Nanostructured Electrodes and the Lithium-Air Battery

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Science in the 20th century

Nature of matter: atom → sub-atomic
Origin of the Universe: Big Bang
Molecular Biology: genetics

Science in the 21st century

Societal Challenges
- Food
- Water
- Global Warming / Energy

Climate change – a challenge for SCIENCE and technology.
New science, new ideas, new approaches, new materials.
Nanostructured Electrodes
Power Density

Li-ion \rightarrow relatively low power device (compared with Pb-acid)

Intrinsic limits to Li$^+$ and e$^-$ mobility

$\tau = \frac{l^2}{2D}$

Li diffusion coefficient

diffusion distance

time for intercalation

BUT

Reduce $l$ micron $\rightarrow$ nano
NANOPARTICULATE ELECTRODES

Advantages

- High surface area in contact with electrolyte
- Short diffusion distances for Li\(^+\) and e\(^-\) (\(t = l^2/2D\))
- Change in chemical potential \(\Rightarrow\) voltage
- Better accommodation of strain accompanying insertion.
- Solid state reactions can occur that are impossible in bulk

Disadvantages

- May be more difficult/expensive to synthesize
- More difficult to fabricate composite electrode
- Lower volumetric energy density of electrode
- Surface reactivity
- Cycling stability
TiO$_2$-(B) nanotubes / wires

NaOH + TiO$_2$(anatase) + H$_2$O $\xrightarrow{\text{hydrothermal synthesis}}$ TiO$_2$-(B) nanotubes / wires

TiO$_2$-(B) nanowires

TiO$_2$-(B) nanotubes


**TiO$_2$-(B) Electrode Performance**

- **1.6 V vs Li$^+/\text{Li}$ - anode**
- Intercalate Li up to Li$_{0.98}$TiO$_2$-(B) (330mAhg$^{-1}$)
- **Twice** that of anatase, Li$_4$Ti$_5$O$_{12}$ and bulk TiO$_2$-B
- >99.9% reversibility

Advantage of 1D nanomorphology

- Micron long wires ensures electron exchange between wires
- Nanometre diameter ensures fast Li$^+$ intercalation
Mesoporous LiMn$_2$O$_4$ spinel

Combining μm and nm dimensions

Mn$_2$O$_4$ (MnO$_2$) $\leftrightarrow$ LiMn$_2$O$_4$ : intercalation

3D Porous Silica e.g. KIT-6

TEM images

Mesostructure preserved throughout !
Li$_{1.12}$Mn$_{1.88}$O$_4$ spinel (composition of current interest)

~1 μm sized particles
BET : 90 m$^2$g$^{-1}$


![Graphs showing discharge time and capacity retention](image)

**Rate capability**
At high rate, 30C, gravimetric capacity 50% and volumetric 10% higher than bulk.

**Stability at 50 °C and 10 mAhg$^{-1}$**

μm particles + nm thin walls + 3D network of identical mesoporous channels for electrolyte + crystal structure
**Lithium-ion Nanobattery**

TiO$_2$(B)-nanowires  
LiNi$_{0.5}$Mn$_{1.5}$O$_4$

1.5 V  
4.7 V

Li-air cell
Progress in Rechargeable Lithium Batteries

Cathode major limiting factor

\[ \text{Li}_x\text{CoO}_2 : 140 \text{mAhg}^{-1} \quad \text{0.5}<x<1 \sim \frac{1}{2}\text{Li}/\text{Co} \]

\[ \text{Graphite Li}_x\text{C}_6 : 370 \text{mAhg}^{-1} \quad \text{0}<x<1 \sim \frac{1}{6}\text{Li}/\text{6C} \]

Best intercalation cathode → double capacity to 300mAhg\(^{-1}\)!
Lithium / Oxygen Battery Schematic

Discharge with intercalation cathode use $O_2$ from air!

Li anode
Electrolyte
Composite porous cathode

Li$^+$

$Li_2O_2$

$O_2$
Lithium / Oxygen Battery Schematic
Dispense with intercalation cathode use O₂ from air!

