Morphological Evolution of Discharge Products in Li-O₂ and Na-O₂ Batteries

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P. Hartmann, Nat. Mat. 12, 228 (2013).
Metal-Ion Battery

Metal-O₂ Batteries

e.g., Li ions reversibly react with O₂ to form lithium peroxide, Li₂O₂

Y.-C. Lu et al., Energy and Environmental Science 4, 2999 (2011).
**Li-O₂ Batteries: Gravimetric Capacity**

- Lithium-air vs Lithium ion: 3-5 times higher capacity
- No intercalation cathode is necessary
Li-O₂ Batteries: Challenges

Y.-C. Lu et al, Energy and Environmental Science 6, 750 (2013)
Li-O₂ Batteries: Cathode

- Li₂O₂ is an insulator
- Scaffold needed:
  - to provide growth sites for Li₂O₂
  - to provide electrical conductivity
Li-O$_2$ Batteries: Cathode

Solution: Carpets of Vertically Aligned Carbon Nanotubes and Nanofibers (VCNT/Fs)
Why VACNT/F Carpets?

- Light-weight
- Highly conductive
- High surface area
- High porosity
- High aspect ratio
- No binder
- Readily modified

Fast O₂ transport

Fast Li transport

high electron conductivity
Both a reducing gas (e.g. H\textsubscript{2}) and a carbon source gas (e.g. C\textsubscript{2}H\textsubscript{4}) are used.

Growth of CNT/Fs catalyzed by metal particles.
**Li-O₂ Cathode: CNF Carpet Grown on Porous Alumina**

- Porous alumina allows transport of O₂
- Metallization on porous alumina serves as current collector
**Li$_2$O$_2$ Discharge Product on CNFs**

As-synthesized CNF electrode

Galvanostatic discharge from OCV

End of discharge: Monolithic Li$_2$O$_2$ structure with characteristic toroidal particles. High Volumetric Capacity
High Gravimetric Energy Approaching 75% of Theoretical in Discharged State

~4-fold improvement compared to Li-ion electrodes at comparable powers

Morphological Evolution – Discharge

Rate Capability

Rate and Nucleation and Capacity

Low discharge rate (100 mA/g_C):
- A few large particles grow to fill space
- High volumetric capacity

High discharge rate (511 mA/g_C):
- CNTs coated quickly by small particles
- Low volumetric capacity
Tuning of Nanotube Diameter and Areal Density through Catalyst Pre-Treatment

Fe oxidized by exposure to air → Fe oxide reduced by exposure to H₂ at growth T → Fe dewets → Fe coarsens until C₂H₄ is introduced

Control of Structure of Carbon Nanotubes

Preheat Zone  Growth Zone

\[ \text{Gas preheating on. Substrate temperature set at 475°C} \]

\[ \text{Gas preheating off. Substrate temperature set at:} \]

\[ Q \approx 0.87 \text{eV} \]

\[ Q \approx 0.1 \text{eV} \]

\[ \text{CNT structure controlled by both preheat and growth T} \]

Growth at low temperatures and rapid substrate heating limits reaction of catalyst and allows CNF growth on metal underlayers

Aligned CNTs: Carpet Heights ~ 100 µm to 1 mm

Multi-walled nanotubes (mostly 2-4 walls) with some amorphous carbon along the sidewalls
Carpet Removal

Growth He/H₂/C₂H₄ at 720°C
Terminate with brief O₂ exposure

Free-standing 1cm² x 1cm² x 500μm CNT carpets
Free Standing CNT electrode

Freestanding CNT Carpet

Separators with Electrolyte

Lithium
500μm thick CNT carpet
Discharged at 50 mA/g<sub>c</sub>, to 1000 mAh/g<sub>c</sub>
Uniform distribution of similarly sized disc particles.
Particle Size Evolution

SEM Measurements of Particle Aspect Ratios

Increasing Aspect Ratio with Particle Diameter (CNTs)
Particle Substructure

Low Rates: Toroid morphology

High Rates: Disc morphology

Plate-like morphologies evident on particle surfaces (CNFs)
Thin plates with dominant (0001) Li$_2$O$_2$ surface
Slight misorientation between plates leading to arc pattern
Surface Energy Anisotropy

