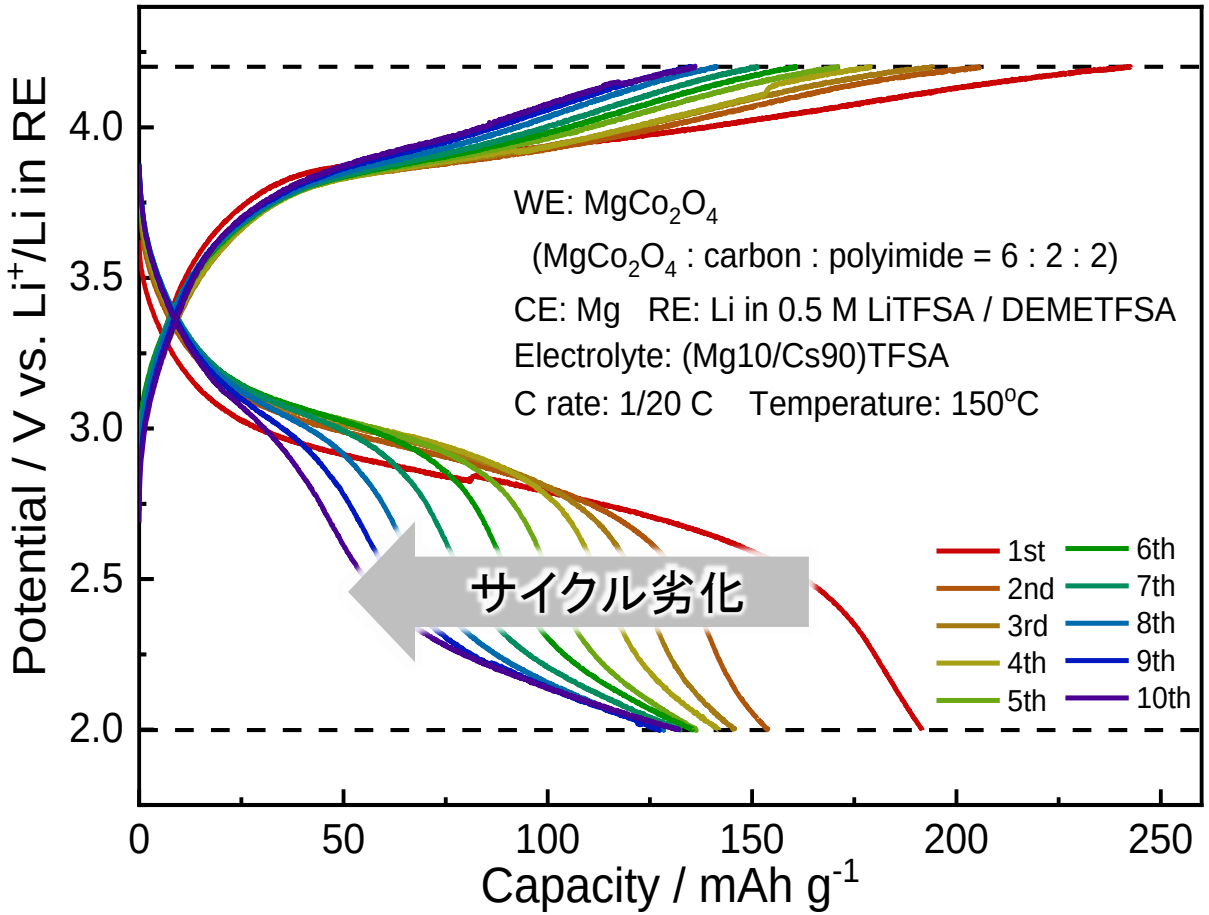
	Normal spinel	Disordered spinel		Rocksalt
				
Mn^{3+}イオンのヤーンテラー効果による歪	$MgMn_2O_4$	$MgFe_2O_4$	$MgCo_2O_4$	$MgNiO_2$
	Tetragonal	Cubic	Cubic	Cubic
理論容量	271 mAh/g	268 mAh/g	260 mAh/g	スピネル型構造をとらない
平衡電位* (vs. Mg^{2+}/Mg)	1.8 V	1.7 V	3.0 V	

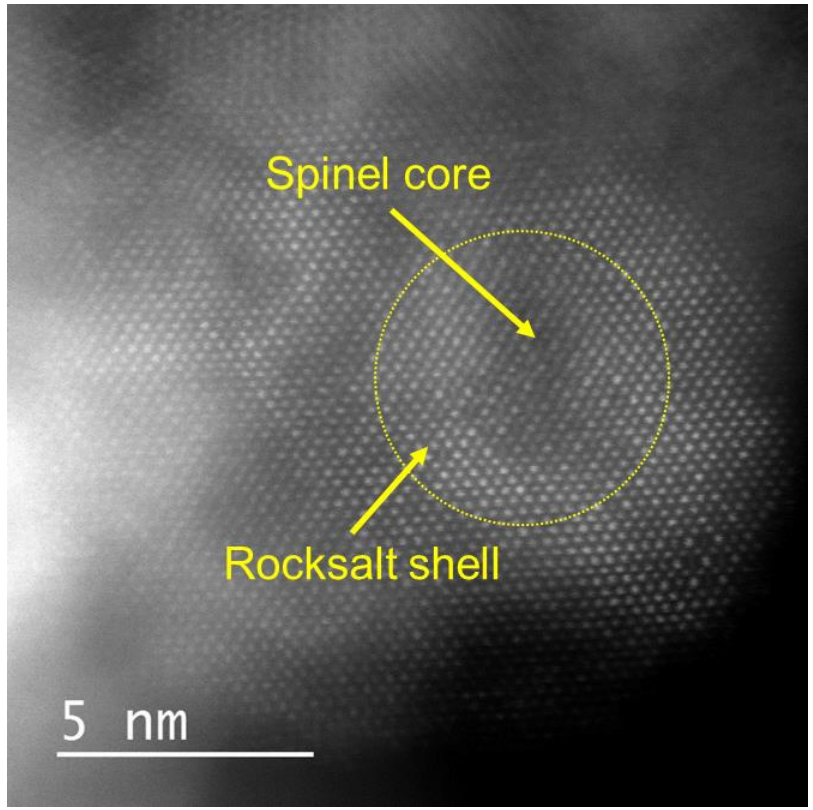
*第一原理計算による値（東工大 大場先生らとの共同研究）

特に$MgCo_2O_4$は高電位（3 V級）が期待されるため
高エネルギー密度を達成する新規正極材料として有望

スピネル酸化物に着目した材料探査

スピネル相と岩塩相の二相共存反応（酸素格子は整合）により充放電が進行





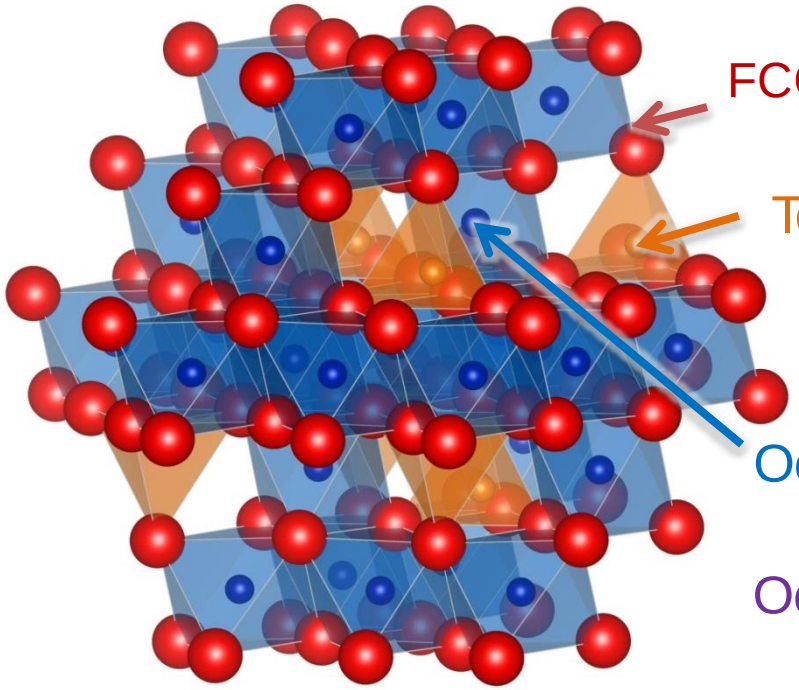
放電後の粒子のSTEM観察結果

サイクル劣化抑制に向けたスピネル型酸化物の新たな設計指針が必要

Structural similarity between Spinel and Rocksalt

Space group #227

Spinel



$A(II)B(III)_2O_4$

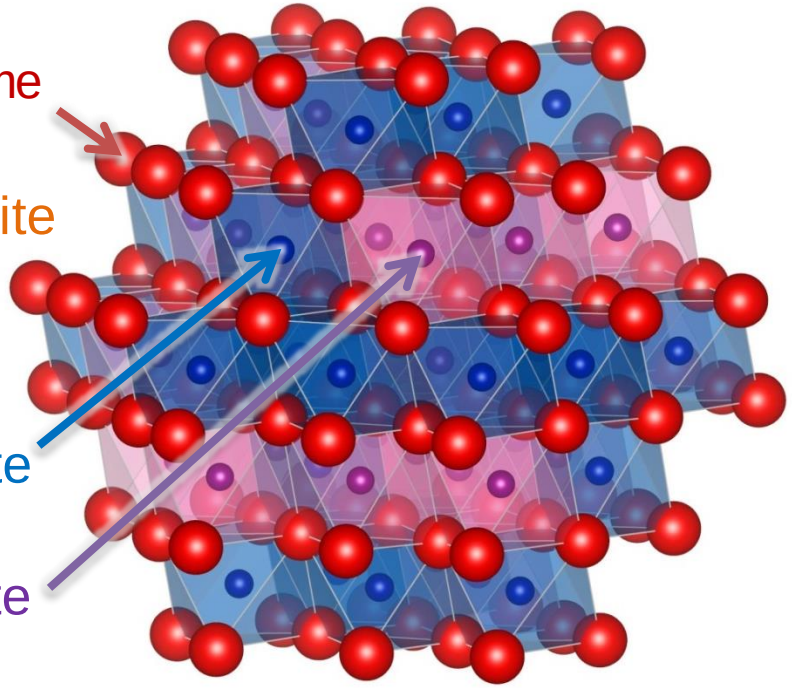
FCC oxygen flame
(32e site)

Tetrahedral site
(8a site)

Octahedral site
(16d site)

Octahedral site
(16c site)

Rocksalt

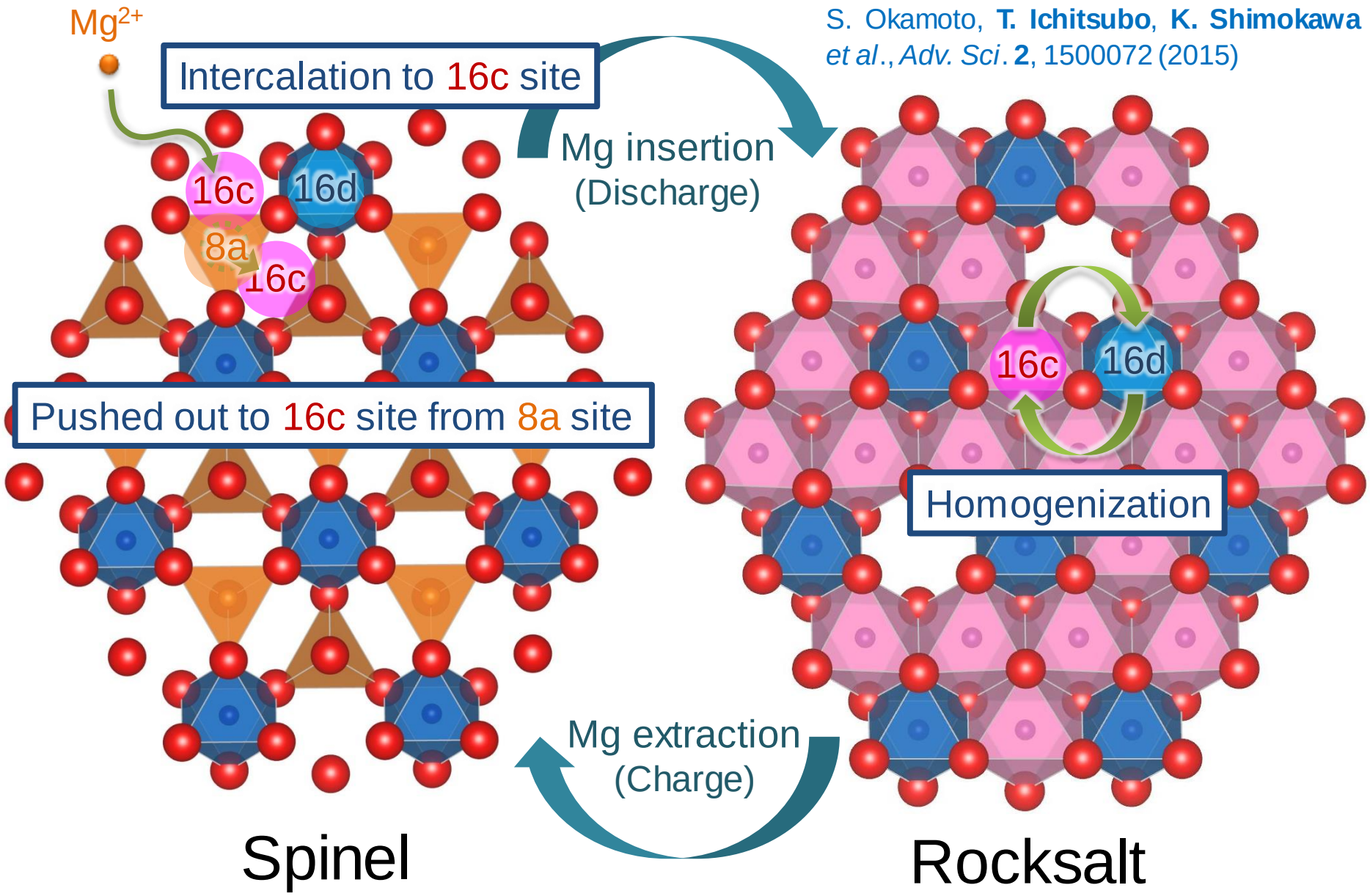


$MgA(II)B(II)_2O_4$

Only difference is the configuration of 8a and 16c

“Intercalation and push-out” mechanism

S. Okamoto, **T. Ichitsubo**, **K. Shimokawa** *et al.*, *Adv. Sci.* **2**, 1500072 (2015)



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www.advancedscience.com

Intercalation and Push-Out Process with Spinel-to-Rocksalt Transition on Mg Insertion into Spinel Oxides in Magnesium Batteries

Shinya Okamoto, Tetsu Ichitsubo, Tomoya Kawaguchi, Yu Kumagai, Fumiyasu Oba, Shunsuke Yagi, Kohei Shimokawa, Natsumi Goto, Takayuki Doi, and Eiichiro Matsubara*

