ナノアーチ構造シリコンアノードを持ったリチウムイオン電池

Silicon Anodes with a Nano-Vault Structure for Lithium-Ion Batteries

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リチウムイオン電池と日本の関わり

Li-Ion Batteries: a Very Japanese Affair

新技術説明会
New Technology Presentation Meetings!

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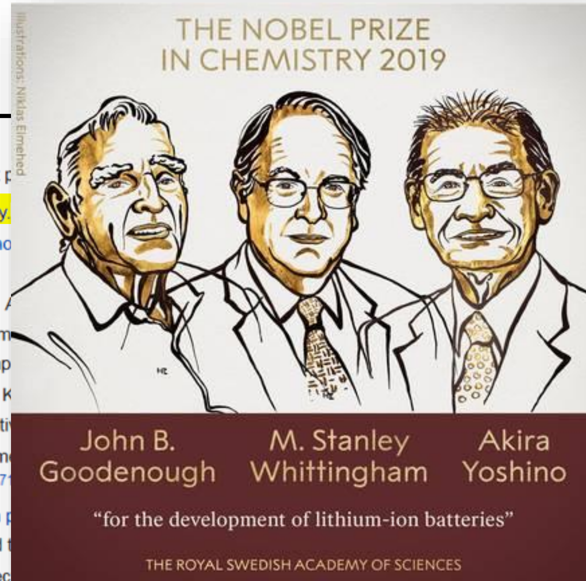
The Free Encyclopedia



Commercialization and advances [edit]

The performance and capacity of lithium-ion batteries increased as development p

- *1991* – Sony and Asahi Kasei released the first commercial lithium-ion battery. … was led by Yoshio Nishi.[13]
- *1996* – Goodenough, Akshaya Padhi and coworkers proposed lithium iron pho… with the same structure as mineral olivine) as positive electrode materials.[62] </nowiki>*Journal of the Electrochemical Society*, 144 (4), p. 1188-1194</ref>
- *1998* – C. S. Johnson, J. T. Vaughey, M. M. Thackeray, T. E. Bofinger, and S. A… ich NMC cathode materials.[63]
- *2001* – Arumugam Manthiram and co-workers discovered that the capacity lim… n be understood based on the relative positions of the metal 3d band relative to the top of the oxygen 2p band.[64][65][66] This discovery has had significant imp… battery layered oxide cathodes, as well as their stability from a safety perspective.
- *2001* – Christopher Johnson, Michael Thackeray, Khalil Amine, and Jaekook K… hium rich cathodes based on a domain structure.
- *2001* – Zhonghua Lu and Jeff Dahn file a patent[69] for the NMC class of positi… nts over the widely used lithium cobalt oxide.
- *2002* – Yet-Ming Chiang and his group at MIT showed a substantial improvem… uctivity by doping it[70] with aluminium, niobium and zirconium. The exact mechanism causing the increase became the subject of widespread debate.[7…
- *2004* – Yet-Ming Chiang again increased performance by utilizing lithium iron p… sed particle density almost one hundredfold, increased the positive electrode's surface area and improved capacity and performance. Commercialization led t… well as a patent infringement battle between Chiang and John Goodenough.[71]
- *2005* – Y Song, PY Zavalij, and M. Stanley Whittingham report a new two-elec…
- *2011* – Lithium nickel manganese cobalt oxide (NMC) cathodes, developed at Argonne National Laboratory, are manufactured commercially by BASF in Ohio.[74]
- *2011* – Lithium-ion batteries accounted for 66% of all portable secondary (i.e., rechargeable) battery sales in Japan.[75]
- *2012* – John Goodenough, Rachid Yazami and Akira Yoshino received the 2012 IEEE Medal for Environmental and Safety Technologies for developing the lithium ion battery.[10]
- *2014* – John Goodenough, Yoshio Nishi, Rachid Yazami and Akira Yoshino were awarded the Charles Stark Draper Prize of the National Academy of Engineering for their pioneering efforts in the field.[76]
- *2014* – Commercial batteries from Amprius Corp. reached 650 Wh/L (a 20% increase), using a silicon anode and were delivered to customers.[77]
- *2016* – Koichi Mizushima and Akira Yoshino received the NIMS Award from the National Institute for Materials Science, for Mizushima's discovery of the $LiCoO_2$ cathode material for the lithium-ion battery and Yoshino's development of the lithium-ion battery.[12]
- *2016* – Z. Qi, and Gary Koenig reported a scalable method to produce sub-micrometer sized $LiCoO_2$ using a template-based approach.[78]
- *2019* – The Nobel Prize in Chemistry was given to John Goodenough, Stanley Whittingham and Akira Yoshino "for the development of lithium-ion batteries".[11]

In 2010, global lithium-ion battery production capacity was 20 gigawatt-hours.[79] By 2016, it was 28 GWh, with 16.4 GWh in China.[80] Production is complicated and requires many steps.[81]