Plate structure consistent with theoretical calculations of the equilibrium Wulff shape


Surface dominated by Li$_2$O$_2$ (001)
TEM Imaging of Particles

Plates at ~4 nm layer pitch
Splayed-Plate Rim Formation

Side-profile of Disc Particle

Suggests additional nucleation of plates during growth (CNTs)
Origin of Shape Evolution

Plates Bend With Increasing Diameter

Increasing Diameter and Aspect Ratio

Aspect Ratio Evolution and Disc to Toroid Transition is Caused by Bending and Growth of Additional Plates
Dark Field Imaging

Dark field imaging reveals the presence of small crystallites comprising the structure of the particles

* Capturing (110) reflections
Mesocrystal Assembly: $\text{Co}_3\text{O}_4$

SEM images of the cobalt precursor prepared with different concentrations of $\text{Co(CH}_3\text{COO)}_2\cdot 4\text{H}_2\text{O}$ at (a) 6, (b) 40, (c) 93, and (d) 160 mM while the concentration of PVP was fixed at 0.23 mM.

**Mesocrystal Assembly: CaCO$_3$**

Similar structures found in other material systems – CaCO$_3$ particles can be synthesized with doughnut/disc shapes exhibiting similar diffraction patterns.

Mesocrystal Assembly

Helmut Coelfen and Markus Antonietti, Mesocrystals and Nonclassical Crystallization, John Wiley and Sons (2008)
Mesocrystal Assembly: $\text{Li}_2\text{O}_2$

Li$_2$O$_2$ grown *chemically* through reaction of KO$_2$ with a solution of LiTFSI.

(lithium bis-trifluoromethanesulfonimide)

Mesocrystal Assembly: Li$_2$O$_2$

Proposed mechanism for electrochemical mesocrystallization of Li$_2$O$_2$.
High O$_2^-$ concentrations promotes nucleation of Li$_2$O$_2$ nanocrystals in solution, and assembly into toroids.


Alternative paths:

\[ O_2 + e^- \rightarrow O_2^- \]
\[ O_2^- + Li^+ \rightarrow LiO_2 \]
\[ LiO_2 + Li^+ + e^- \rightarrow Li_2O_2 \]
\[ 2LiO_2 \rightarrow Li_2O_2 + O_2 \]
Mesocrystal Assembly

Nucleation of plate-shaped nanocrystals

Assembly of nanocrystals to form plates and mesocrystals
Calcite (Calcium Carbonate) Growth Morphologies

$[\text{Ca}^+]$

$[\text{PSS}]$

PSS = polystyrenesulfonate

Li-O$_2$ vs. Na-O$_2$

- High gravimetric energy (3505 Wh/kg$_{Li2O2}$)
- High charge overpotential (~1000mV)

- Low gravimetric energy (1108Wh/kg$_{Na2O2}$ or 1605Wh/kg$_{Na2O2}$)
- Lower charge overpotential (~100mV)
Discharge and charge voltage profiles of Na-O₂ cells to a fixed capacity (1000 mAh g⁻¹). Dotted line: $E^0 (\text{NaO}_2) = 2.27$.

Voltage vs. capacity of CNT electrodes discharged galvanostatically between 10 and 1000 mA g⁻¹ in 0.1M NaClO₄ in DME.

Discharge Product

Discharged at 1000 mAg$_c^{-1}$ to 1000 mAhg$_c^{-1}$

Discharged at 10 mAg$_c^{-1}$ to 1000 mAhg$_c^{-1}$

in 0.1 M NaClO$_4$ DME

Na-O$_2$ / VACNTs
Discharge Product

- Discharged at 10, 100 and 1000 mA g$_c$\(^{-1}\) to 1000 mAh g$_c$\(^{-1}\) and after being discharged and fully charged at 1000 mA g$_c$\(^{-1}\) to 1000 mAh g$_c$\(^{-1}\) in 0.1M NaClO$_4$ in DME.
- D and G bands of the CNTs and the NaO$_2$ peak at 1156 cm$^{-1}$ are indicated in the Raman spectra.
**Na-O₂ / VACNTs**

**Discharge Product**

- Only NaO₂ is observed
- Na₂O₂ · H₂O observed only after air exposure (not in up to 6000 ppm H₂O in solution)
• Very similar Tafel plots
• Same rate-determining step (i.e. electron transfer to O$_2$ to form LiO$_2$ or NaO$_2$)?