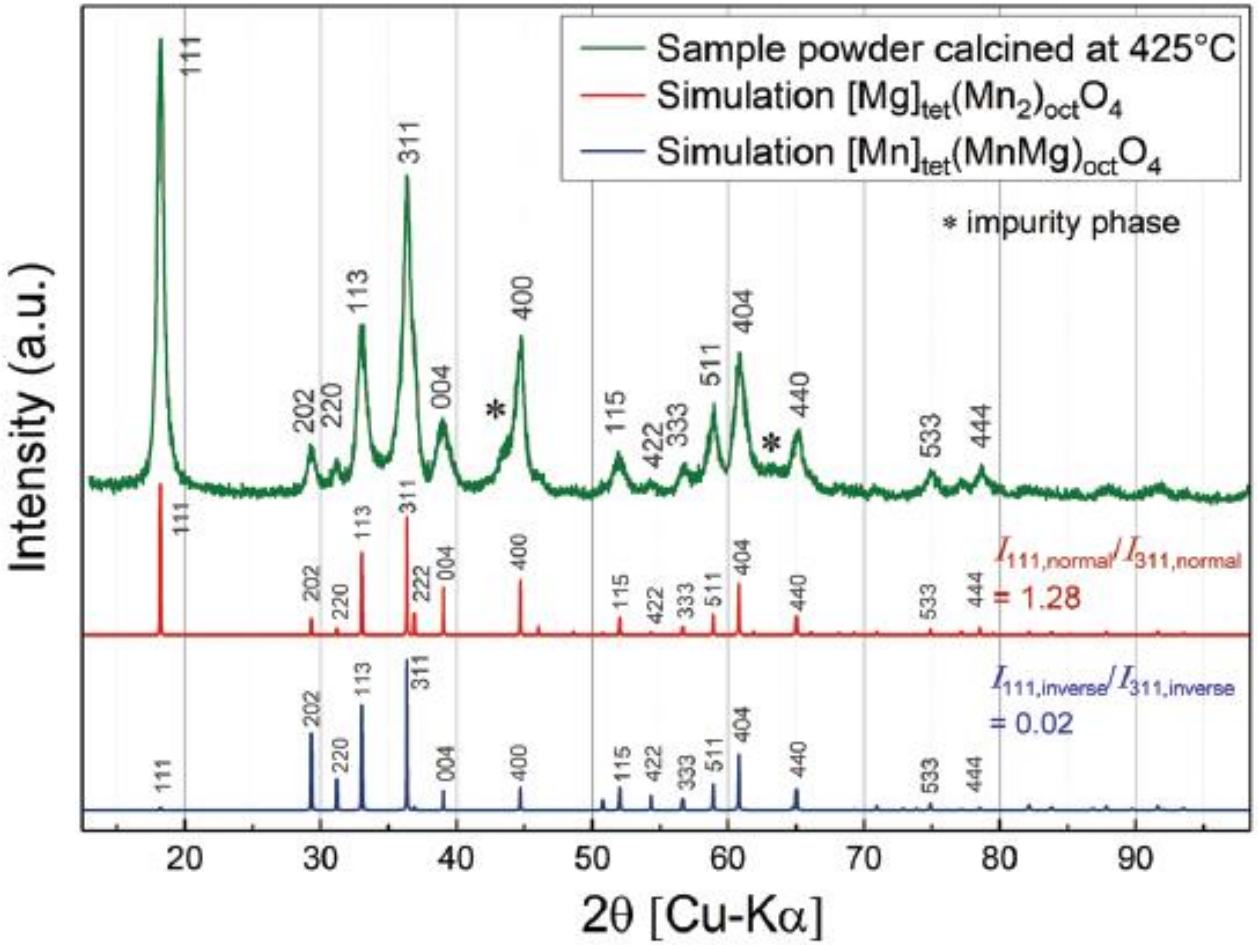
$MgMn_2O_4$からのMgの脱離挙動について

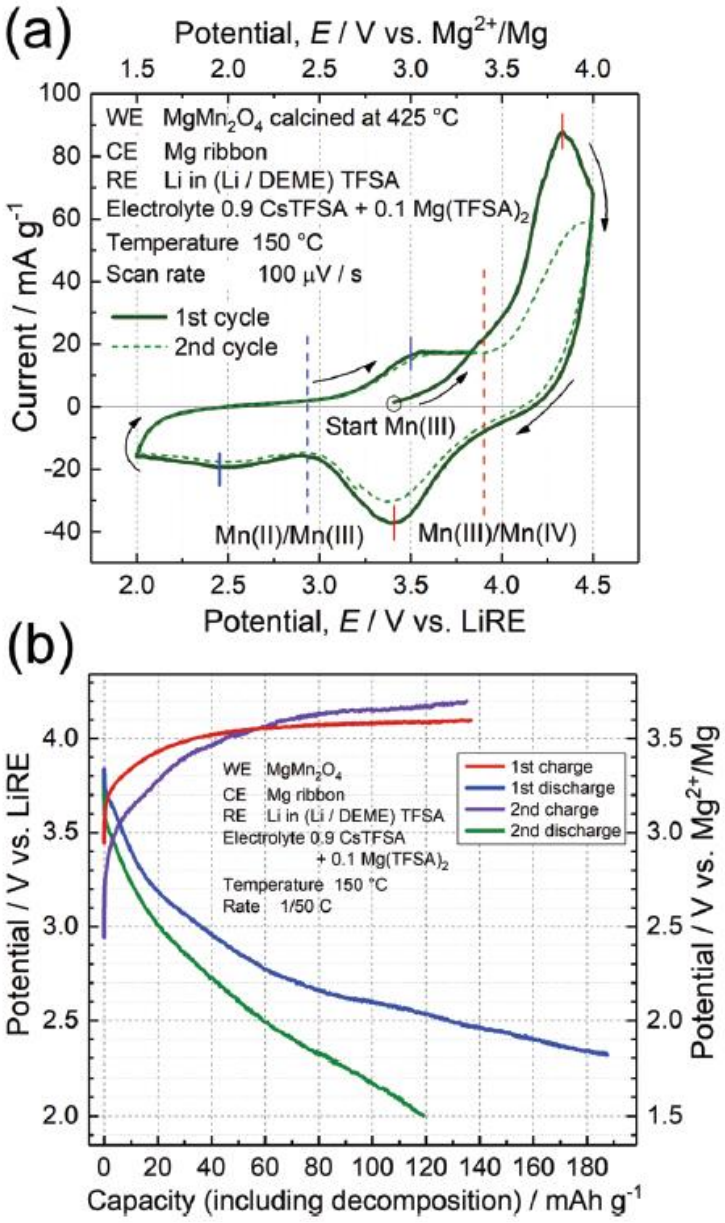
Check for updates

Cite this: *Phys. Chem. Chem. Phys.*, 2019, 21, 23749

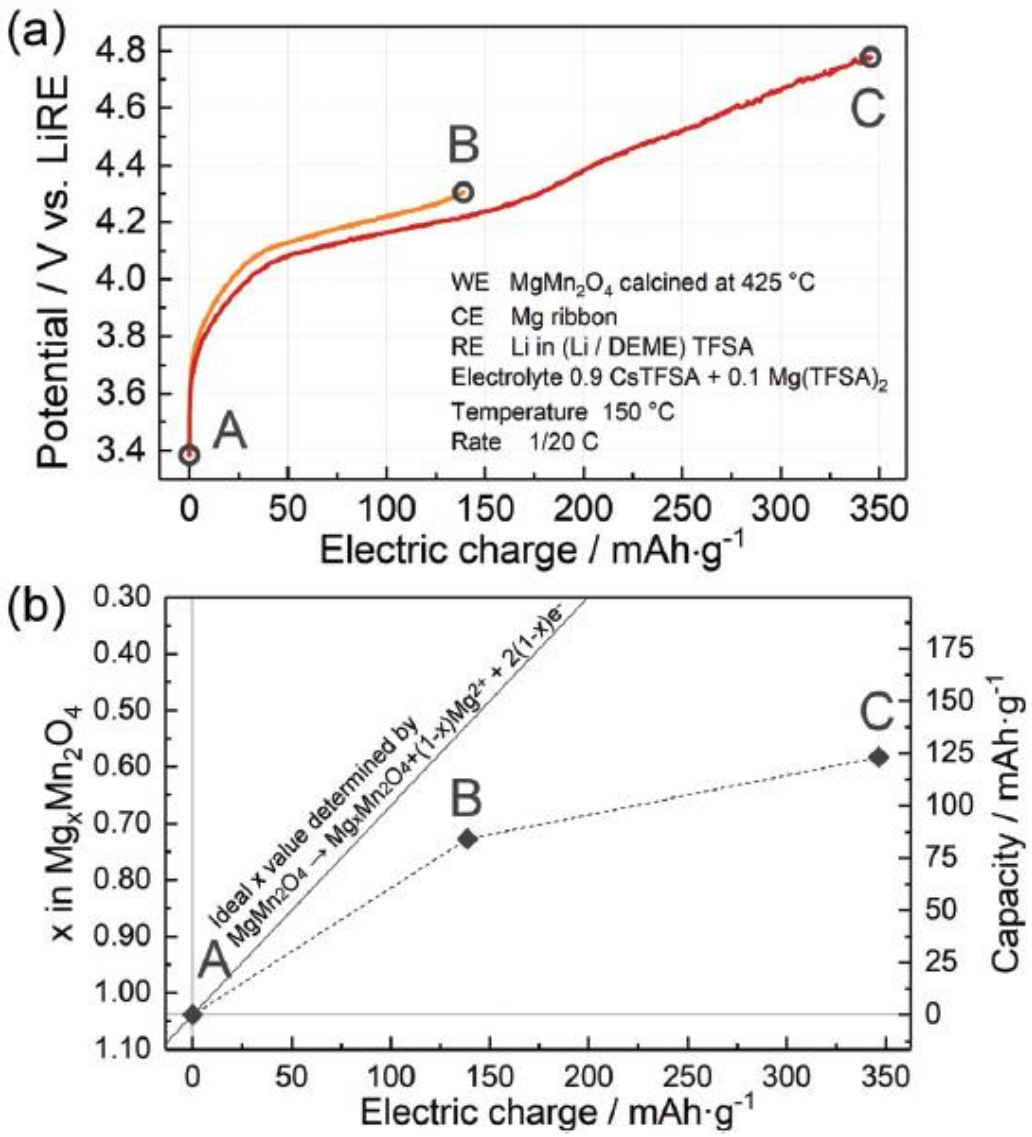
Electrochemical phase transformation accompanied with Mg extraction and insertion in a spinel $MgMn_2O_4$ cathode material†

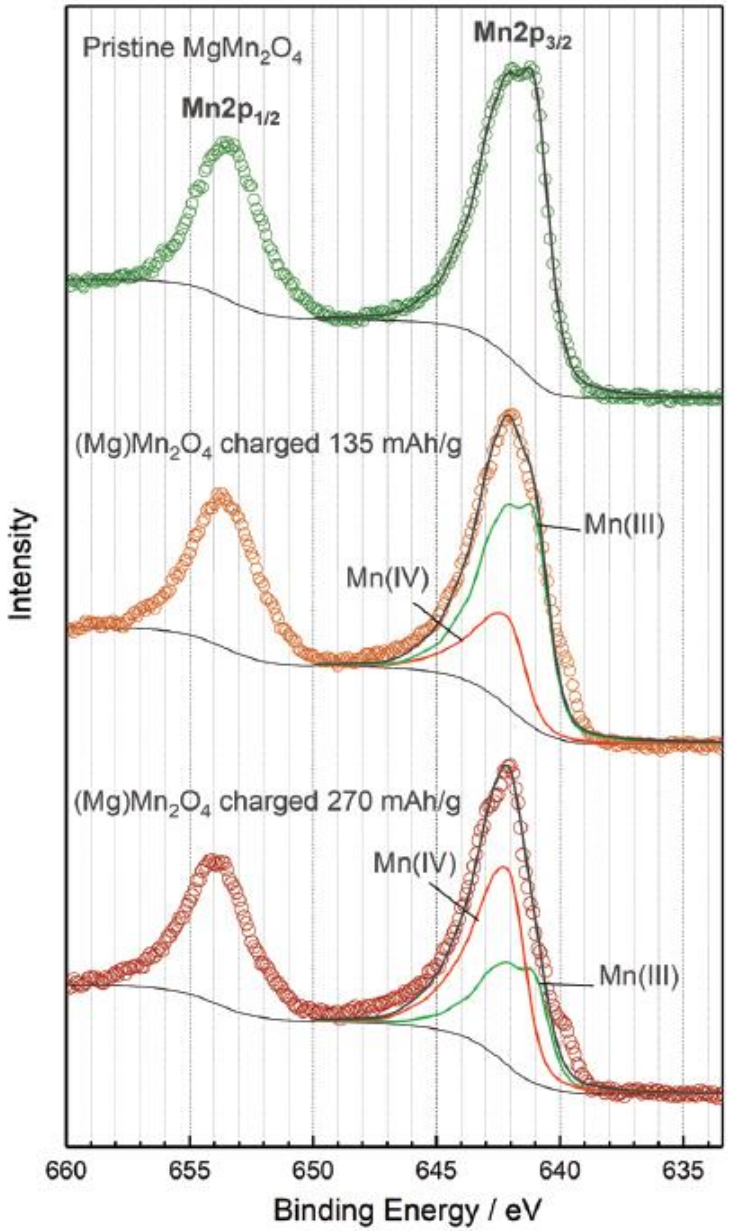
Takuya Hatakeyama,*[a] Norihiko L. Okamoto,[a] Kohei Shimokawa,[a] Hongyi Li,[a] Aiko Nakao,[b] Yoshiharu Uchimoto,[c] Hiroshi Tanimura,[a] Tomoya Kawaguchi[a] and Tetsu Ichitsubo*[a]