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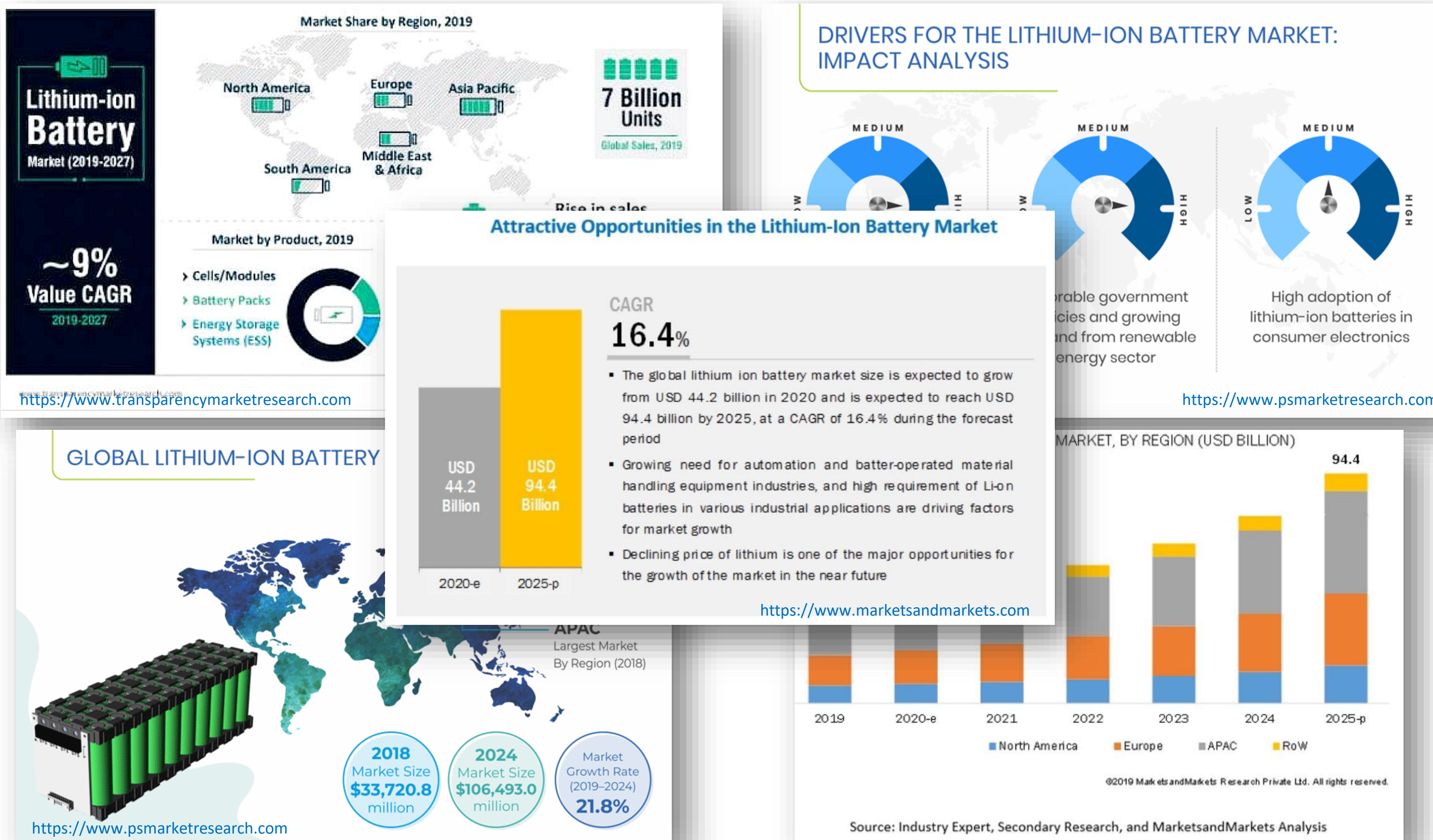
リチウムイオン電池市場
Economics of Li-Ion Batteries



- アノードのコスト：全体の**10–15%**　Anode worth **10-15%** of total cost
- アノード市場：2025年には**100億ドル**（1兆円）規模に　Anode market worth **~$10 billion** by 2025

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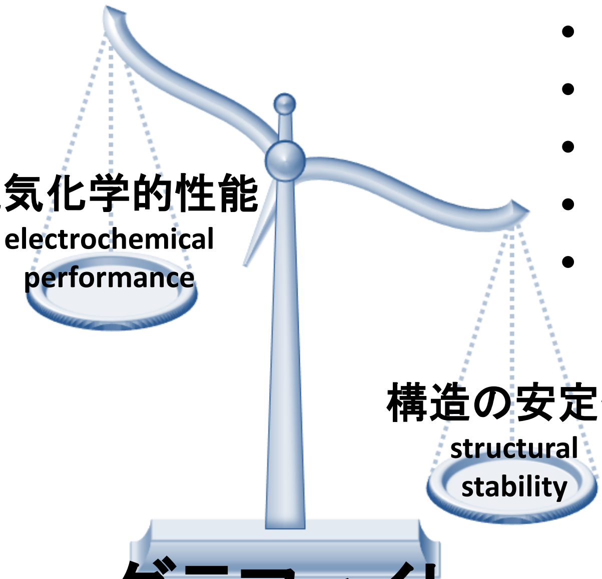
アノード材料の採用基準