Rotating Ring Disk Electrode (RRDE)
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![Diagram of RRDE with reactions](image)
**Na-O₂ vs. Li-O₂**

*Rotating Ring Disk Electrode (RRDE)*

- 50 mV/s in DME at 1600 rpm
- 0.1 M NaClO₄ or 0.1 M LiClO₄

Current response on the **ring** held potentiostatically at 3.0 V vs Na⁺/Na or 3.5 V vs Li⁺/Li

CVs on the **disk** at 50 mV/s between 1.8 - 4.0 V vs Na⁺/Na and 2.0 – 4.5 vs Li⁺/Li

Li-O$_2$ vs. Na-O$_2$

RRDE: Superoxide Solubility

Estimated soluble and insoluble fractions of the total ORR charge as a function of rotation rate

NaO$_2$ Morphology and Distribution Through CNT Carpet

Discharged at 10mA/g$_c$

Discharged at 1000mA/g$_c$

$\text{NaO}_2 \text{ Morphology and Distribution Through CNT Carpet}$

Low rate

Discharged at 10mA/g$_c$

High rate

Discharged at 1000mA/g$_c$
Li$_2$O$_2$ Morphology and Distribution Through CNT Carpet

Low discharge rate

High discharge rate

CNTs coated by small particles Throughout carpet
Transport-Limited at High Discharge Rates?

Calculated $O_2$ concentration profile
Low Barrier to Nucleation?

Nucleation at O\textsubscript{2}/carpet and separator/carpet interfaces consumes all or most of the O\textsubscript{2}, ‘starving’ the interior of the carpet.
**Nucleation: NaO$_2$ vs. Li$_2$O$_2$**

Energy barrier for nucleation:

\[
\Delta G_{nuc} \propto \frac{\bar{\gamma}^3}{(-RT \ln(\sigma))^2}
\]

\[
\bar{\gamma} = \sum_i \alpha_i \gamma_i = \text{surface energy averaged over the facets } i
\]

\[\sigma = \text{supersaturation}\]

\[
\bar{\gamma}_{Li_2O_2} = 28.2 \text{ meV/Å}^2
\]

\[
\bar{\gamma}_{NaO_2} = 11.7 \text{ meV/Å}^2
\]

\[
\sigma_{Li_2O_2} = 4.6 \times 10^{16}
\]

\[
\sigma_{NaO_2} = 1.6 \times 10^{15}
\]

\[
(\Delta G_{nuc})_{NaO_2} \approx 12 \times (\Delta G_{nuc})_{Li_2O_2}
\]

Particle Formation Mechanism

• Morphology is reminiscent of FeS$_2$ (pyrite) morphology which grows via a layer-by-layer mechanism (including penetration twins).

• However, a fully analogous mechanism would require O$_2$ reduction to O$_2^-$ followed by stepwise Na$^+$ addition on the solid NaO$_2$ surface.

• This is unlikely here because NaO$_2$ is insulation and O$_2^-$ is highly soluble in the electrolyte.

• Therefore, in analogy with other insulating metal oxide crystals...mesocrystal self assembly?
Summary

• For Li-O₂, only Li₂O₂ forms; For Na-O₂, only NaO₂ forms
• Copious formation of Li₂O₂ within CNT carpet limits capacity at high rates
• Copious formation and rapid growth of NaO₂ at surfaces of CNT carpet limits capacity at high rates
• Li₂O₂ appears to grow through mesocrystal assembly, leading to complex toroidal particles
• NaO₂ might also grow through mesocrystal assembly
• Growth of Li₂O₂ and NaO₂ appears to be rate limited by the same process, perhaps electron transfer to O₂ to form O₂⁻
• In both cases, (M⁺, O₂⁻) is present in the electrolyte, more in the case of Na⁺ than Li⁺
• The barrier to nucleation of Li₂O₂ appears to be higher than the barrier for NaO₂ nucleation