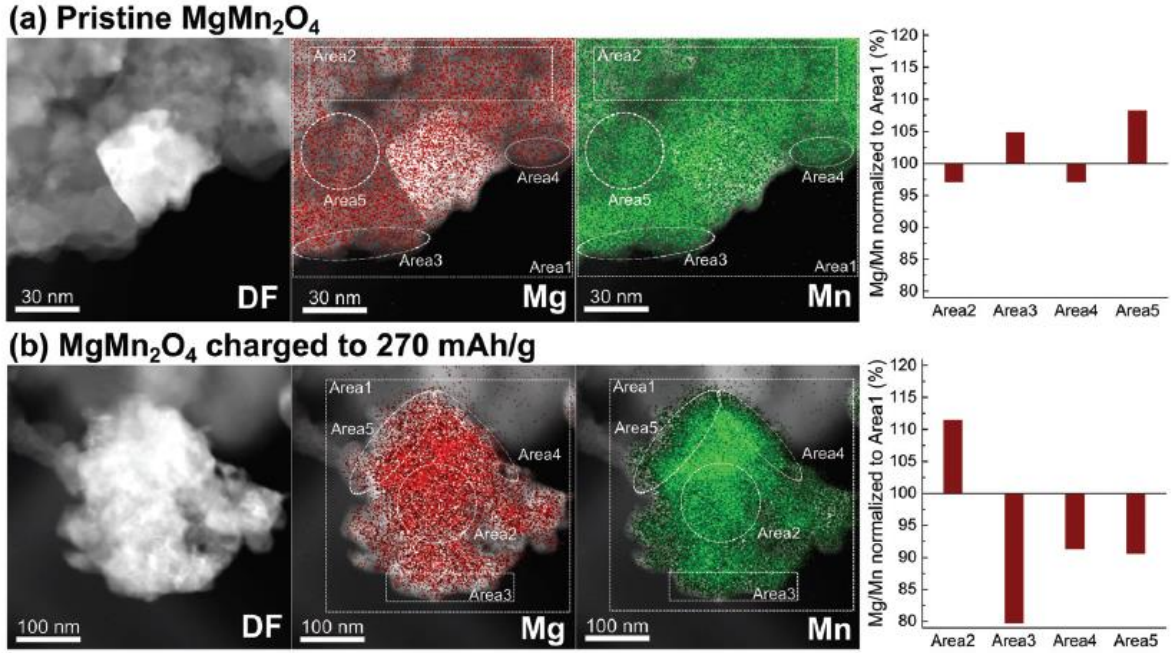


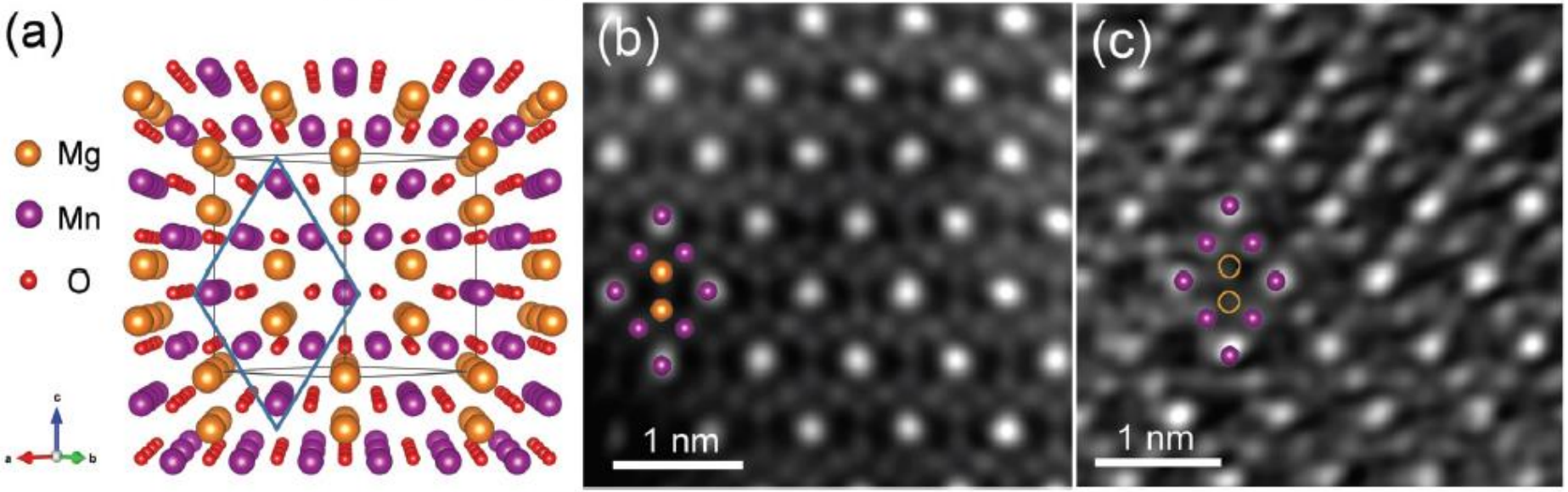
$MgMn_2O_4$からのMgの脱離挙動について



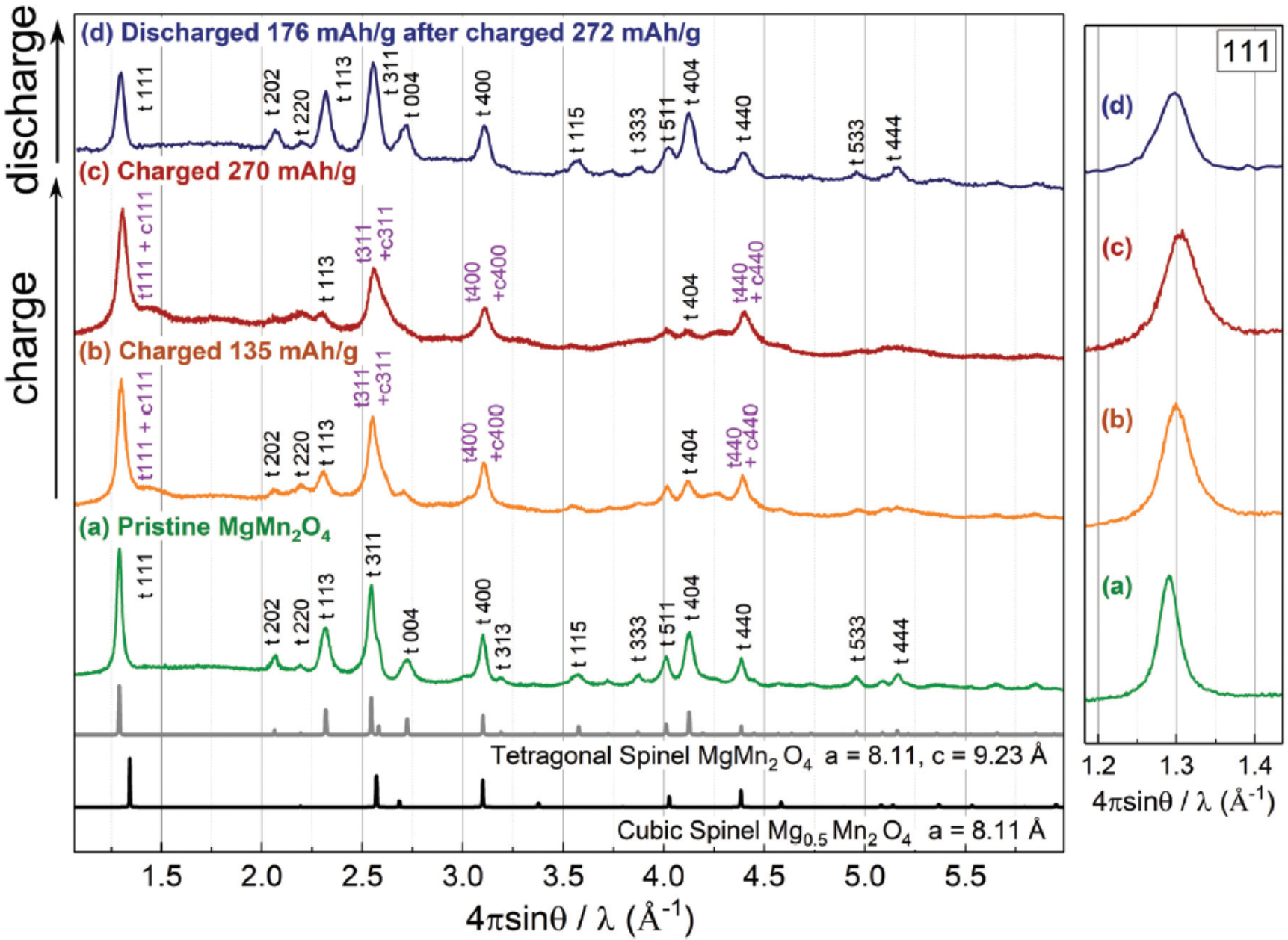


$MgMn_2O_4$からのMgの脱離挙動について

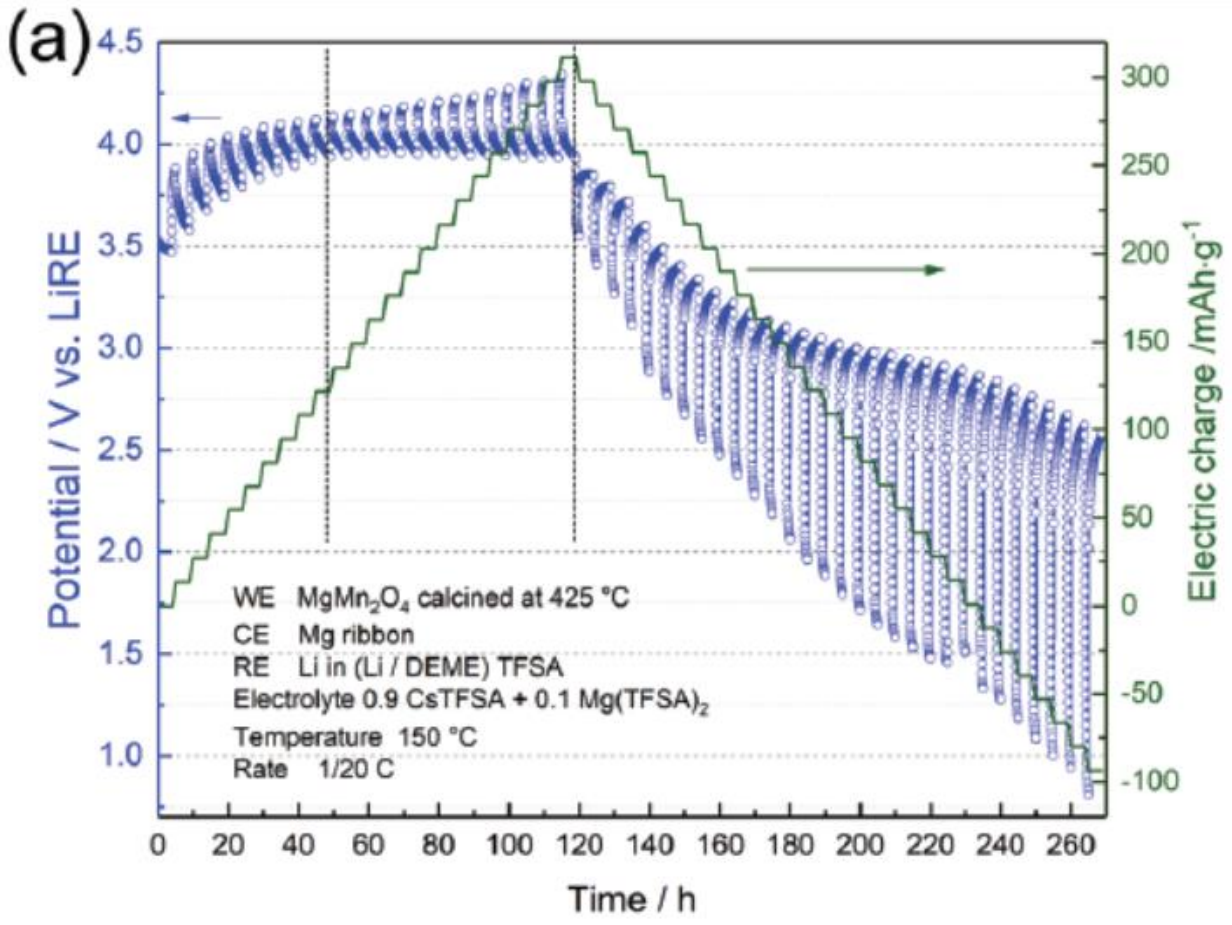


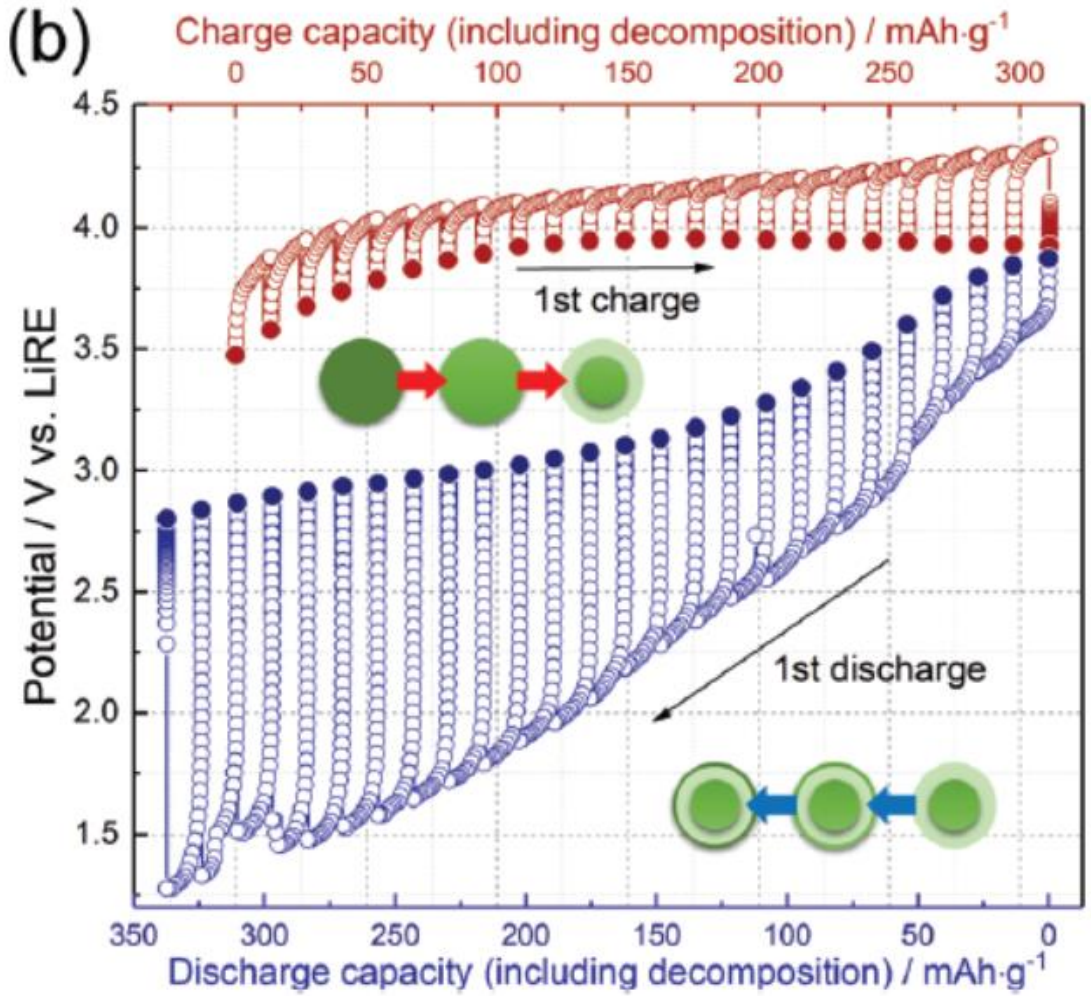


$MgMn_2O_4$からのMgの脱離挙動について



$MgMn_2O_4$からのMgの脱離挙動について





発表論文

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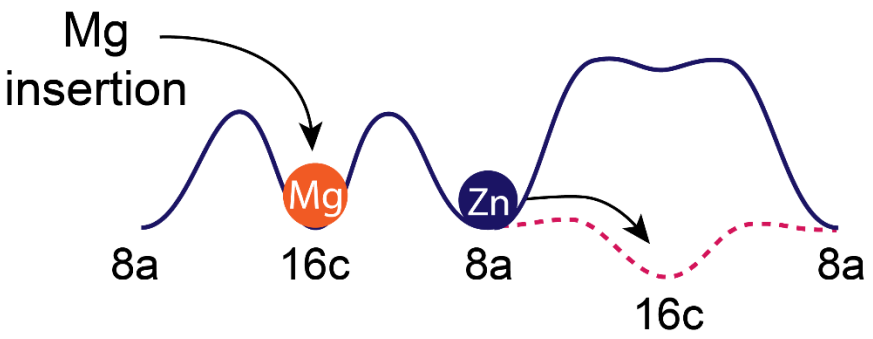
Cite this: *Phys. Chem. Chem. Phys.*, 2019, **21**, 23749

Electrochemical phase transformation accompanied with Mg extraction and insertion in a spinel $MgMn_2O_4$ cathode material†

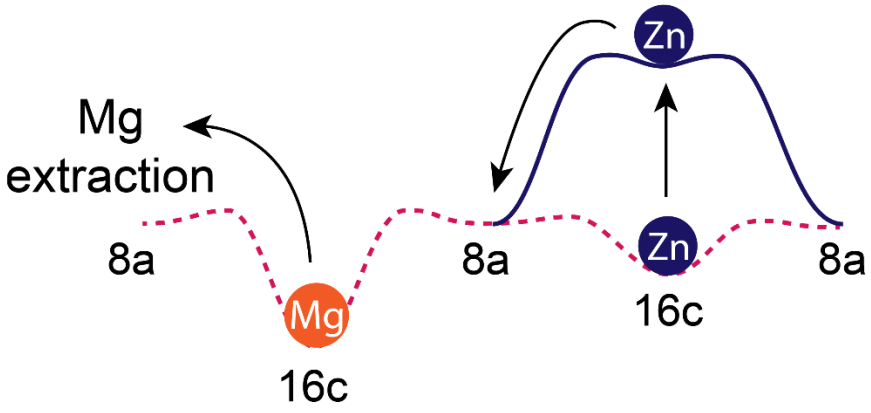
Takuya Hatakeyama, *[a] Norihiko L. Okamoto, [a] Kohei Shimokawa, [a] Hongyi Li, [a] Aiko Nakao, [b] Yoshiharu Uchimoto, [c] Hiroshi Tanimura,[a] Tomoya Kawaguchi [a] and Tetsu Ichitsubo *[a]

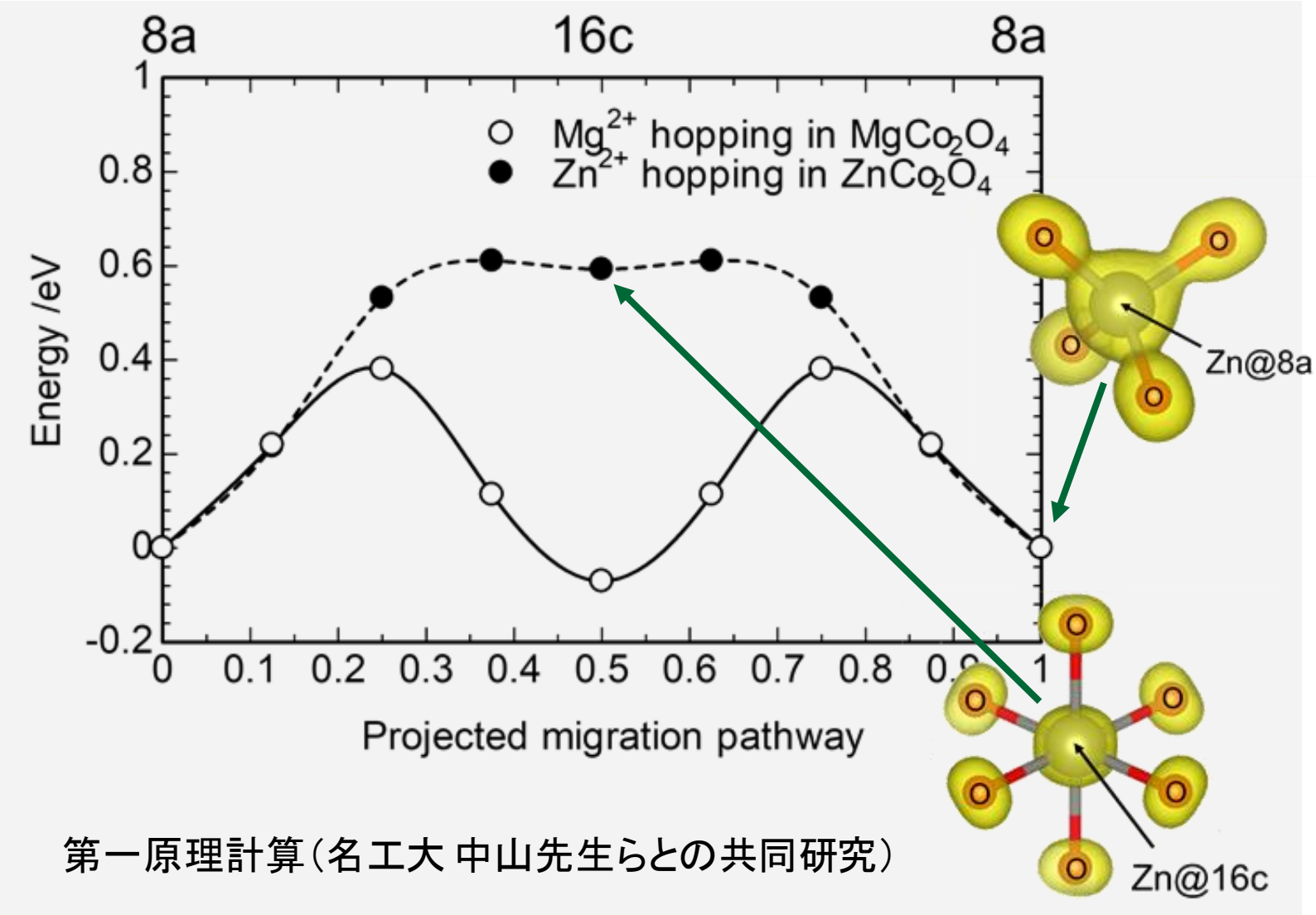
四面体配位を好むZnの利用による「岩塩→スピネル」逆変態の促進

Discharge: spinel → rocksalt



Charge: rocksalt → spinel

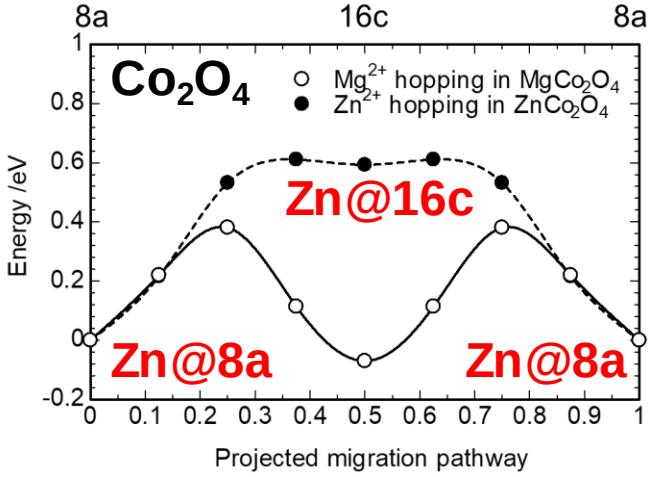


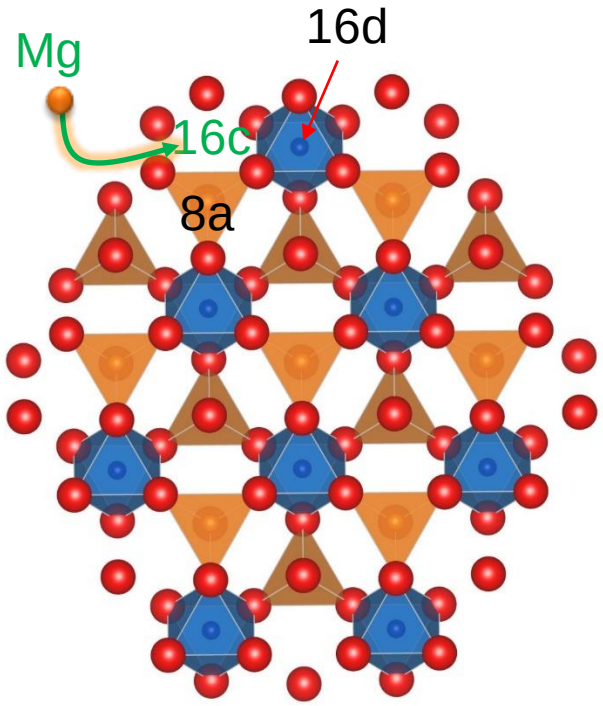


第一原理計算（名工大 中山先生らとの共同研究）

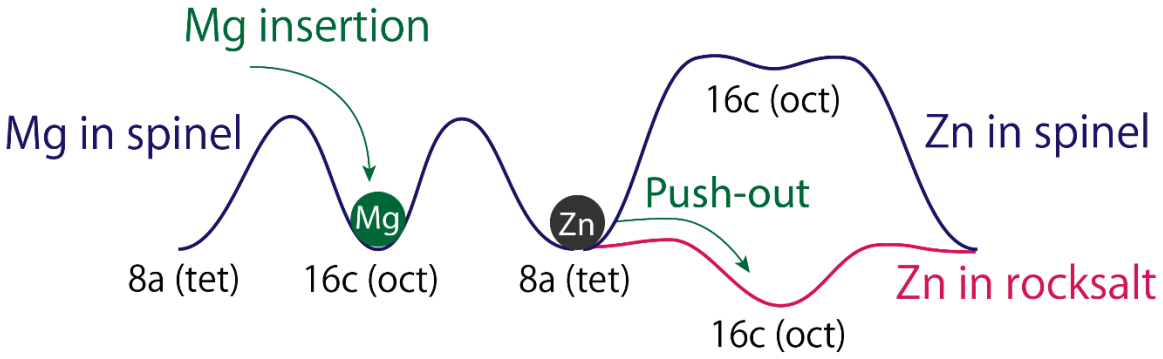
Znは充電時に「16c→8a」の移動（スピネル型構造への復帰）が速やかに生じると期待される.

四面体配位を好むZnの利用

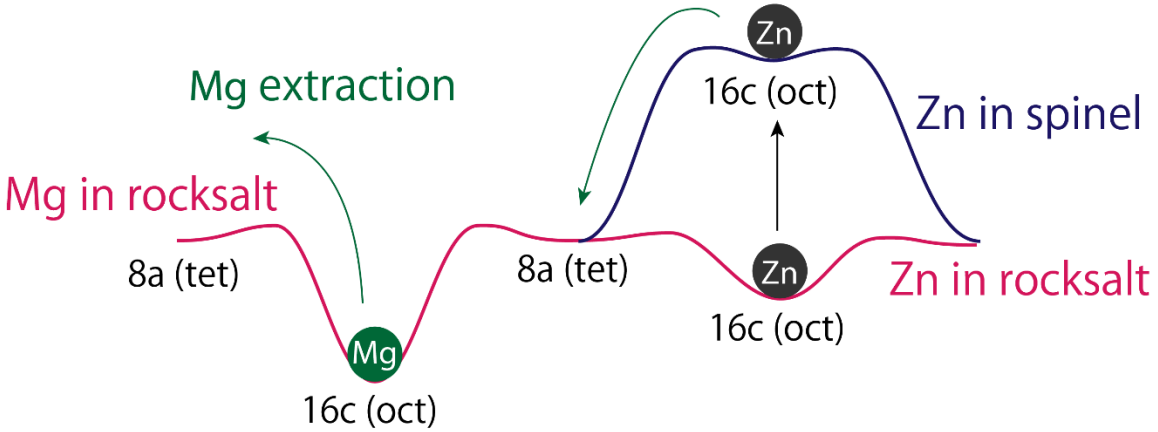




Discharge: spinel → rocksalt

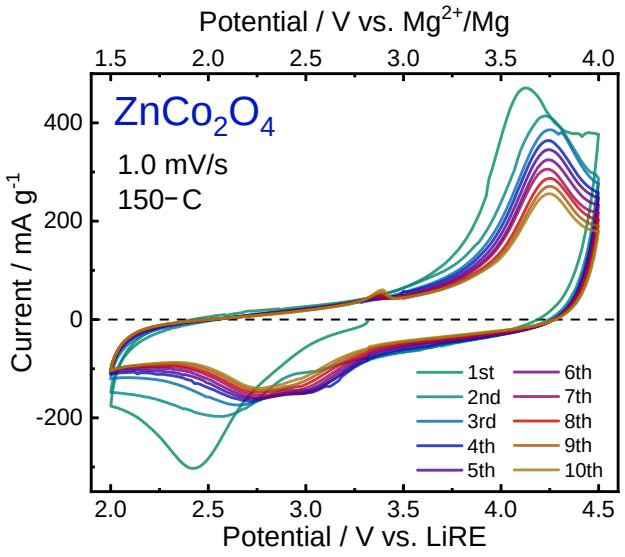


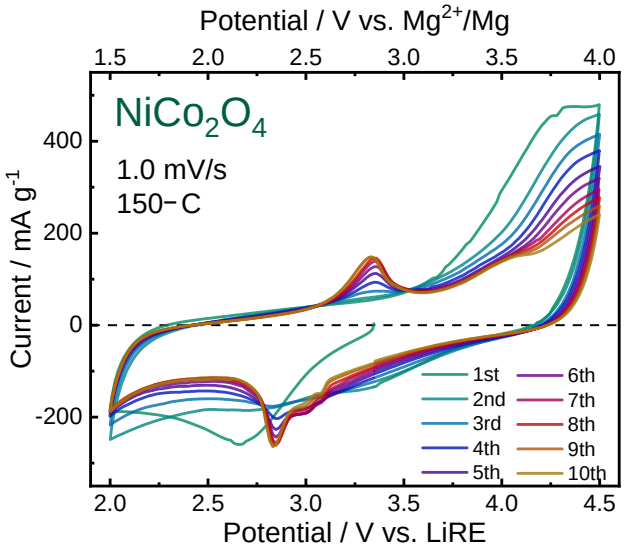
Charge: rocksalt → spinel

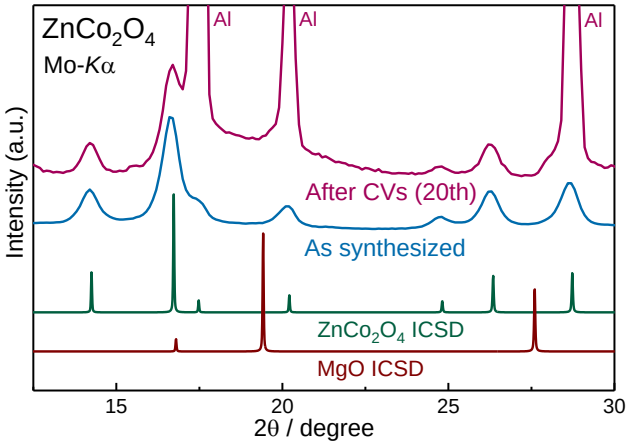


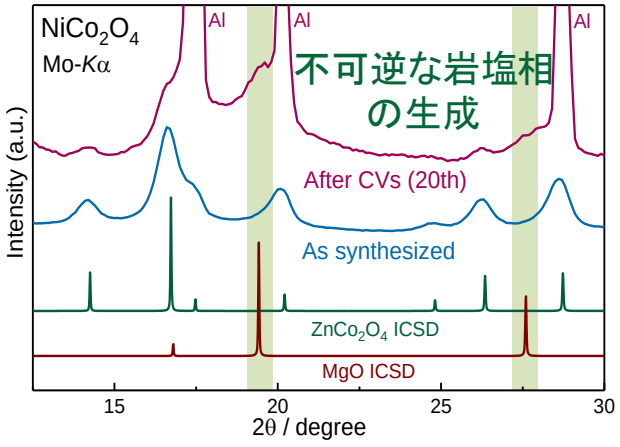
A(II)B(III)$_2$O$_4$（A: Zn, Ni; B: Co, Fe）の比較実験結果