Criteria for Anode Material Selection

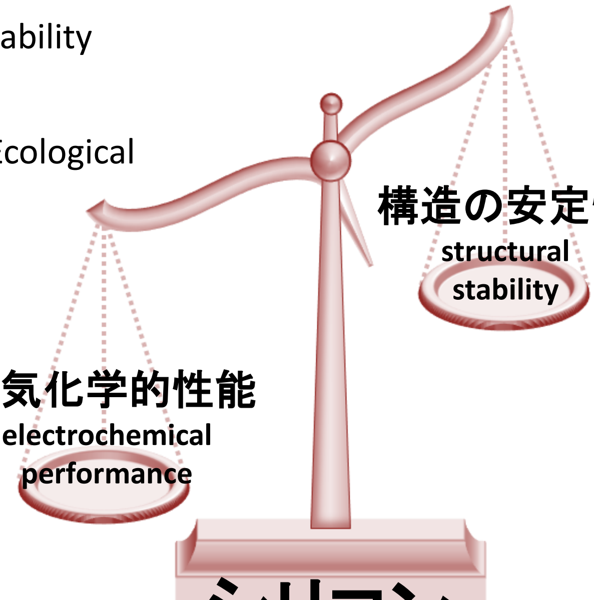
- エネルギー容量　Energy capacity
- 性能　Performance
- サイクル性　Cycleability
- サイズ　Size
- 環境への影響　Ecological
- 安全性　Safety
- コスト　Cost



グラファイト
Graphite

- 安価
  cheap
- 拡張可能
  scalable
- ロバスト性
  robust

- **低容量**
  low capacity
- 重い
  heavy



シリコン
Silicon

- **大容量**
  very high capacity
- 材料が安価
  cheap material
- 軽量
  lightweight
- インテグレーション可能
  integrateable

- 大きく膨張
  huge swelling
- **SEIが安定しない**
  unstable SEI
- **亀裂発生**
  fracture

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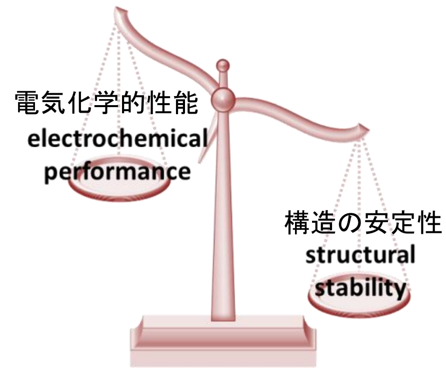
アノード材料の採用基準
Criteria for Anode Material Selection

テスラ　Battery Day　2020年9月22日

Tesla Battery Day, September 22, 2020

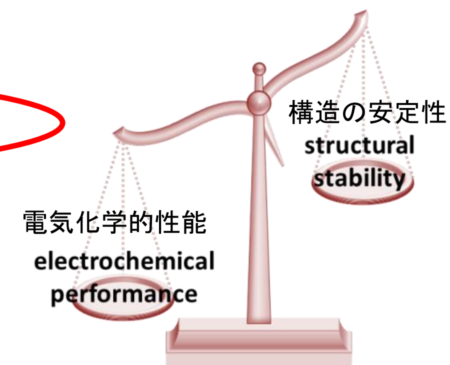
シリコンアノードの安定化させる方法
Strategies to Stabilise Si Anodes

- **リチウム化による膨張を制限 Restrict lithiation swelling**
  - シリコン混合アノード Silicon-composite anodes
  - 土台でのカプセル化 Encapsulation in matrices
  - 非活性物質の添加 Addition of inactive material



- 安定するが**シリコンの割合は低下**
  increased stability but **reduced Si content**

- **リチウム化による膨張を収容 Accommodate lithiation swelling**
  - 構造(例：薄膜、ナノ粒子、ナノチューブ、ナノワイヤ等)
    Structuring (e.g., thin films, nanoparticles, nanotubes, nanowires, etc.)



- 安定性が向上**することも**
  sometimes increased stability
- 製造過程が**複雑**
  extra fabrication **complexity**

例：Amprius社(シリコンナノワイヤ) Ramot社(ステンレス鋼上のシリコンナノワイヤ)
e.g., Amprius (Si nanowires), Ramot (Si nanowires on stainless steel)

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OISTアノード：成長工程

OIST Anode: Growth

適した基材／集電体
appropriate substrate / collector

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OISTアノード：成長工程

OIST Anode: Growth

新技術説明会
New Technology Presentation Meetings!