Li anode

Electrolyte

Composite porous cathode

Li⁺

O₂

Li₂O₂

Charge

Li anode

Electrolyte

Composite porous cathode
Capacity of Lithium-air

Li/LiPF$_6$ in propylene carbonate/porous carbon-MnO$_2$-binder

Swagelok Li / O₂ Cells

- Aluminium grid
- Composite Electrode: Porous Carbon-MnO₂
- Electrolyte: PC-LiPF₆

O₂ filled tube

Li
Li-O₂ Cell

Porous (super P:EMD:binder) cathode

2Li⁺ + 2e⁻ + O₂ ⇌ Li₂O₂

Overall Cell Capacity / mAh g⁻¹

Voltage

Capacity of Super P / mAh g⁻¹

Cycle number

2 - 4.1 V
70 mA/g

0 250 500 750 1000
0 250 500 750 1000

0 5 10 15 20
0 500 1000 1500 2000

discharge
charge

Porous (super P:EMD:binder) cathode

2Li⁺ + 2e⁻ + O₂ ⇌ Li₂O₂
Direct gas exchange between electrolyte and gas phase
**Li$_2$O$_2$ decomposition on charge**

In situ DEMS (Differential Electrochemical Mass Spectrometry)

- **Cell reaction**: $2\text{Li} + \text{O}_2 \leftrightarrow \text{Li}_2\text{O}_2$

Oxygen evolution during the decomposition of Li$_2$O$_2$ on charge

Powder X-ray Diffraction

- **After charging (100%)**
  - Li$_2$O$_2$
  - EMD
  - PTFE
- **Before charging**
  - Li$_2$O$_2$
  - EMD
  - PTFE

Charge passed corresponding to Li$_2$O$_2$ decomposition

**Powder X-ray Diffraction**

- **Intensity / arbitrary units**
- **2θ (FeKα) / degree**

- **Charge of Li$_2$O$_2$ electrode**

- **Oxygen evolution (m/z = 32)**

**In situ DEMS**
### Role of Catalyst

**Differential Electrochemical Mass Spec – On Charging**

<table>
<thead>
<tr>
<th>m/z</th>
<th>Relative amounts of gas evolved for</th>
<th>Li$_2$O$_2$</th>
<th>Li$_2$O$_2$ / MnO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 (from CO &amp; CO$_2$)</td>
<td>-</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>16 (from O$_2$, CO &amp; CO$_2$)</td>
<td>0.3</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>28 (CO)</td>
<td>1.6</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>32 (O$_2$)</td>
<td>1.1</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>44 (CO$_2$)</td>
<td>0.6</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>

- Most abundant process with MnO$_2$ catalyst is **O$_2$ formation (m/z = 32)**
- MnO$_2$ catalyses Li$_2$O$_2$ decomposition
Catalyst type influences performance:
- overall capacity
- charge potential
Effect of MnO$_2$ catalyst type

- Surface area and crystal structure important for performance
- Nanowire $\alpha$-MnO$_2$ gives highest capacity so far, 3000 mAhg$^{-1}$

$\alpha$-MnO$_2$ Catalyst

$\alpha$-MnO$_2$ catalyst ⇒ Lower charge potential

Limit window for cycling ⇒ avoid deep discharge

⇒ Negligible capacity fade on cycling, $\sim$2000 mAh$^{-1}$ (10+ cycles)

Limit window for cycling: 2400 mAh$^{-1}$

LiCoO$_2$
O₂ reduction on glassy carbon electrode in 0.1 M TBAPF₆-PC

O₂ + e⁻ = O₂⁻

E⁰ = 2.32 V
k⁰ = 0.9x10⁻³ cm/s
[O₂] = 1.45 mM
D₀₂ = 5.7x10⁻⁵ cm²/s
• Air cathode: gain in gravimetric > volumetric energy.
• Must couple with high capacity anode to realize benefits in a cell.
• \( \text{Li}_2\text{O}_2 \) to \( \text{Li}_2\text{O} \) >> capacity.
• Better understanding needed for more accurate predictions.
Conclusions Li-air

Opportunity
• High capacity
• Low cost

Challenges
• Charge potential greater than discharge
• Cycle life
• Electrolyte
• O₂ selective membrane
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