Znの利用による「岩塩→スピネル」逆変態の促進

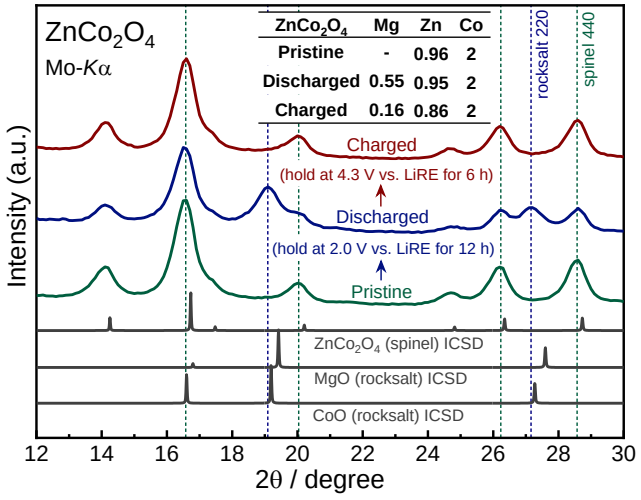


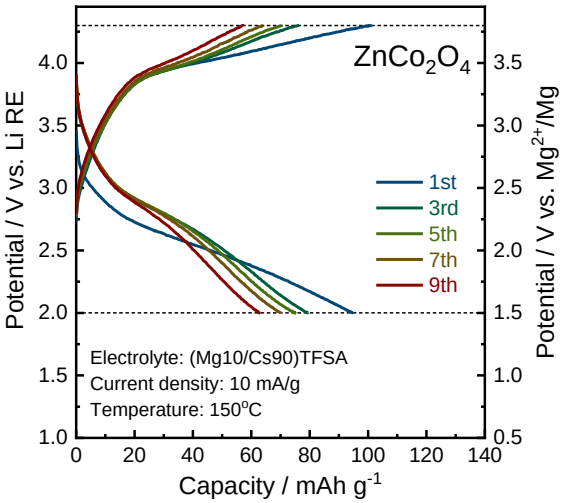


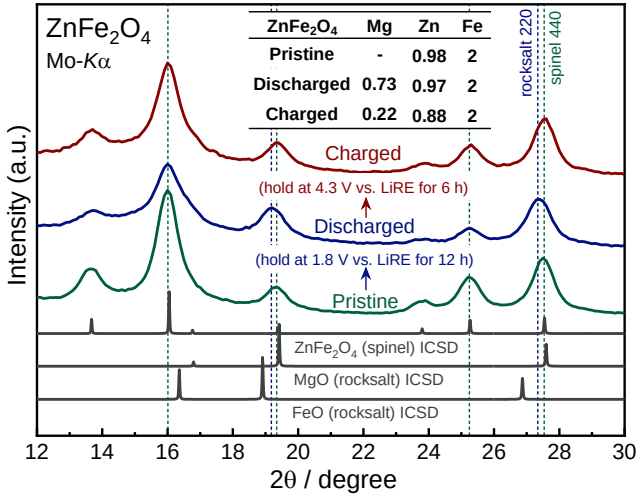


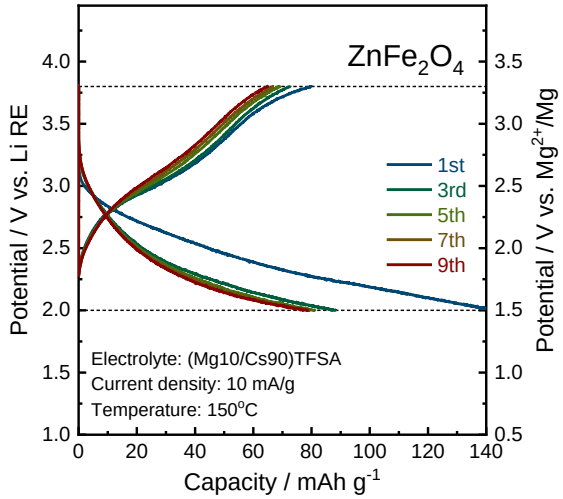


Feの利用による充放電時の体積変化率の低減





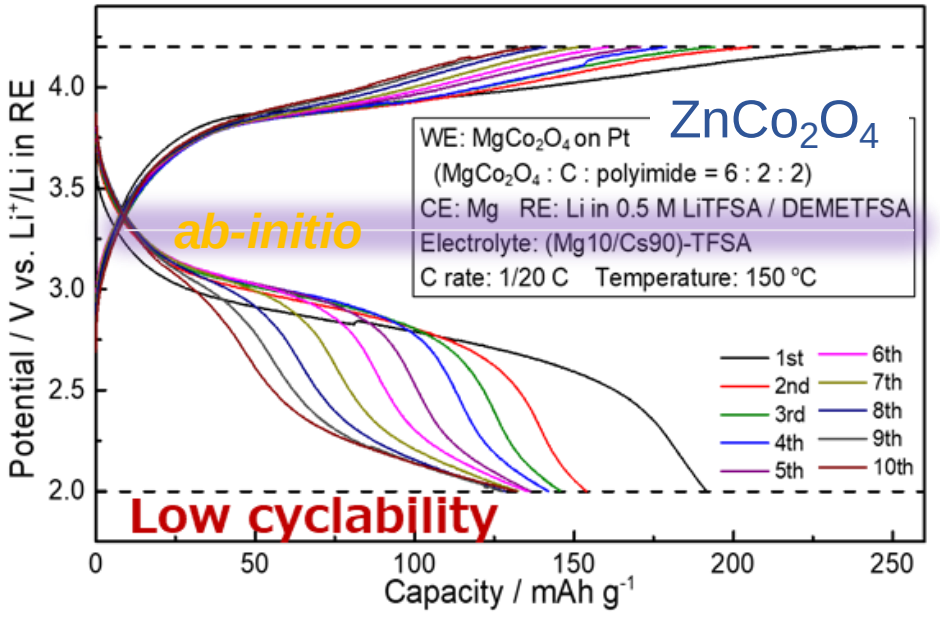




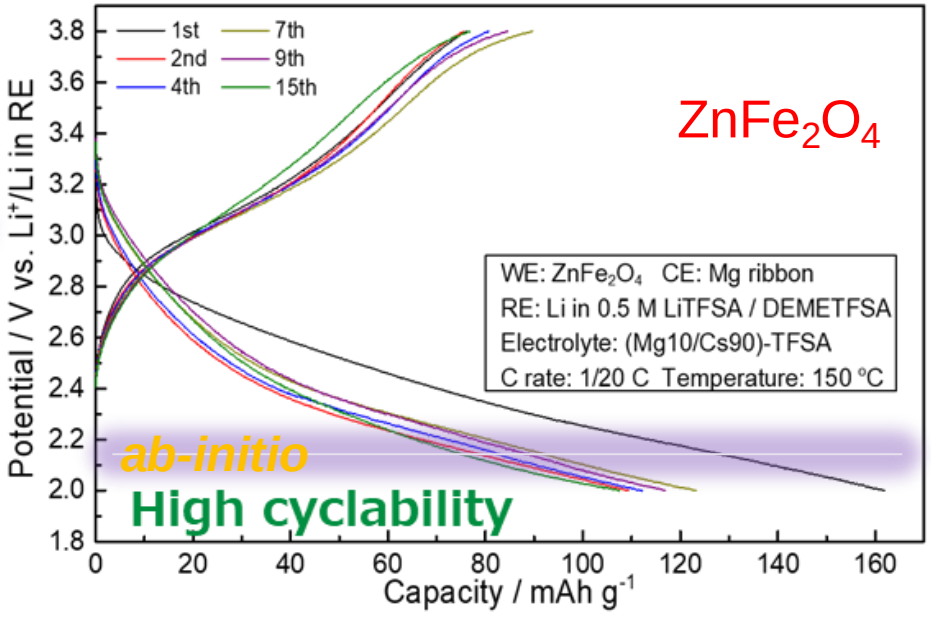
高サイクル特性の実現に向けたスピネル型酸化物の構造設計（カチオン選択）指針を構築

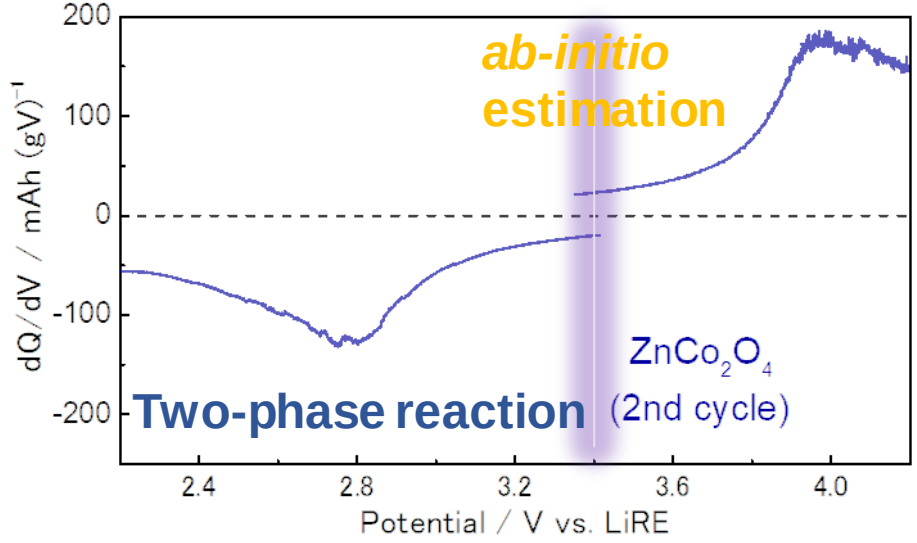
$ZnCo_2O_4$ vs $ZnFe_2O_4$ in cyclability

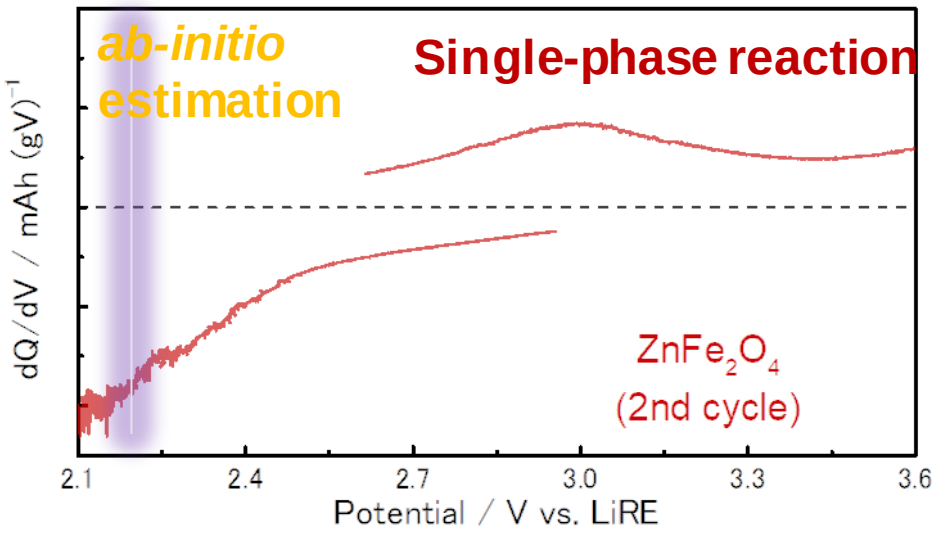
Large volume expansion and contraction



Almost zero strain







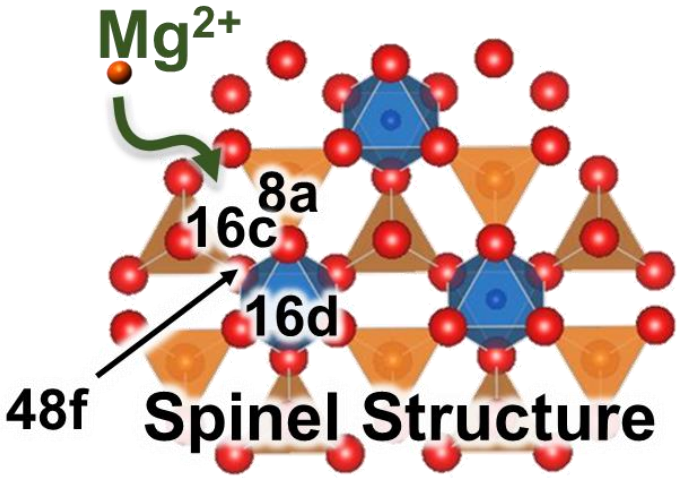
Materials design for MRB cathode

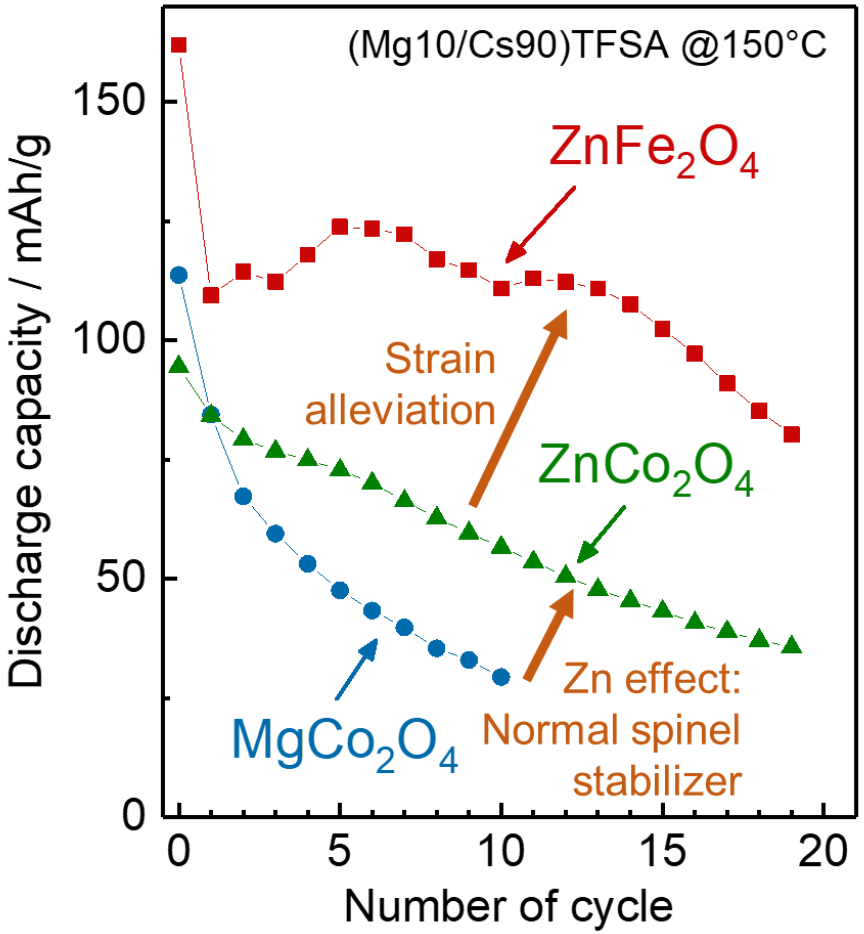
Spinel ⇔ Rocksalt

Evidence of Mg insertion

1. Two-phase reaction
2. In spinel, 8a instead of 16c
   In rocksalt, 16c instead of 8a
3. Coherent strain is inevitably caused

Degrade of cyclability





Although cyclability is markedly improved, the degrade of cyclability is still observed. How to circumvent this phenomenon?

K. Shimokawa, T. Atsumi, M. Harada, R. E. Ward, **M. Nakayama**, Y. Kumagai, F. Oba, N. L. Okamoto, **K. Kanamura**, **T. Ichitsubo**, Journal of Materials Chemistry A 7, 12225-12235 (2019).

発表論文

Journal of Materials Chemistry A

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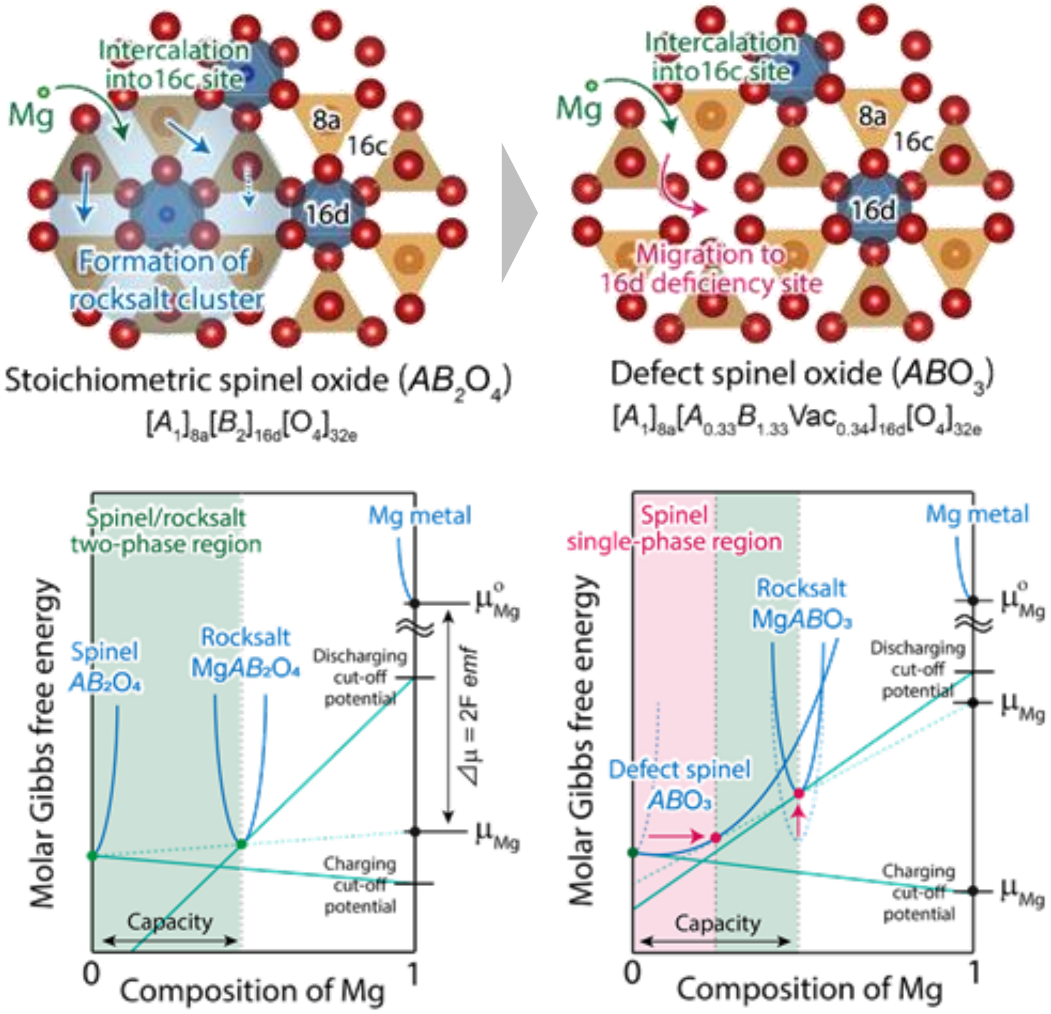
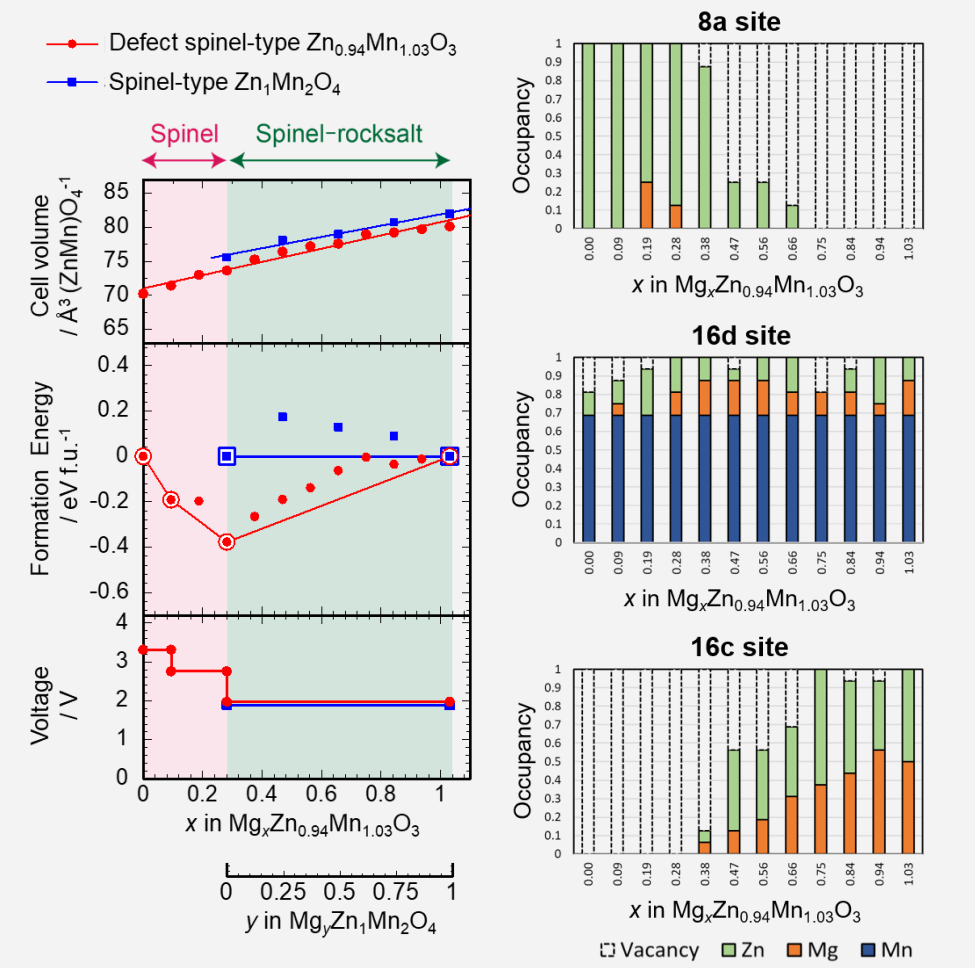
Cite this: *J. Mater. Chem. A*, 2019, **7**, 12225