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OISTアノード：成長工程
OIST Anode: Growth

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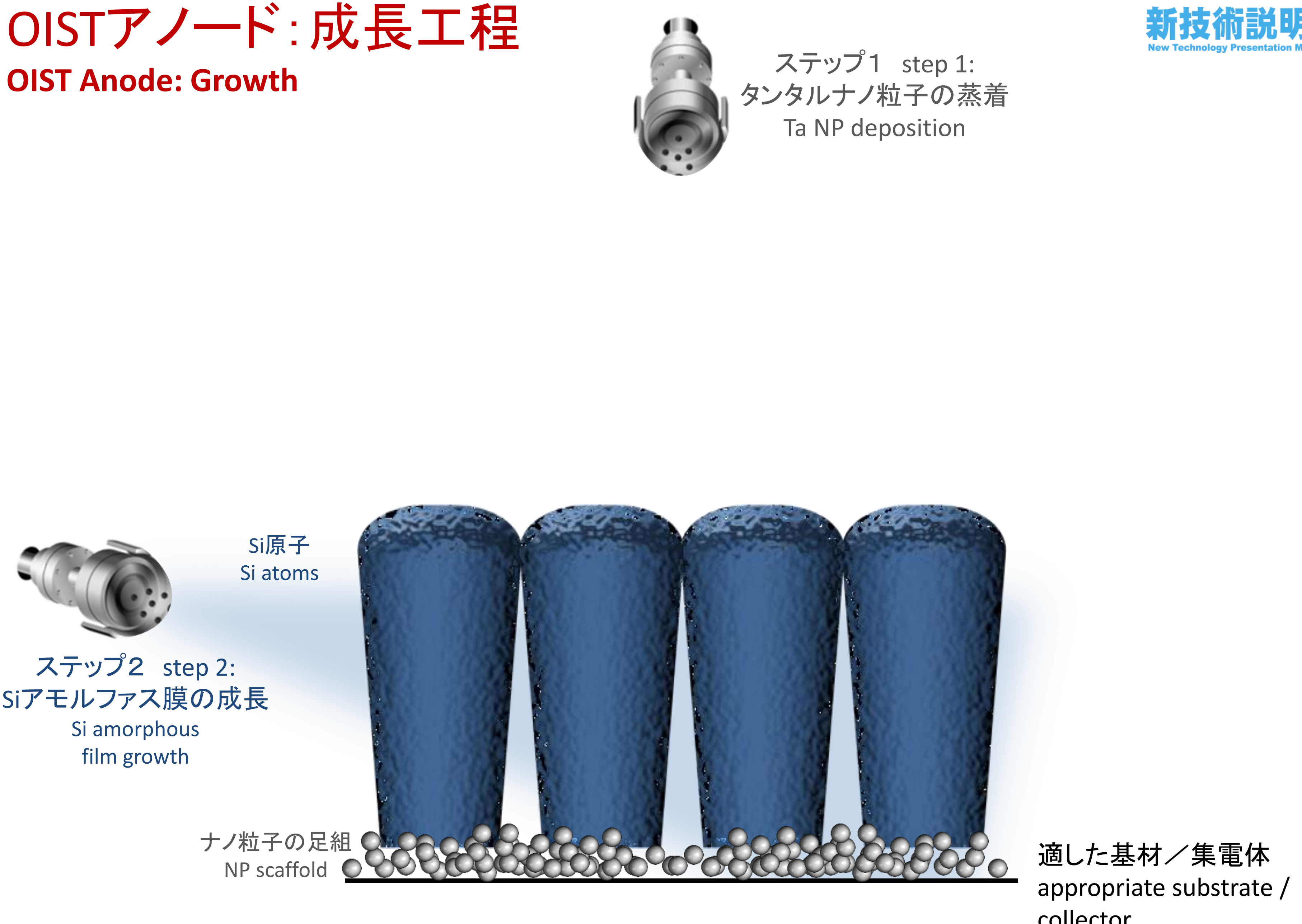