Zinc-based spinel cathode materials for magnesium rechargeable batteries: toward the reversible spinel–rocksalt transition†

Kohei Shimokawa, *[a] Taruto Atsumi,[b] Maho Harada,[b] Robyn E. Ward,[c] Masanobu Nakayama,[bc] Yu Kumagai,[d] Fumiyasu Oba,[ce] Norihiko L. Okamoto,[a] Kiyoshi Kanamura[f] and Tetsu Ichitsubo *[a]

欠陥スピネル型酸化物$ZnMnO_3$の利用を提案

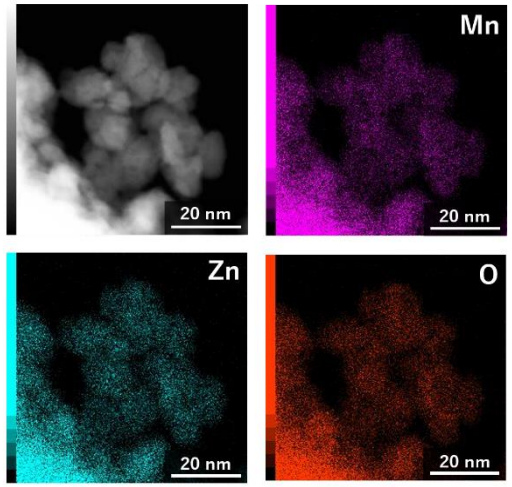


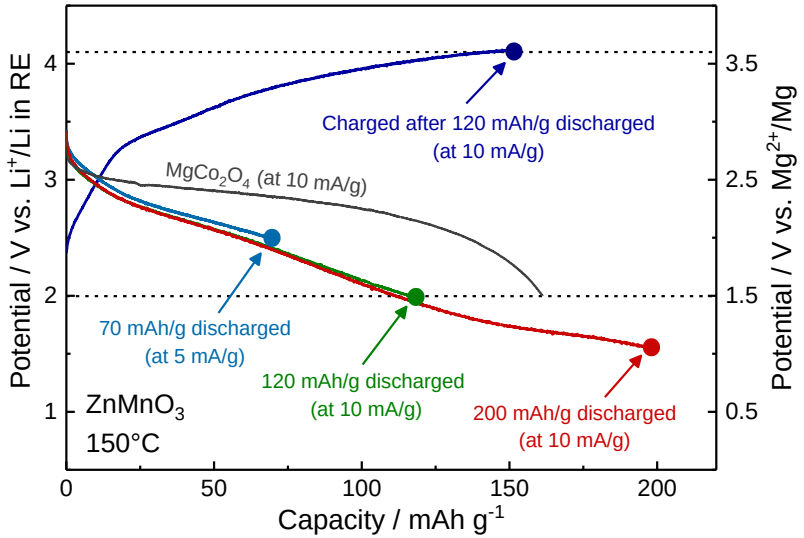


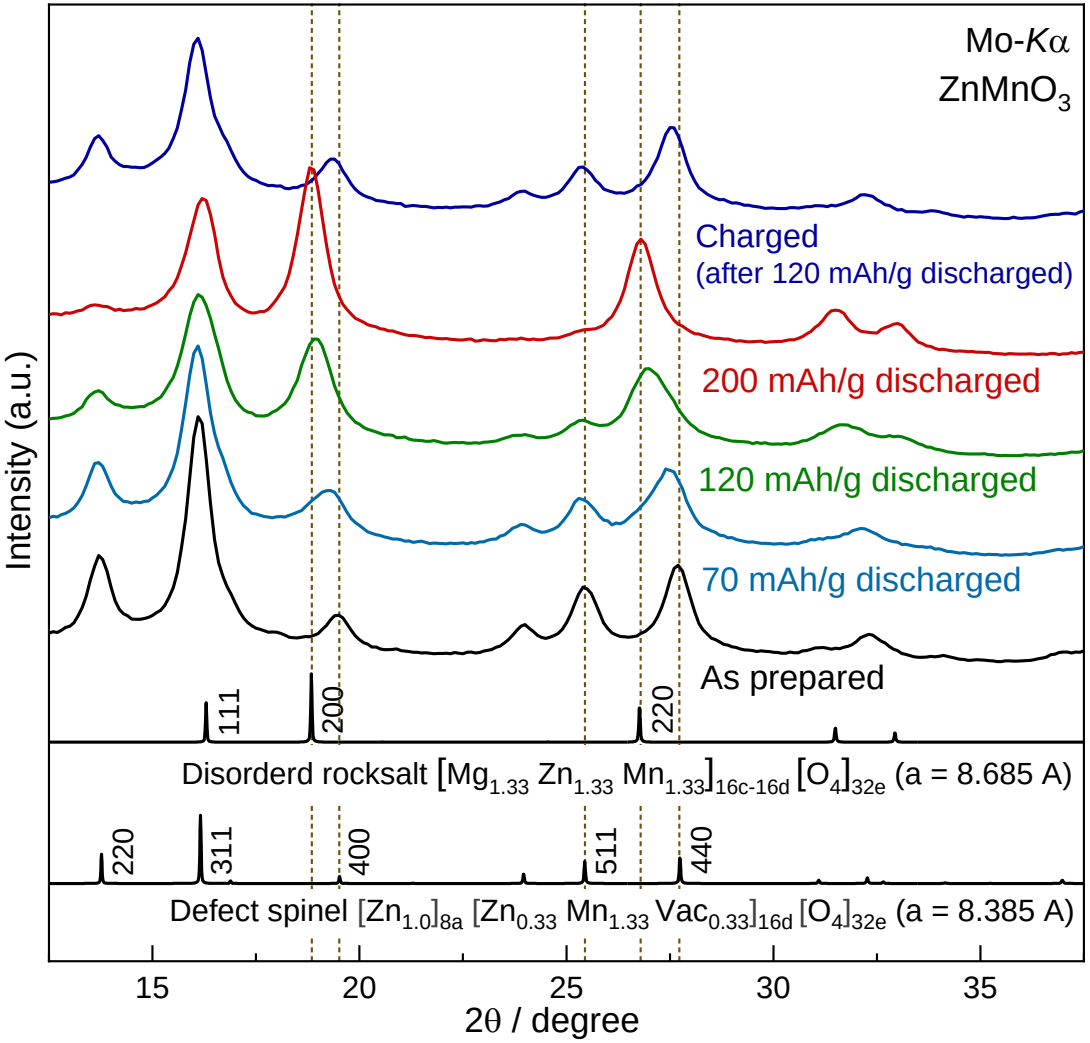
第一原理計算（名工大 中山先生らとの共同研究）

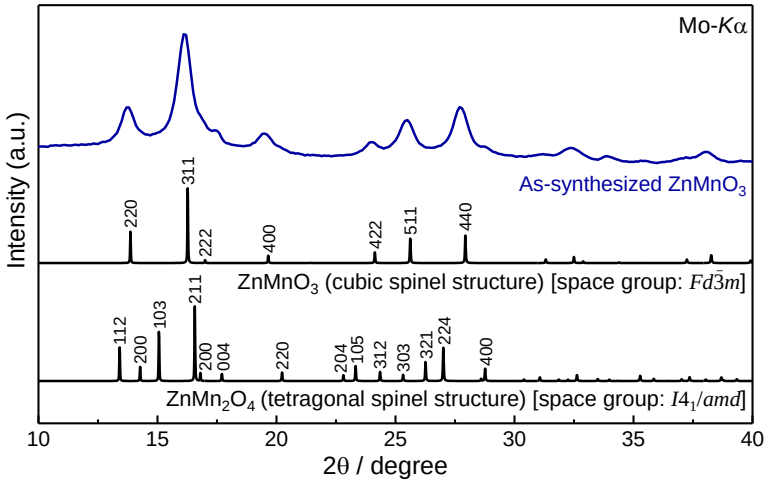
カチオン欠損サイトを利用することで岩塩相への二相共存反応による構造相転移を抑制し，サイクル特性の向上を狙う.