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アーチ構造　vaulted structure

利点
Advantages

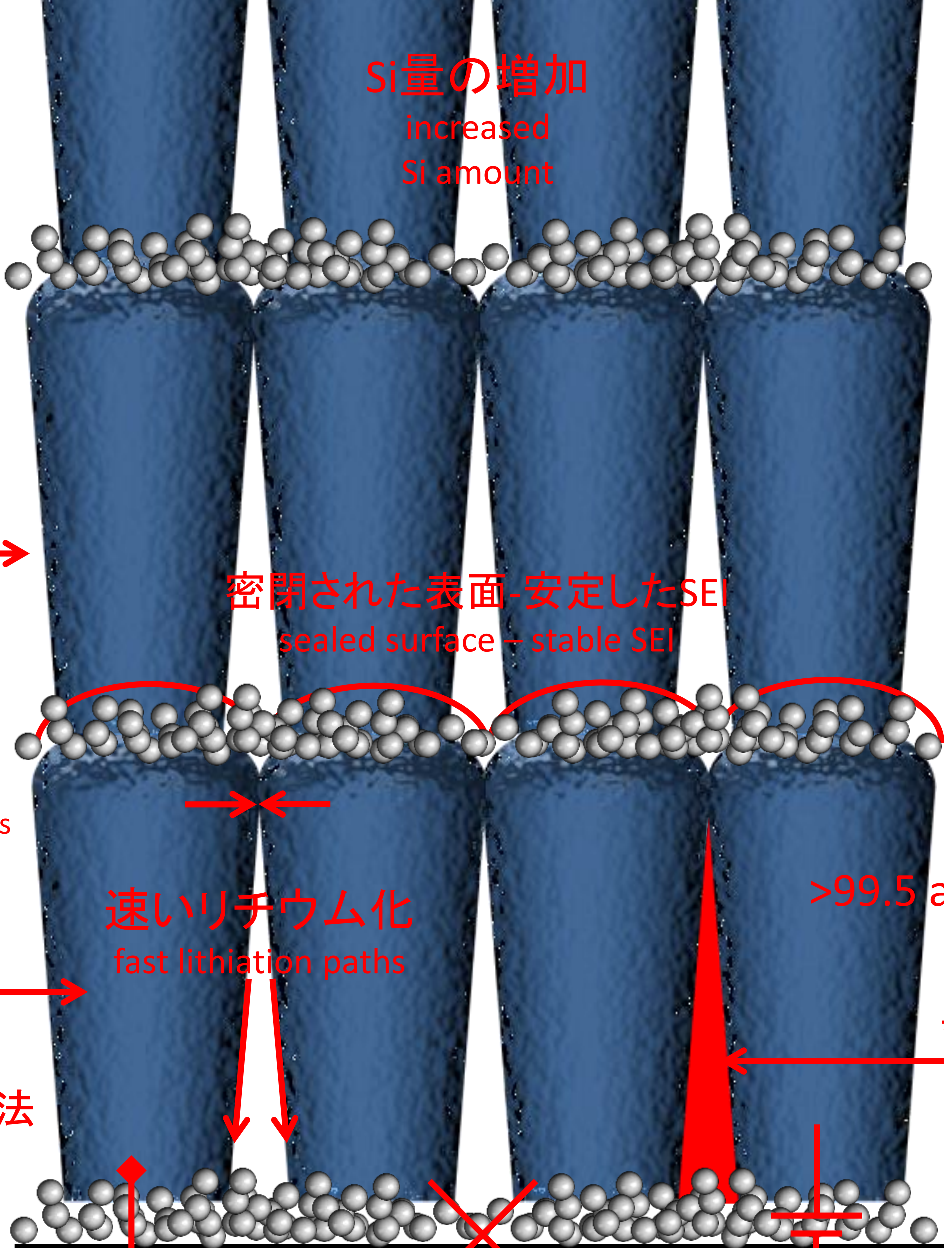
フレキシブル、制御可能、スケールアップ可能なデザイン
flexible, controllable, scalable design

重ねられる
possibility to stack vertically

剛性の増加
increased stiffness

アモルファスシリコン柱
amorphous Si pillars

インテグレーション可能、環境負荷の少ない製造方法（バインダー、溶液不要）
integratable, eco-friendly fabrication (no binders/solvents)



もっと重ねられる
and beyond...

水道橋のような多層構造
aqueduct structure

広い表面積
high surface area

異方性膨張のためのスペース
space for anisotropic swelling

密着性の向上
improved adhesion

相互拡散なし
no interdiffusion

向上した電気接点
enhanced electrical contact

アーチ構造 vaulted structure

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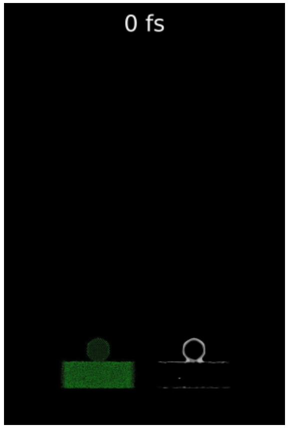
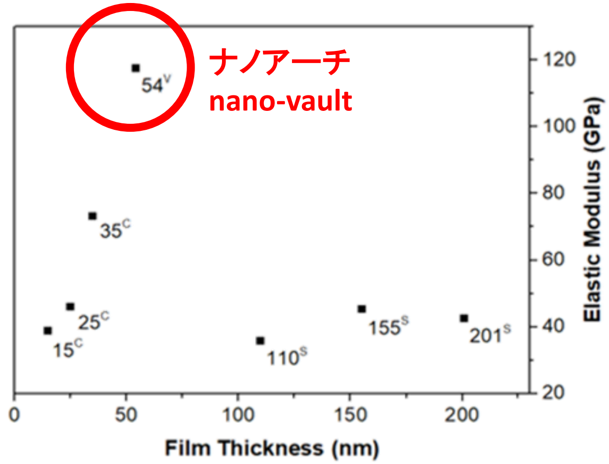
OISTアノード：特徴