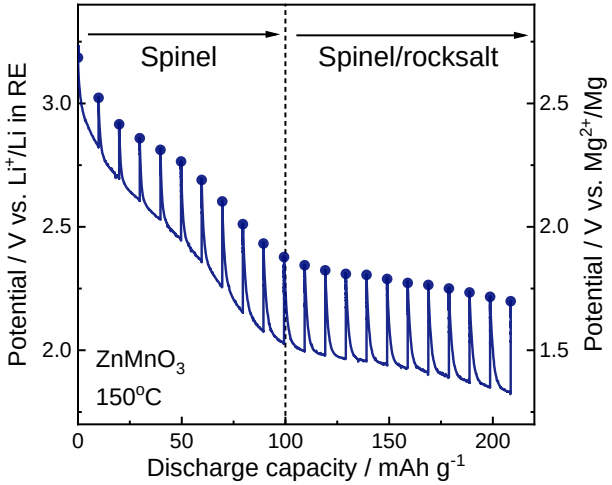
$ZnMnO_3$の合成と充放電挙動（初回サイクル）





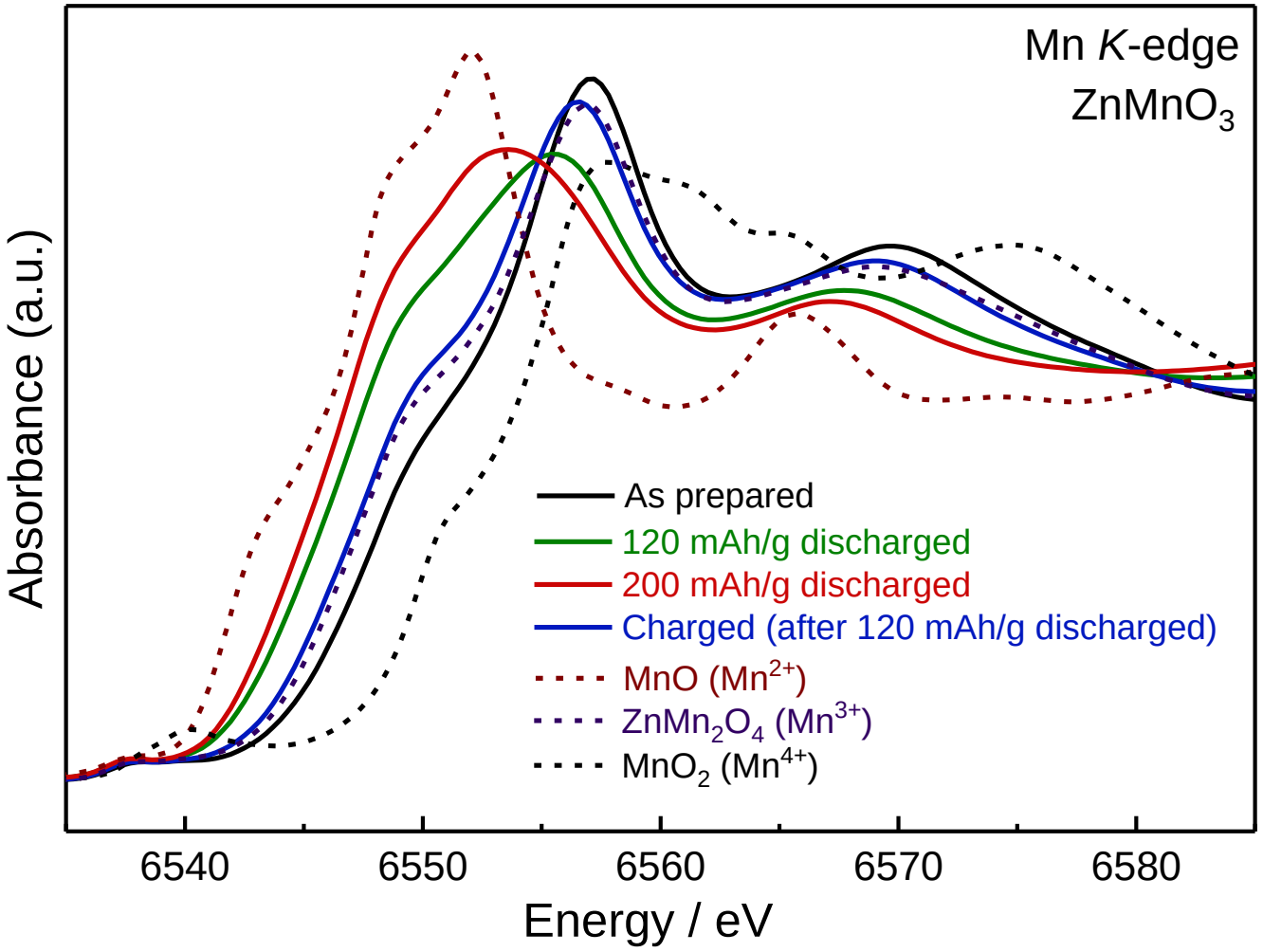


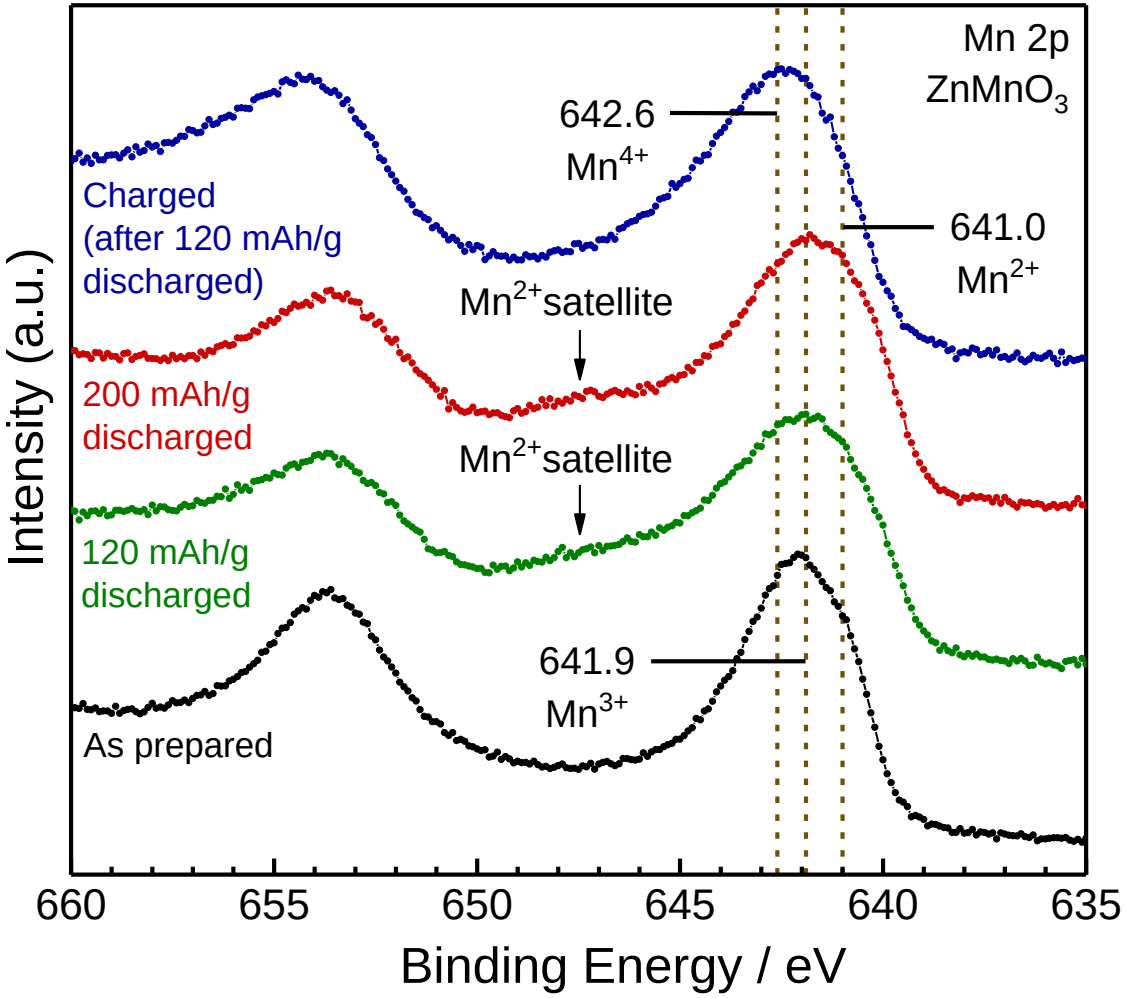




単相の$ZnMnO_3$ナノ粒子の合成に成功．放電初期の約100 mAh/gで単相反応を示唆．

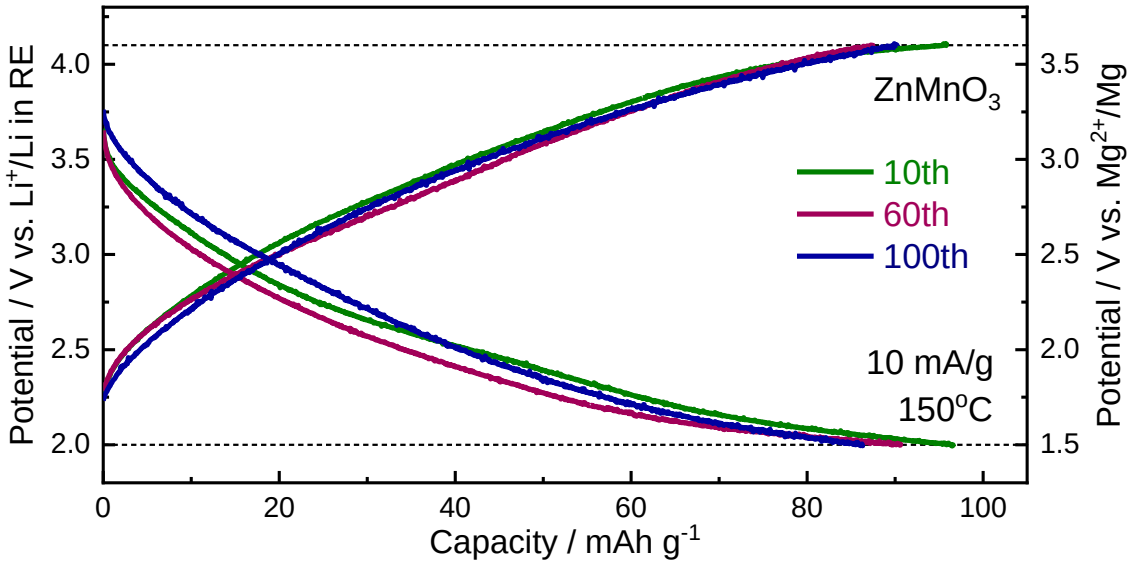
充放電前後のMnの価数変化（XANES, XPS）

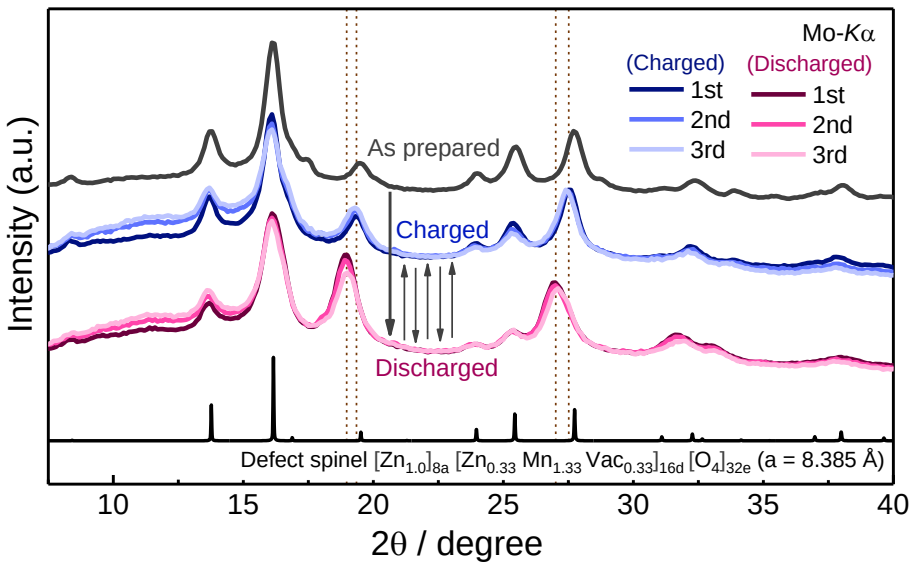


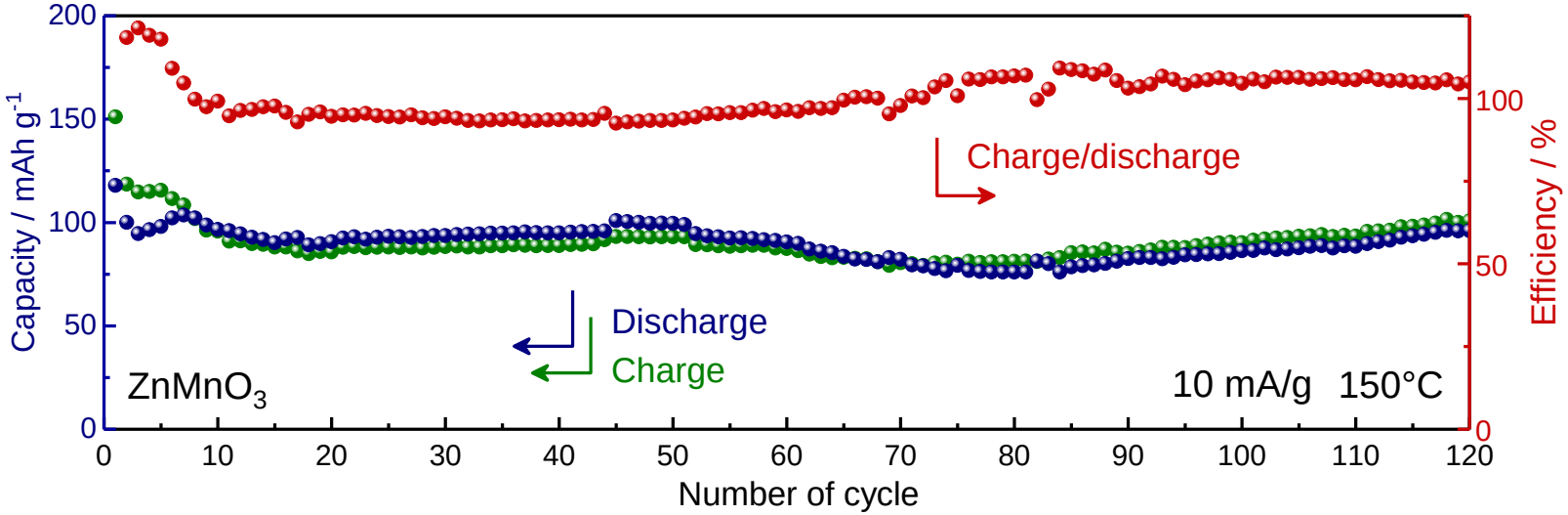


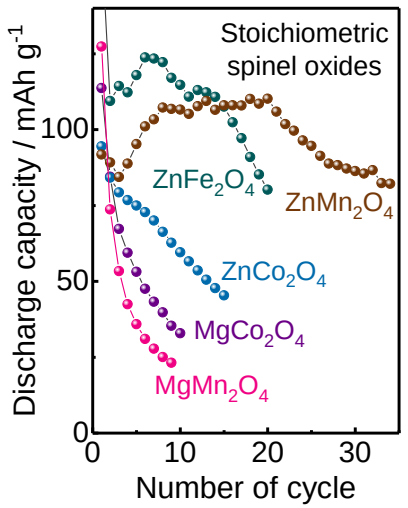
バルクと表面で多少の不均一性があるものの，可逆的なMnの価数変化を確認.

欠陥スピネル$ZnMnO_3$の充放電試験結果（150℃）



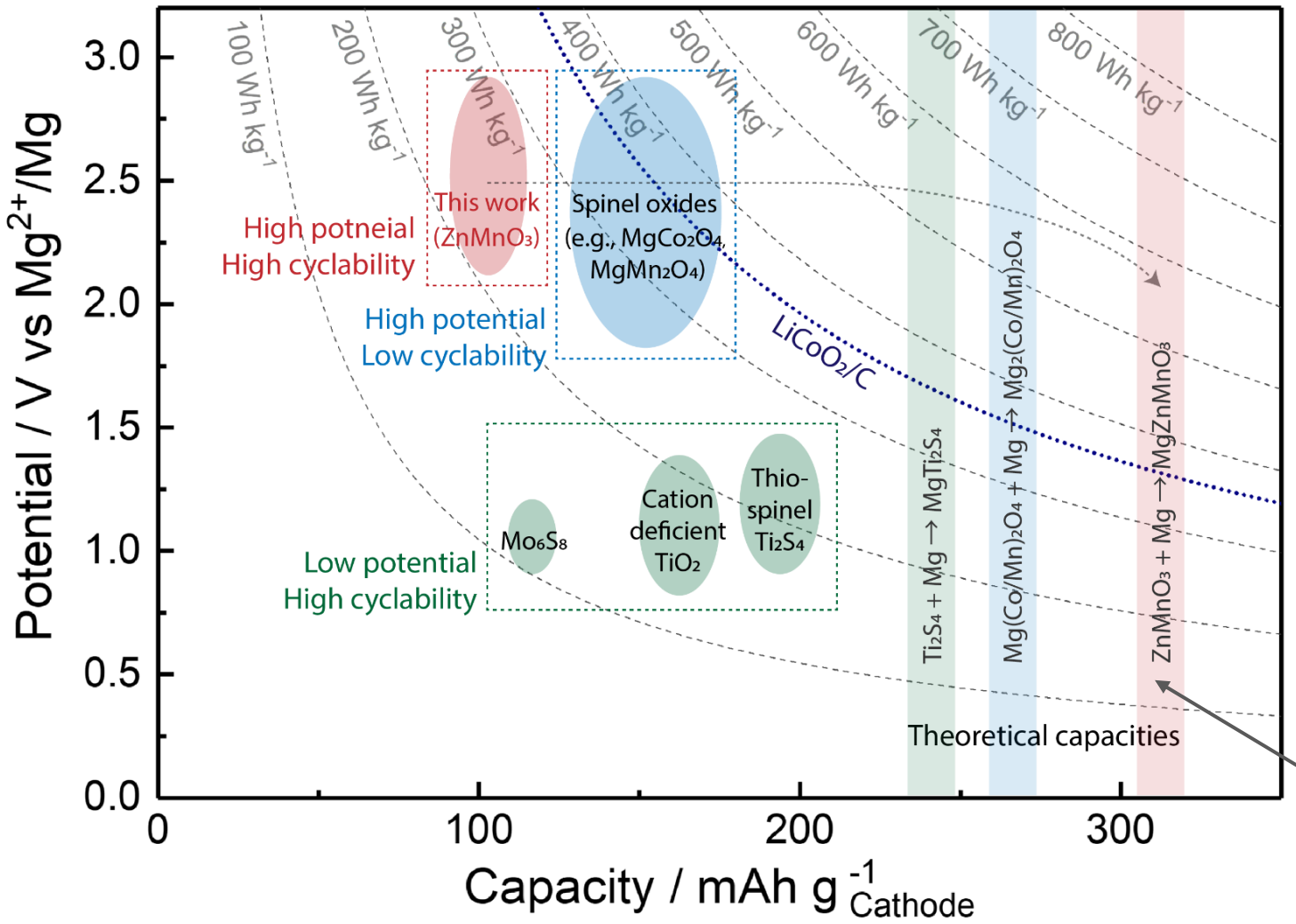




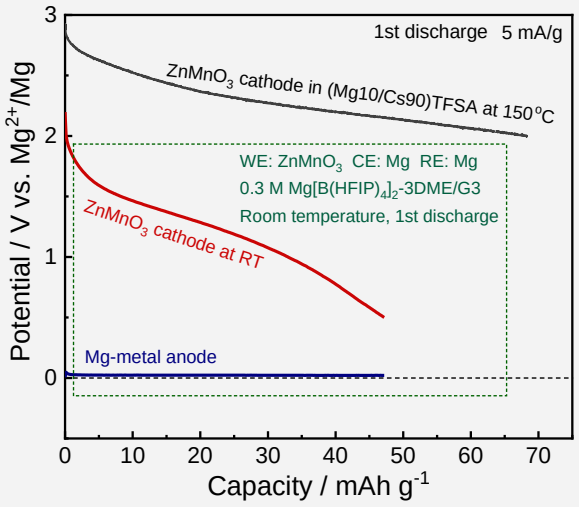


高電位・高容量・高サイクル特性を兼ね備えた正極特性を実現

Liイオン電池に迫る理論エネルギー密度



フルセル（室温）構築の試み



小林先生・万代先生よりご提供いただいた $Mg[B(HFIP)_4]_2$-3DME/G3電解液を使用

※ スピネル/岩塩の二相共存領域も含めた理論容量

残された課題: ①作動温度の低減, ②正極/負極と適合性のある電解液の開発

COMMUNICATION

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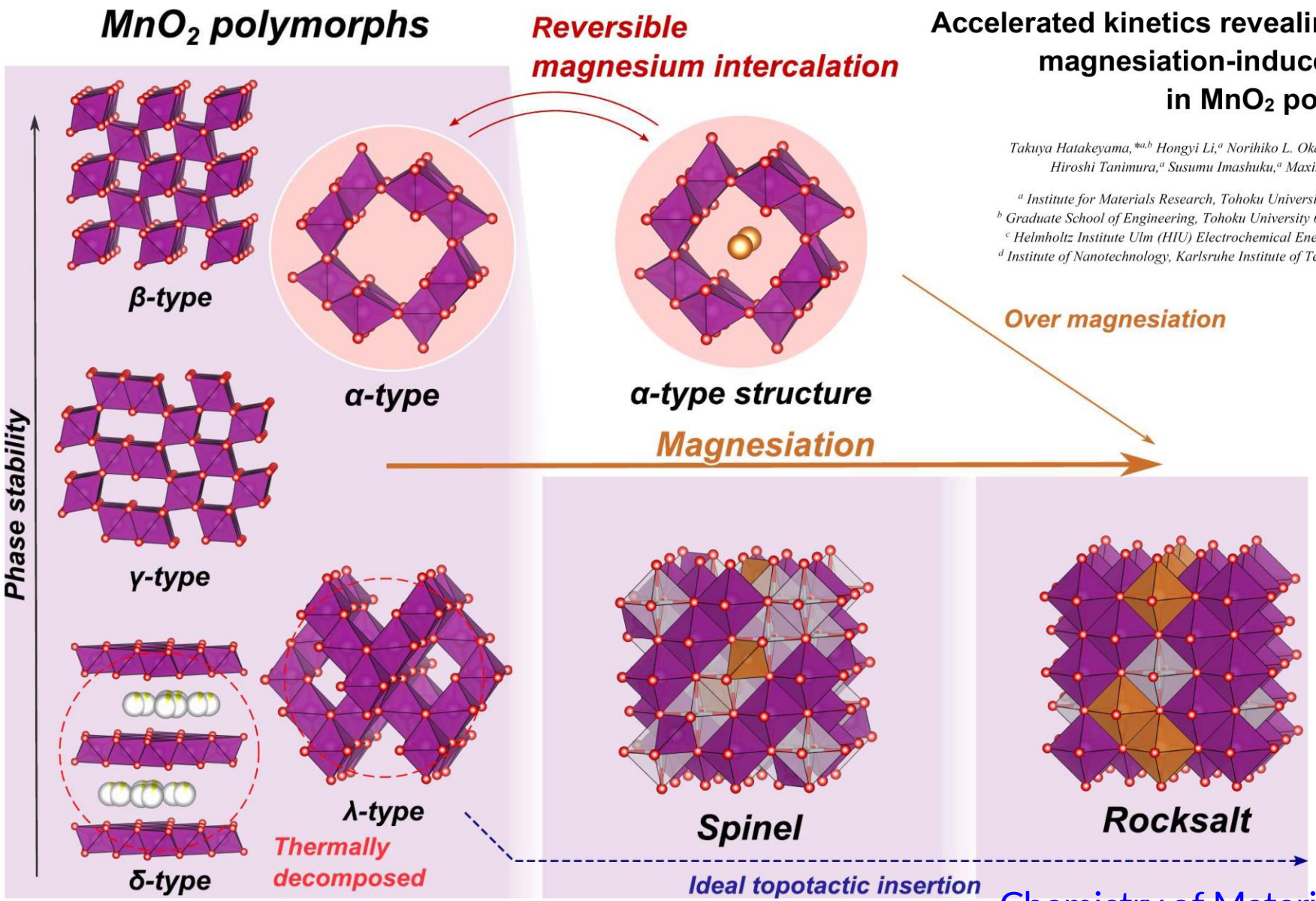
Structure Design of Long-Life Spinel-Oxide Cathode Materials for Magnesium Rechargeable Batteries

Kohei Shimokawa, Taruto Atsumi, Norihiko L. Okamoto, Tomoya Kawaguchi, Susumu Imashuku, Kazuaki Wagatsuma, Masanobu Nakayama, Kiyoshi Kanamura, and Tetsu Ichitsubo**

DOI: 10.1002/adma.202007539

Adv. Mater. **2021**, *33*, 2007539

MnO2多形のMgイオン蓄電池正極に対する総合的研究



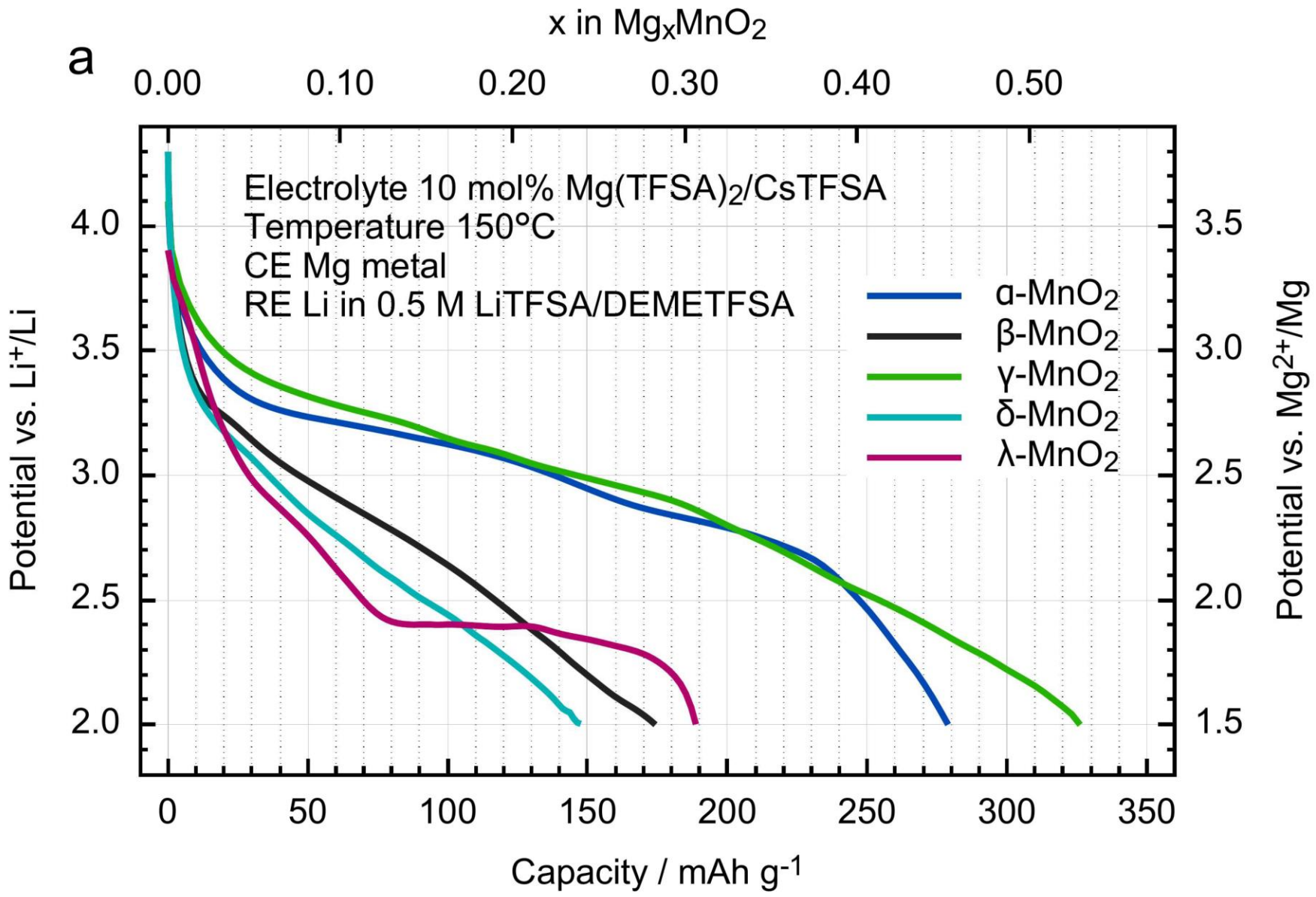
Accelerated kinetics revealing metastable pathways of magnesiation-induced transformations in MnO_2 polymorphs