OIST Anode: Features



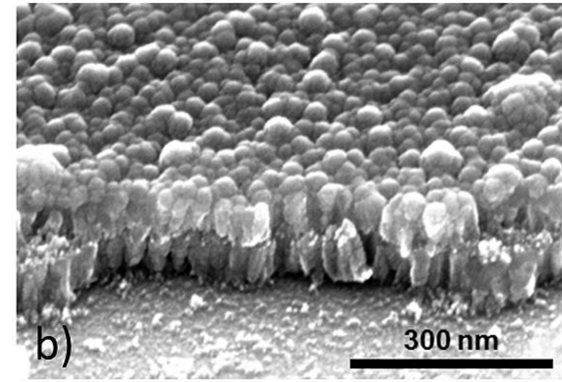
大型の分子動力シミュレーションで証明

proven by large-scale
Molecular Dynamics simulation



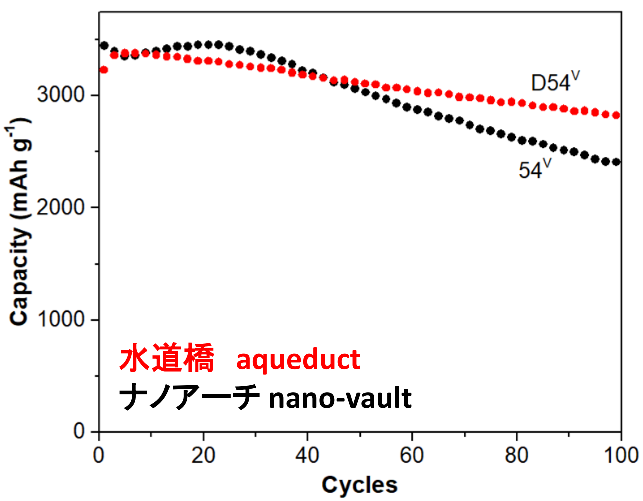
弾性係数の向上

elastic modulus enhancement



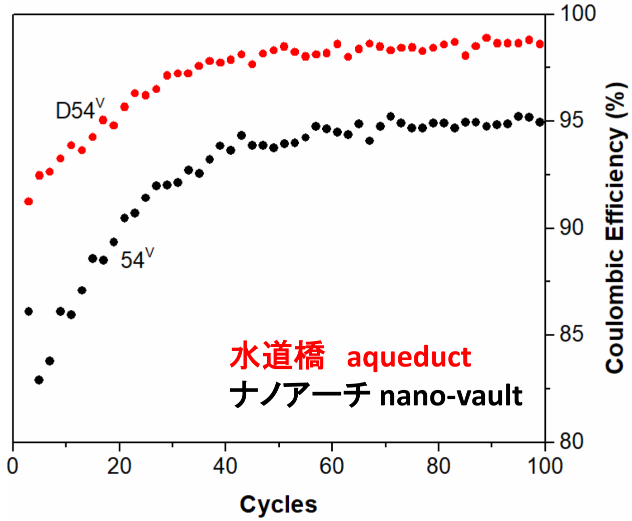
SEM：水道橋のような多層構造

SEM: aqueduct structure



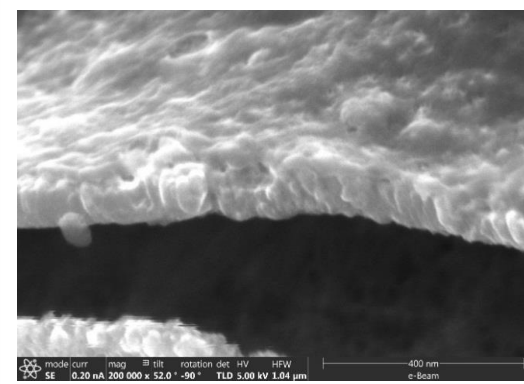
100サイクル後の
エネルギー容量保持

energy capacity retention
after 100 cycles



100サイクル後に
～100%のクローン効率

～100% Coulombic efficiency
after 100 cycles



SEM：サイクル後の構造の安定性

SEM: mechanical stability
after cycling

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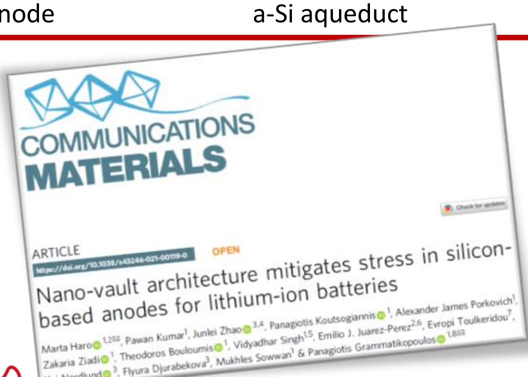
従来技術とナノアーチ構造の比較