Takuya Hatakeyama,[a,b] Hongyi Li,[a] Norihiko L. Okamoto,[a] Kohei Shimokawa,[a] Tomoya Kawaguchi,[a] Hiroshi Tanimura,[a] Susumu Imashuku,[a] Maximilian Fichtner[c,d], and Tetsu Ichitsubo*[a,e]*

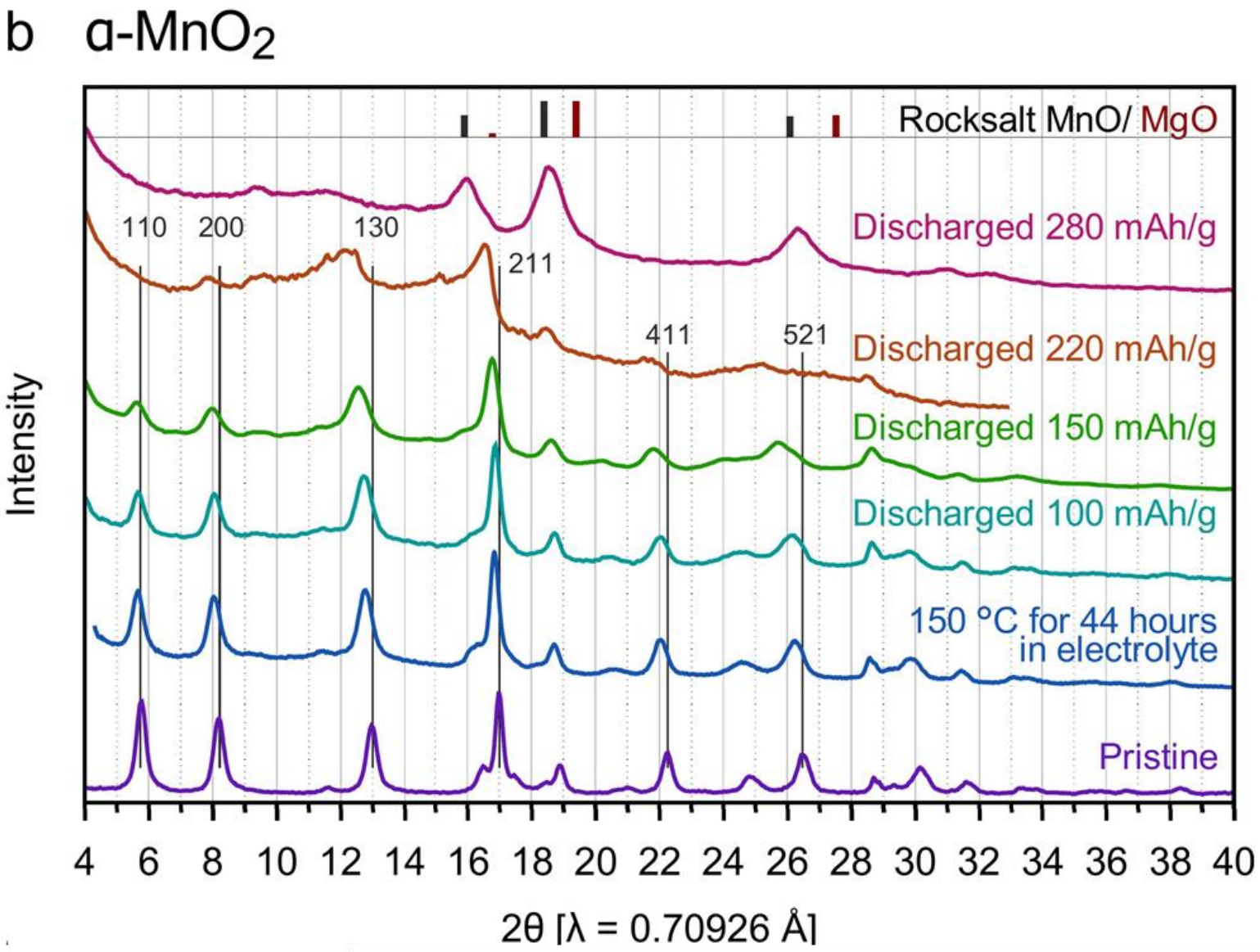
[a] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*
[b] *Graduate School of Engineering, Tohoku University 6-6-01 Aoba, Aramaki, Aoba-ku, Sendai 980-8579, Japan*
[c] *Helmholtz Institute Ulm (HIU) Electrochemical Energy Storage, Helmholtzstraße 11, 89081 Ulm, Germany*
[d] *Institute of Nanotechnology, Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany*

Chemistry of Materials 33, 6983–6996 (2021).