Comparison of nano-vault architecture with existing technology

Zuo et al. *Nano Energy* 31 **(2017)** 113-143

2016	Anode アノード	Synthesis method 合成方法	Cycling stability サイクル安定性 Discharge capacity [mA h g^{-1}] 放電能力	After nth cycle Nサイクル後	Current rate [mA g^{-1}] 電流レート
0D Si NPs	Si NPs/graphene composite	Top-down dispersion and bottom-up synthesis	>1200	600	500
0D Si NPs	Si NPs/rGO-hybrid	Sol-gel reaction followed by magnesiothermic reduction	1165	100	2100
0D Si NPs	SNPs@void@ mGra	Melting self-assembly route	1287	500	500
0D Si NPs	Si@C-rGO	Stirring and vacuum filtration	930	400	300
0D Si NPs	Si NPs/graphene foam	Freeze-drying method	1295	180	500
0D Si NPs	Si-nanolayer-embedded graphite/carbon hybrids	CVD	496	100	0.5C
Si microparticles (1–3 µm)	Graphene cages/um silicon	Using a dual-purpose Ni template	2805	300	210
3D Si	Granadilla-like silicon/carbon composite	Templating method	1100	200	250
OISTアノード OIST anode	**アモルファスSi水道橋（多層構造）** a-Si aqueduct	**CBD-PVD コンビネーション** CBD-PVD combination	**2832**	**100**	**0.5C**

CBD - クラスタビーム蒸着 cluster beam deposition
PVD - 物理蒸着 physical vapour deposition


COMMUNICATIONS MATERIALS

ARTICLE OPEN

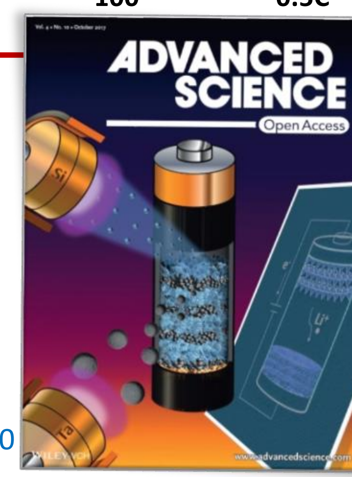
Nano-vault architecture mitigates stress in silicon-based anodes for lithium-ion batteries

Marta Haro, Pawan Kumar, Junlei Zhao, Panagiotis Koutsogiannis, Alexander James Porkovich, Zakaria Ziadi, Theodoros Bouloumis, Vidyadhar Singh, Emilio J. Juarez-Perez, Evropi Toulkeridou, Kai Nordlund, Flyura Djurabekova, Mukhles Sowwan & Panagiotis Grammatikopoulos

Commun Mater 2 **(2021)** 16

最適化前でも既に高性能を示す！

NOTICE: OIST anode not fully optimised yet!



Adv Science 4 **(2017)** 1700180

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想定される用途
Expected application

- **エネルギー密度が重要な**電子機器向けの
  ハイエンドリチウム電池
  （航空・宇宙産業など）
  It can be applied for **high-end** Li-ion batteries for electronic applications, where **energy density over weight** is important (e.g., aeronautics and space).

- 電池以外では、高ストレスサイクルへの耐性が必要な用途にも
  ナノアーチ構造自体を利用可
  （水素貯蔵、バイオインプラントなど）
  Other than batteries, the nano-vault architecture itself can be used in applications requiring endurance over variable high-stress cycling (e.g., hydrogen storage, bioimplants, etc.).

実用化に向けた課題

Challenges for commercialisation

- 達成していること

（1）ナノ構造ユニットの**電気化学的および機械的応答**の改善

（2）**垂直方向に積み重ねる**多重構造による性能の向上

We have demonstrated (1) the **improved electrochemical and mechanical response** of the nanostructure unit
(2) performance enhancement due to **vertical repetition** in multilayers.

- これから取り組むこと

（1）構造（サイズ、材料、層数など）のさらなる最適化

（2）製造プロセスのスケールアップ

（例：マグネトロンスパッタリングから化学蒸着法への変更）

We need to (1) further **optimise the structure** (e.g., dimensions, materials, number of layers)
(2) **scale up** fabrication process (e.g., by replacing magnetron sputtering with other CBD method)

- このナノアーチ構造を、類似技術と比較し、性能やコスト（例：PVDかCVDか）、環境への影響を要評価

For commercialisation, our nano-vault structure needs to be benchmarked against other, similar approaches (e.g., Amprius Si nanowire anodes) in terms of performance, cost (e.g., PVD vs. CVD), and environmental impact.

企業への期待
Potential ways for technology transfer

- パラメータの最適化と概念実証は(POC: Proof-of-concept)は大学で行い、スケールアップは企業での実施を希望。

  Parameter optimisation and proof-of-concept should be conducted in academic environment.
  Scale-up should be proven at industrial scale.

- マイクロバッテリーに関心を持つ企業との共同研究を希望。
  (1)最適化の実現:ポスドク雇用の資金提供など
  (2)スケールアップ:ライセンス契約

  Looking for a company focusing on micro-batteries for research collaboration:
  (1) optimisation round (e.g., post-doc funding)
  (2) production upscale (technology licencing)

- **高密度バッテリー**を開発中の企業や、**ハイエンド製品市場**への参入を目指す企業(ドローンなど)は、本技術の導入が有効。

  Companies which are developing **high-density batteries** or which want to enter into **high-end application market** (e.g., drones) can benefit from this technology.

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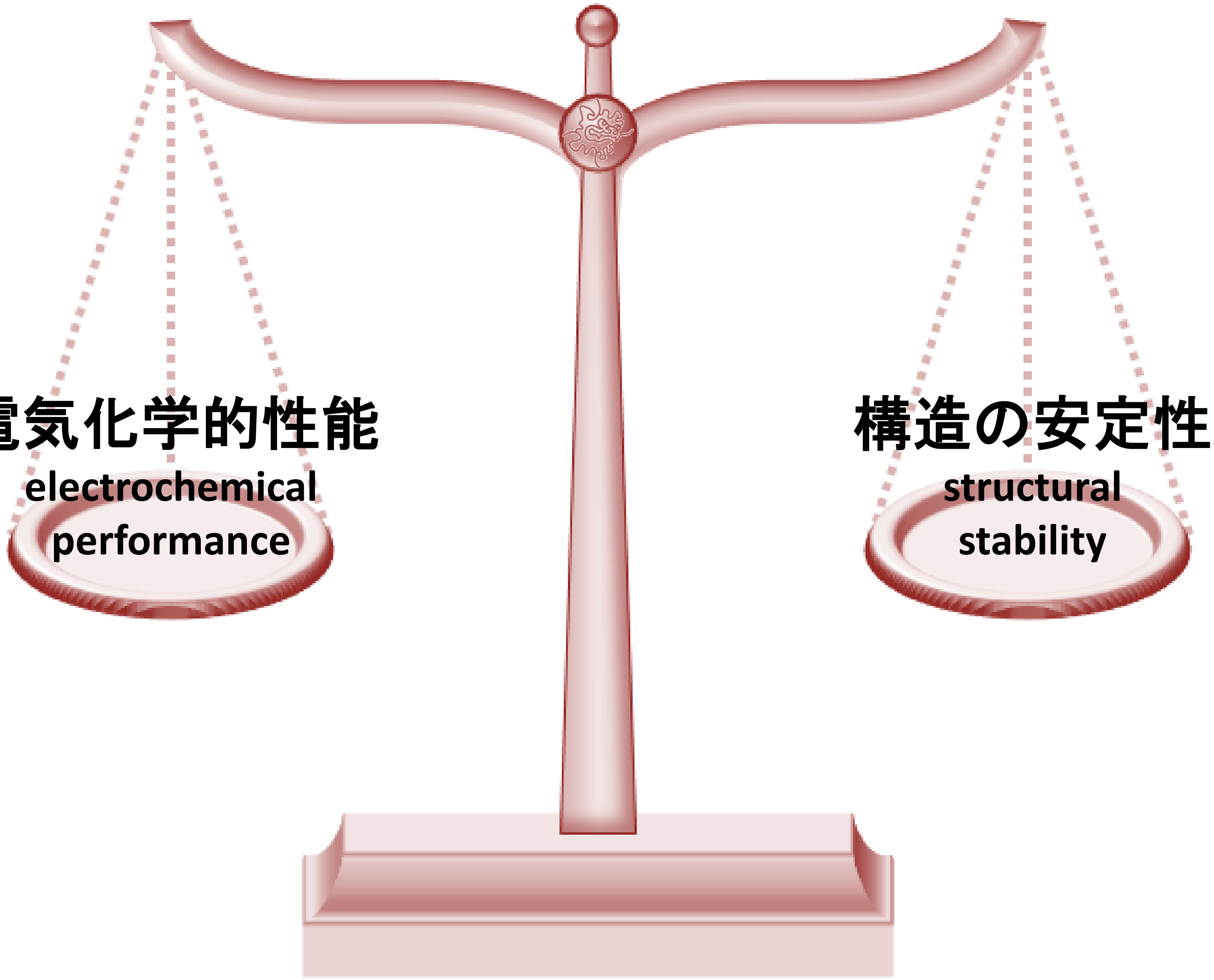
OISTのアノード:総合評価
OIST anode: Assessment



特許
Patent

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出願番号	:米国　仮出願　63/075,455
出願人	:沖縄科学技術大学院大学（単独）
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