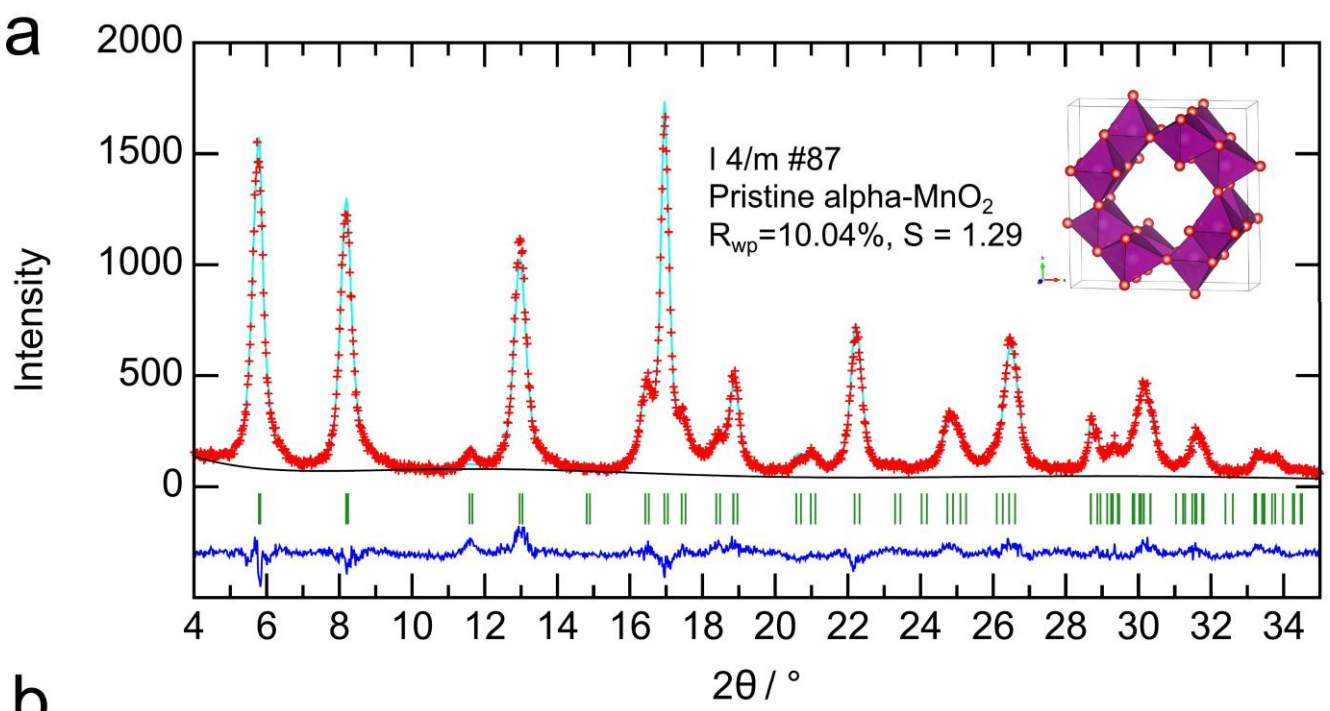
MnO2多形のMagnesiation挙動



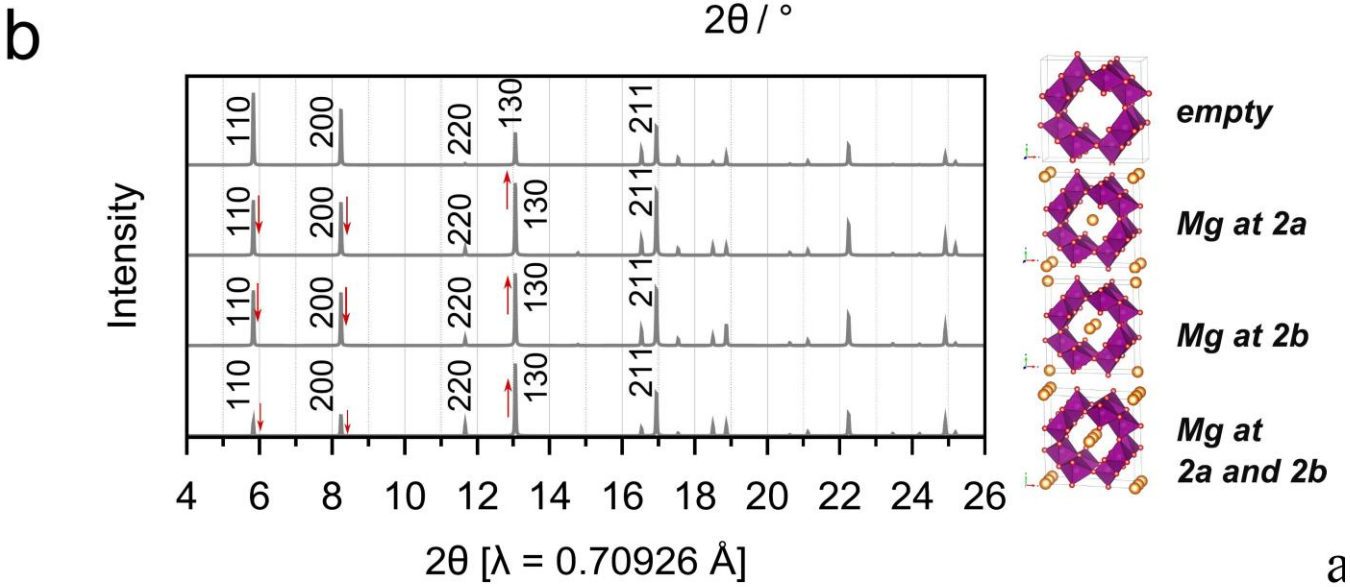
Magnesiation後の構造変化:α型



Mgの挿入位置による構造変化：α型



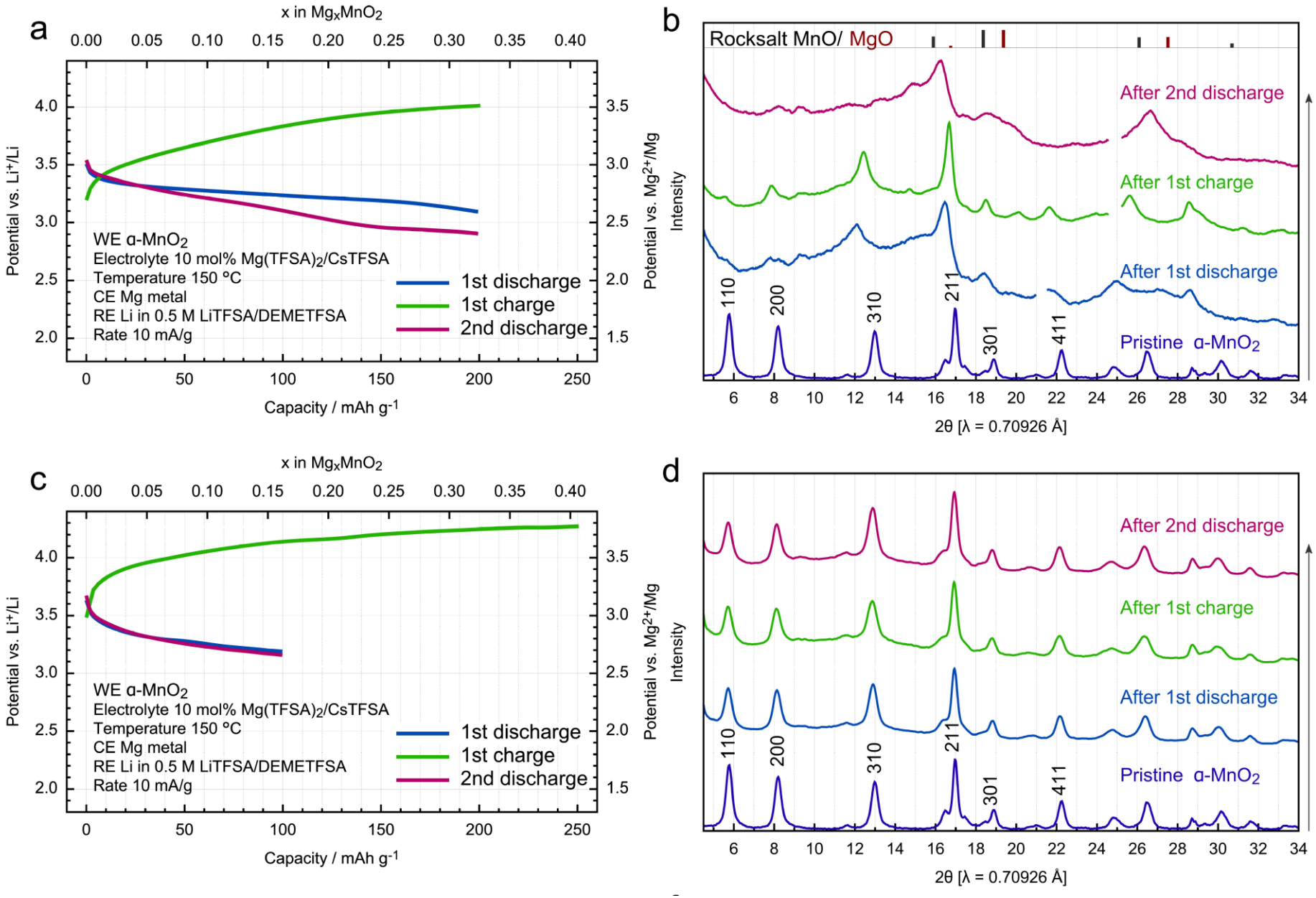
初期構造



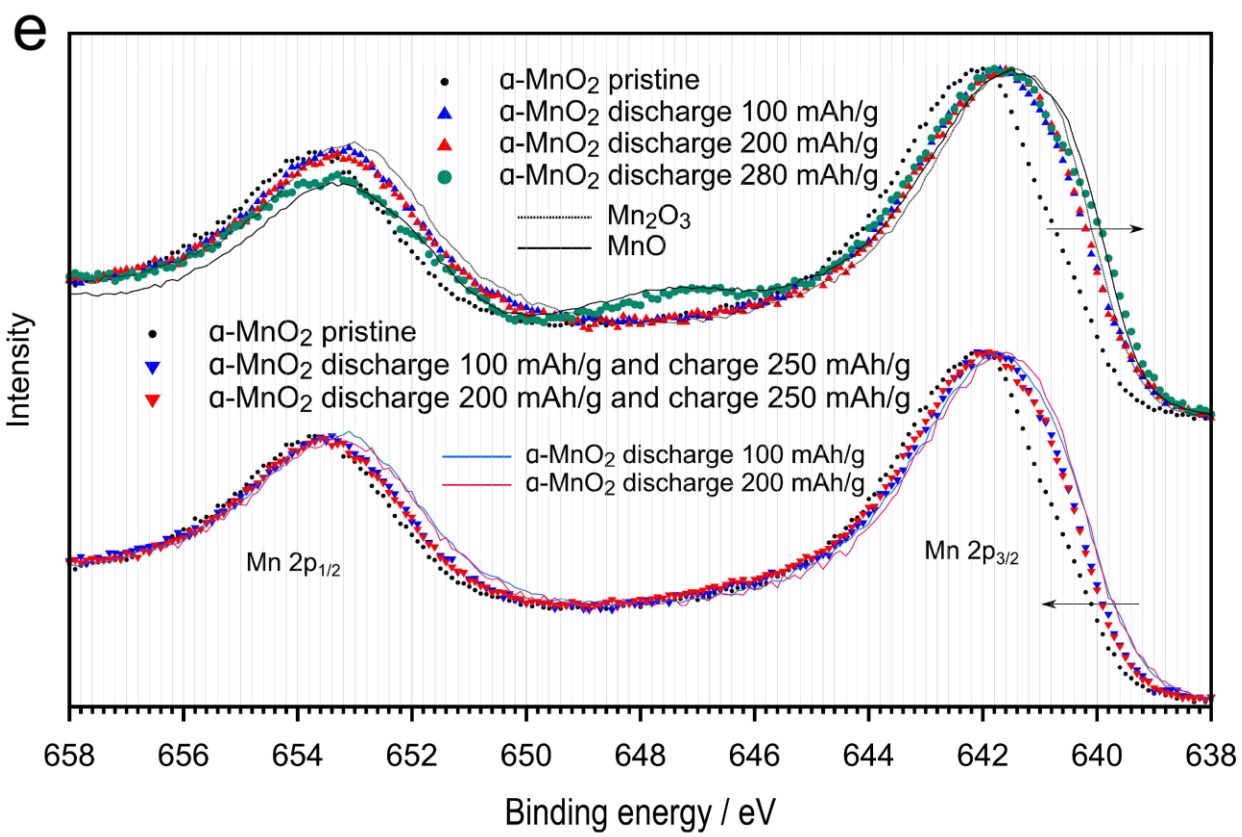
Mg挿入による
構造変化
シミュレーション

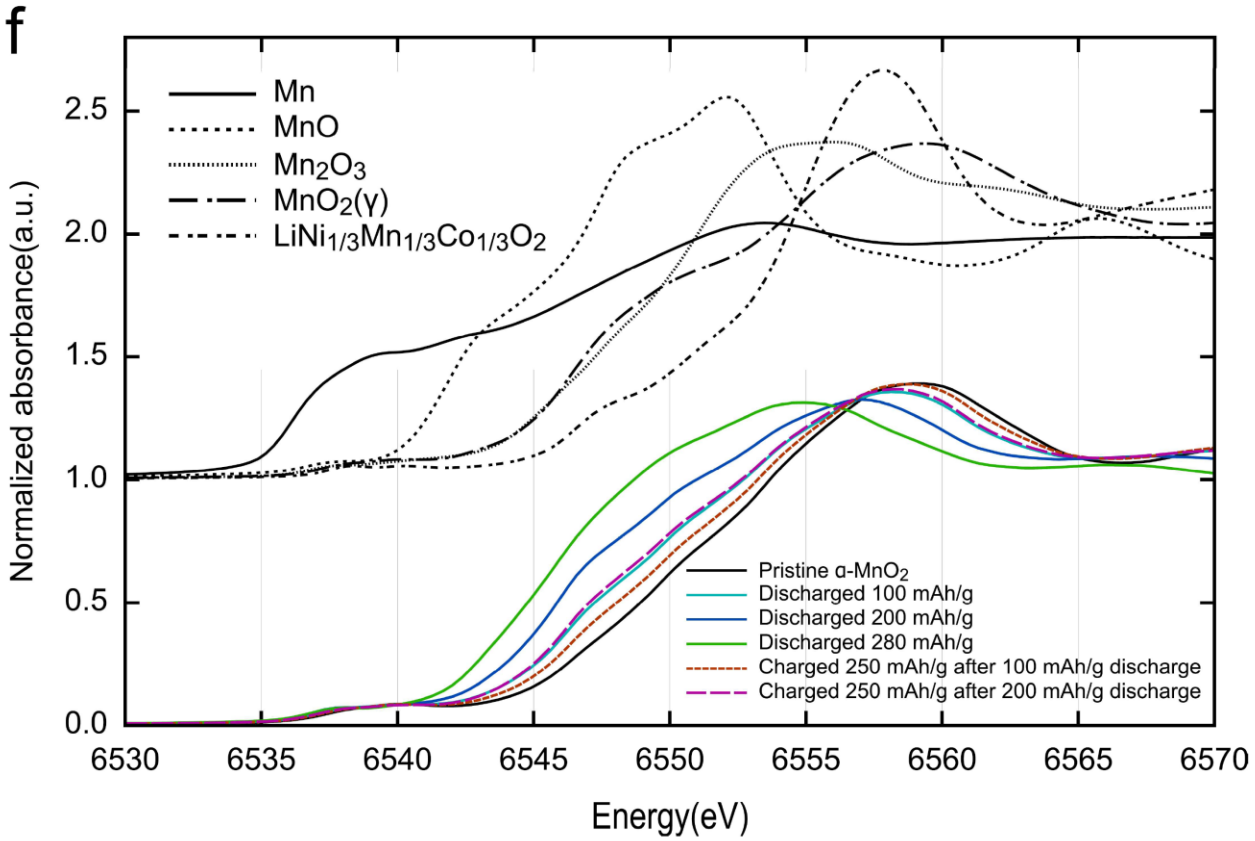
a

α型のMg挿入・脱離実験と構造変化



α型のMg挿入・脱離実験と価数変化 XPS & XANES





α型のMg挿入脱離の相変態過程

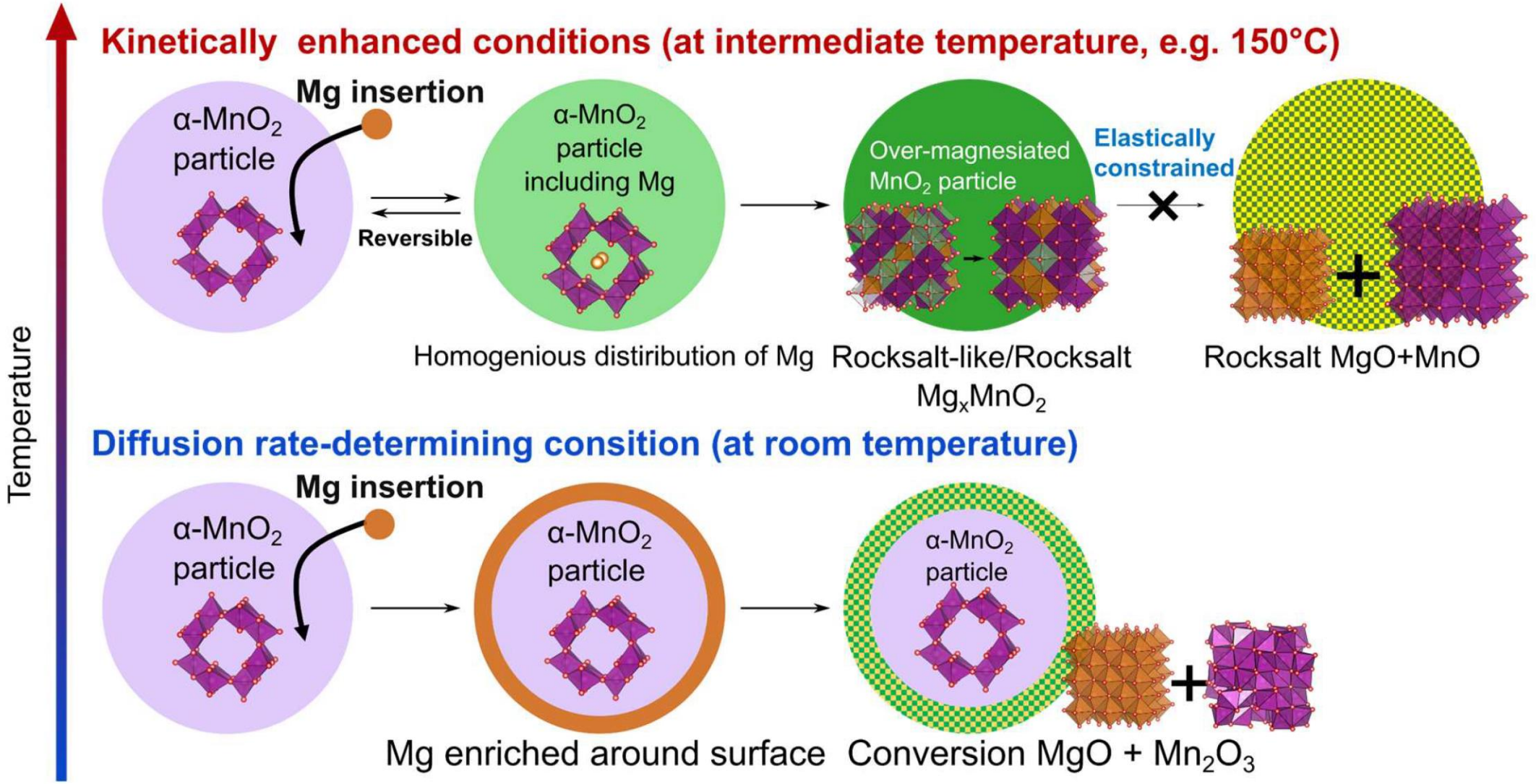
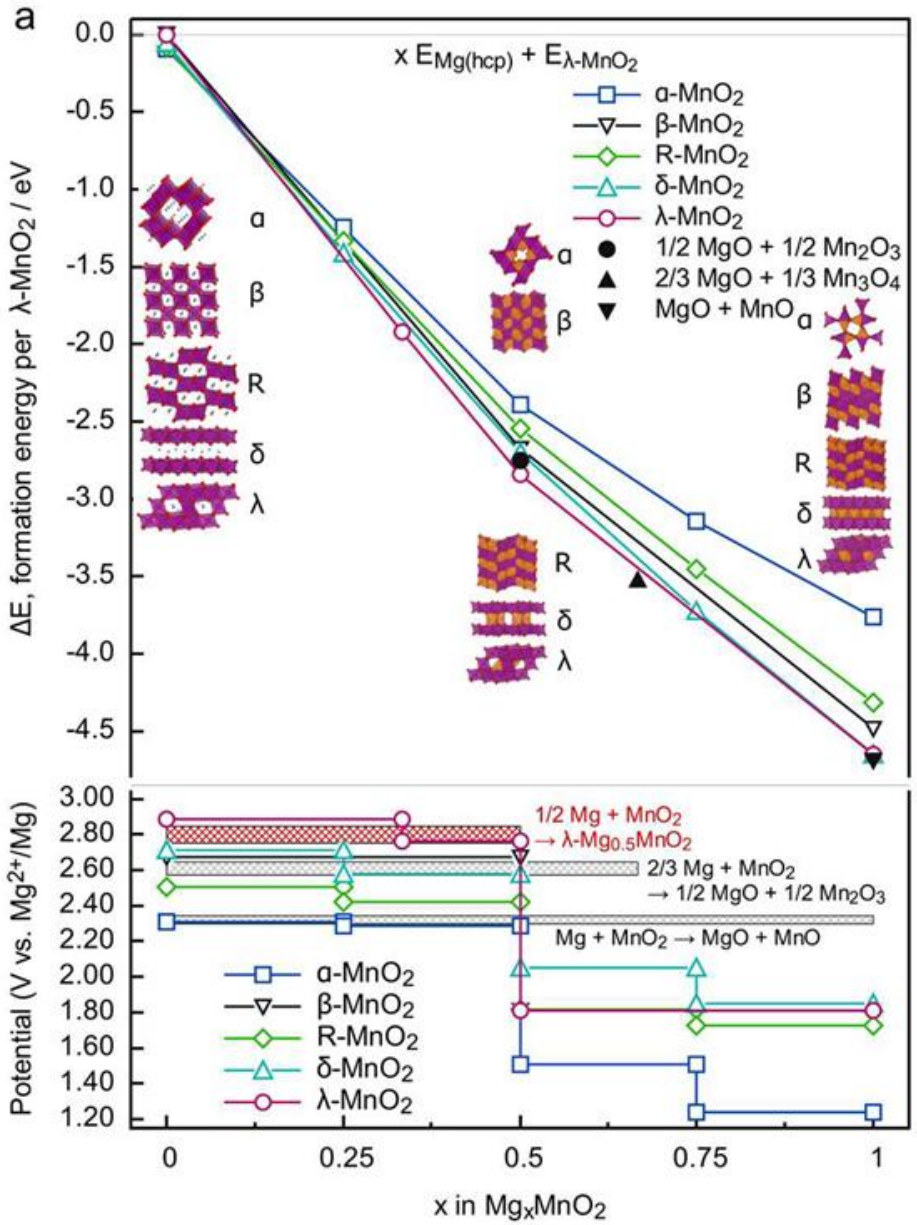
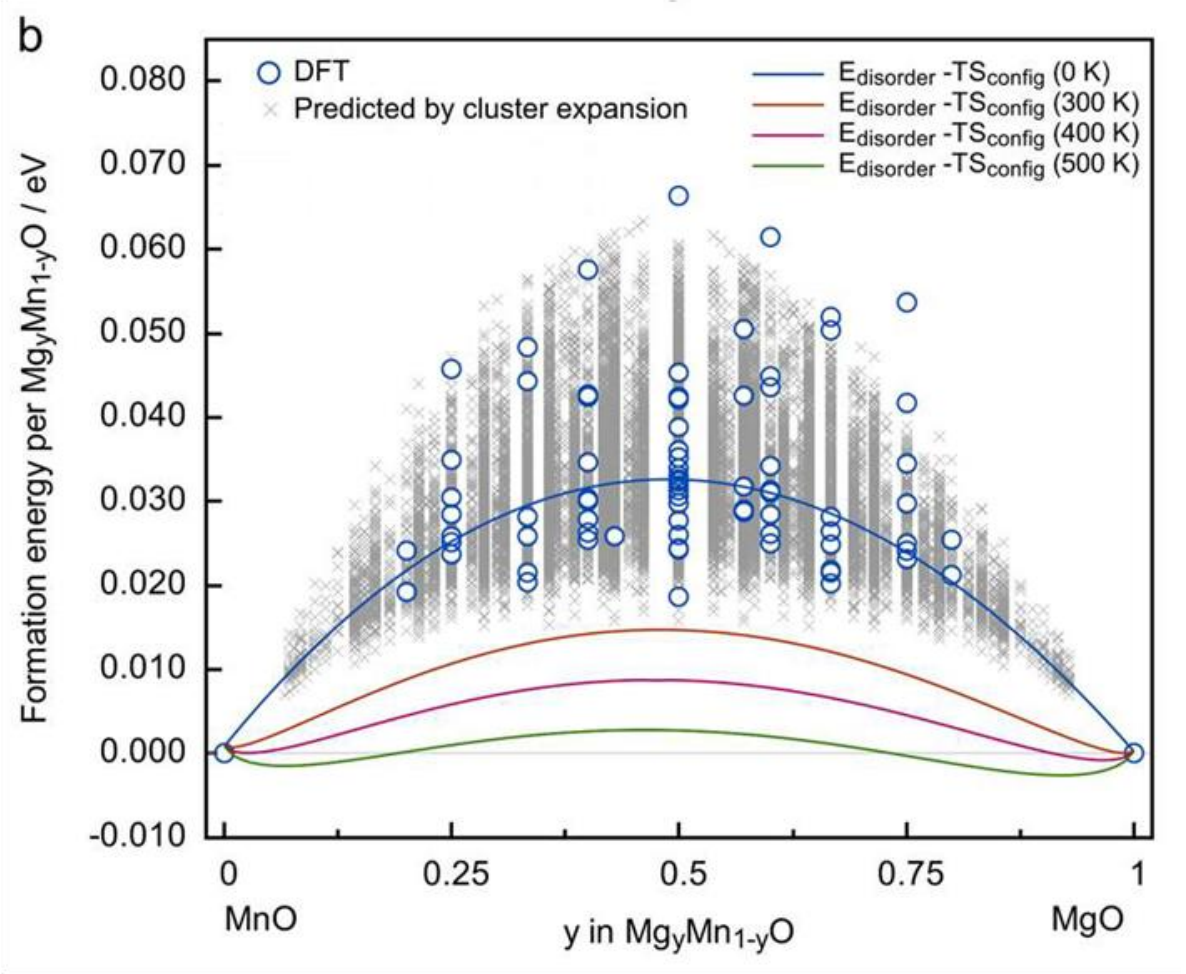


Figure 8. Schematic illustration showing the two kinds of magnesiation pathways of α-MnO_2 particles at intermediate temperature and room temperature, where the latter pathway was based on the previous work by Arthur et al.[25]

第一原理計算によるエネルギーと電位





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Article

Accelerated Kinetics Revealing Metastable Pathways of Magnesiation-Induced Transformations in MnO_2 Polymorphs

Takuya Hatakeyama,* Hongyi Li, Norihiko L. Okamoto, Kohei Shimokawa, Tomoya Kawaguchi, Hiroshi Tanimura, Susumu Imashuku, Maximilian Fichtner, and Tetsu Ichitsubo*

Cite This: *Chem. Mater.* 2021, 33, 6983–6996

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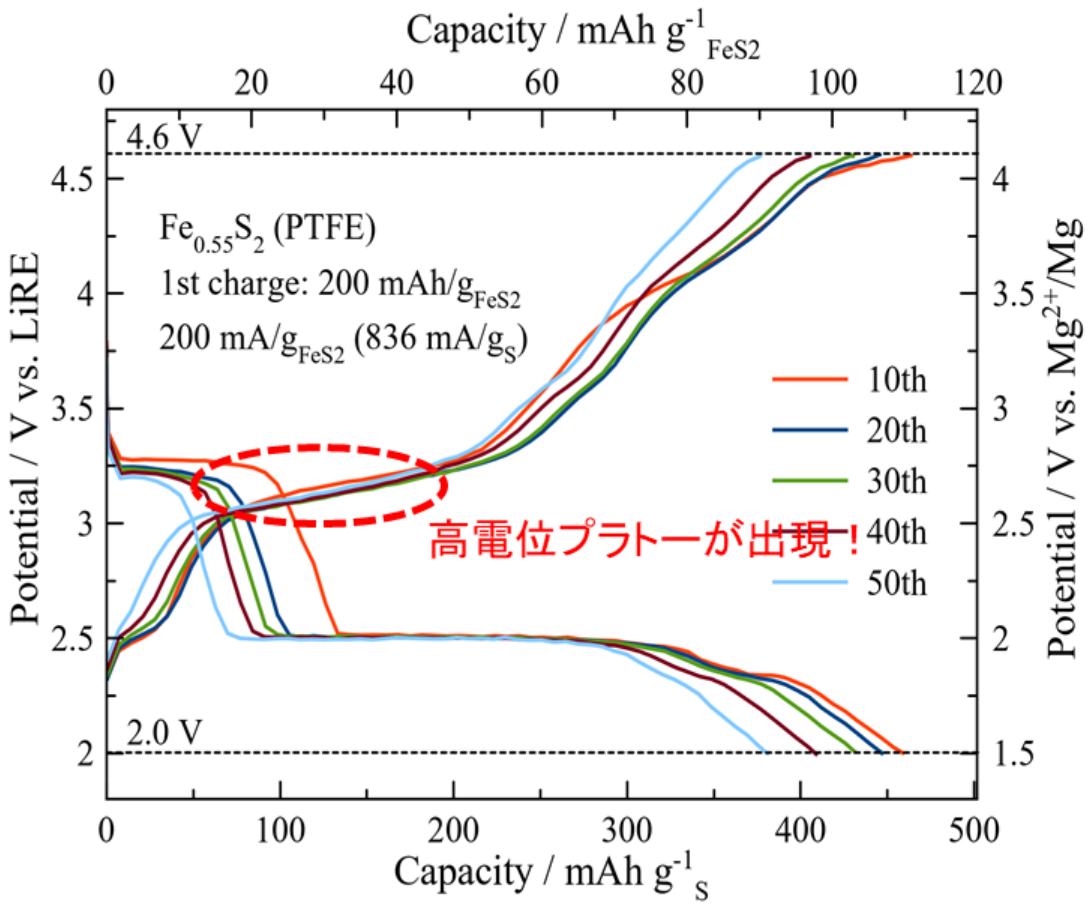
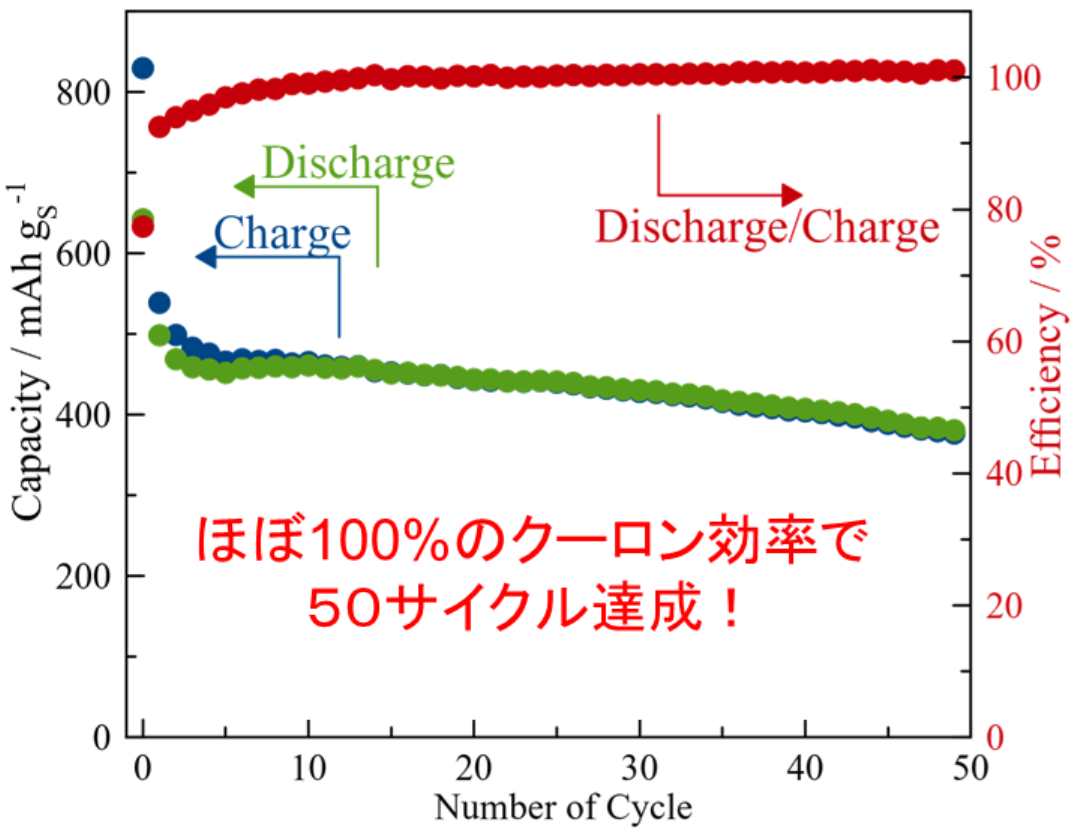
液体S/硫化物複合正極

バインダーをPVdFからPTFEに変更（FeS_2 : Carbon : PTFE = 70 : 25 : 5）





高電位プラトーを利用した可逆的なサイクルを実現

発表論文

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Cite this: *J. Mater. Chem. A*, 2021, **9**, 16585

Electrochemically synthesized liquid-sulfur/sulfide composite materials for high-rate magnesium battery cathodes†

Kohei Shimokawa, *[ab] Takuya Furuhashi,[a] Tomoya Kawaguchi,[a] Won-Young Park,[a] Takeshi Wada,[a] Hajime Matsumoto,[c] Hidemi Kato[a] and Tetsu Ichitsubo *[a]

Mg/S batteries are some of the most promising rechargeable batteries owing to their high theoretical energy density. Their development is, however, hindered by (i) low electronic conductivity of S, (ii) sluggish Mg^{2+} diffusion in solid Mg–S compounds formed by discharge, and (iii) dissolubility of polysulfides into electrolytes. To address these problems, we propose liquid-S/sulfide composite cathode materials in combination with an ionic liquid electrolyte at intermediate temperatures (~150 °C). The composite structure is spontaneously fabricated by electrochemically oxidizing metal sulfides, yielding liquid S embedded in a porous metal-sulfide conductive frame. This concept is demonstrated by a S/FeS_2 composite cathode, which shows a significantly high-rate capability of, *e.g.*, 1246 mA $g^{-1}_{(S)}$ with a capacity of ~900 mA h $g^{-1}_{(S)}$. In addition, non-equilibrium liquid S formed by fast charging results in an unexpected higher discharge potential. This work provides a new strategy to design S-based cathodes for achieving high-rate multivalent rechargeable batteries.

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