The Need for Li Metal Protection in Li – O₂ Batteries with Redox Mediators

Seongmin Ha, Dongho Koo, Kyu Tae Lee*
Chemical and Biological Engineering
Seoul National University (ktlee@snu.ac.kr)
1) Introduction

2) Failure mechanism of a redox mediator in Li–O₂ batteries

3) LiNO₃ as a scavenger of oxidized redox mediators in Li–O₂ batteries
Failure mechanism of Li–O$_2$ batteries with a redox mediator
MPT as a model for Li–O₂ batteries

10-Methylphenothiazine (MPT)

- Reversible redox reaction in Ar and O₂ atmospheres (LiSO₃CF₃ + MPT in tetraglyme)

\[
\begin{align*}
\text{CH}_3 & \quad \text{CH}_3 \\
\text{N} & \quad \text{N}^+ \\
\text{S} & \quad \text{S}^+ \\
\end{align*}
\]

1st Redox center

2nd Redox center


A. A. Golriz et al., *Nanoscale* (2011) 3 5049-5058

![Graphs and diagrams showing current vs. voltage for Ar and O₂ atmospheres with MPT oxidation cell](image-url)
Reaction mechanism of Li – O₂ batteries with MPT

Full discharging and charging

- Smaller polarization for MPT
- Reversible formation/decomposition of Li₂O₂

Ex situ XRD patterns w/ and w/o MPT
Cycle performance of Li–O₂ batteries with MPT

Constant capacity: 1000 mA h g⁻¹

Improved cycle performance, but still fading
Degradation of MPT in Li-O_2 batteries with Li metal

Reversible redox reaction of MPT in O_2 atmosphere w/o Li metal

Failure mechanism of MPT attributable to Li metal
Li/Li symmetric cells in Ar atmosphere (LiSO$_3$CF$_3$ w/ and w/o MPT in tetraglyme)

- Stable voltage profiles for Li/Li cells containing no MPT
- Unstable voltage profiles and voltage fluctuation for Li/Li cells containing MPT

→ Decomposition of MPT when in contact with Li metal
MPT stability when in contact with Li metal

- ~ 1.3 V additional peak → reductive decomposition of MPT
Decomposition of MPT when in contact with Li metal

- Appearing new $^1$H NMR peaks after the storage with Li metal → decomposition of MPT
Li/Li symmetric cells in $\text{O}_2$ atmosphere (LiSO$_3$CF$_3$ w/ and w/o MPT in tetraglyme)

- Unlike Ar, stable voltage profiles despite the addition of MPT in $\text{O}_2$
  - Suppressed MPT decomposition in $\text{O}_2$
Improved stability of Li metal in O\textsubscript{2}

Role of O\textsubscript{2} for Li metal electrodes

- Dissolved O\textsubscript{2} in the electrolyte formed the lithium oxides-based protective layer on the Li metal surface

- Lithium oxides-based protective layer
  1) Suppressing dendrite growth
  2) Enhancing electrochemical performance

<table>
<thead>
<tr>
<th>Electrolyte (THF)</th>
<th>Average cycling efficiency (5~10 cycles)</th>
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<tbody>
<tr>
<td></td>
<td>Bare</td>
</tr>
<tr>
<td>0.2 M LiClO\textsubscript{4}</td>
<td>~ 50 %</td>
</tr>
<tr>
<td>0.5 M LiClO\textsubscript{4}</td>
<td>75 %</td>
</tr>
<tr>
<td>0.5 M LiAsF\textsubscript{6}</td>
<td>95 %</td>
</tr>
</tbody>
</table>

More lithium oxides (Li$_2$O, Li$_2$O$_2$) were formed in O$_2$ atmosphere compared to Ar atmosphere.
Role of oxidized MPT\(^+\) in failure

What happen on the Li metal surface in Li-O\(_2\) batteries?

- Li/Li symmetric cell with MPT in O\(_2\)
  → stable cycle performance

- Reduced form of MPT
  → stable when in contact with lithium oxides-protected Li metal surface in O\(_2\)

- Oxidized form of MPT\(^+\)
  → related to the degradation of Li metal and MPT
The Li/Li cell was degraded as soon as MPT$^+$ was formed
The degradation of the Li/Li cell is attributable to the formation of oxidized MPT$^+$

$\rightarrow$ MPT$^+$ broke the lithium oxide protective layer on Li
Role of MPT\textsuperscript{+} in the degradation of Li metal

1) MPT\textsuperscript{+} decomposes the lithium oxides protection layer on the Li metal

2) MPT is exposed to fresh Li metal, thus being decomposed on the Li metal

3) Thick passivation layer forms on the Li metal surface, resulting in the failure of Li metal
LiNO$_3$ as an MPT$^+$ scavenger
Role of LiNO₃ in Li–O₂ batteries with MPT

Constant capacity: 1000 mA h g⁻¹

- Improved cycle performance when LiNO₃ was used instead of LiSO₃CF₃
- Best for LiNO₃ in DMA
  → stable solvent against oxygen radical
  → stable cycle performance over 120 cycles
The Li/Li cell was stable even after the formation of oxidized MPT+.

\[ \text{NO}_3^- \text{ protected the Li metal against the attack of MPT}^+ \]
The reaction between NO$_3^-$ and Li metal
→ forms soluble NO$_2^-$ and lithium oxides on Li metal

NO$_2^-$
→ A redox couple with a redox potential of ~ 3.6 V vs. Li/Li$^+$

CV of MPT with Li metal (MPT + tetruglyme, Li metal reference)

- At fast scan rate:
  - the reduction peak was observed
  - Redox potential:
    - $\text{NO}_2^-$: ~ 3.6 V
    - MPT: ~ 3.7~3.8 V
- At fast scan rate:
  - the reduction peak disappeared
  - MPT+ was consumed slowly by $\text{NO}_2^-$
  - $\text{NO}_2^- + \text{MPT}^+ \rightarrow \text{NO}_2 + \text{MPT}$
Even at slow scan rate:
\[ \Rightarrow \text{the reduction peak disappeared when } \text{NO}_2^- \text{ from NaNO}_2 \text{ was added} \]
\[ \Rightarrow \text{MPT}^+ \text{ was consumed by } \text{NO}_2^- \]
Proposed mechanism of LiNO₃ for Li–O₂ batteries with MPT

- **Redox potential:**
  - $\text{NO}_2^-$: $\sim 3.6 \text{ V}$
  - MPT: $\sim 3.7-3.8 \text{ V}$

- $\text{NO}_2^- + \text{MPT}^+ \rightarrow \text{NO}_2 + \text{MPT}$

(1) Formation of the protection layer on Li metal and NO₂⁻ scavenger

(2) The reaction between NO₂⁻ and MPT⁺
1) MPT$^+$ decomposes the lithium oxides protection layer on the Li metal
2) MPT is exposed to fresh Li metal, thus being decomposed on the Li metal
3) Thick passivation layer forms on the Li metal surface, resulting in the failure of Li metal
Suggestions for the Li–O$_2$ batteries with redox mediators

To overcome the failure of MPT and Li metal

1) Stable protective layer on Li metal anode against redox mediators

2) Stable redox mediators against Li metal anode
Thanks for your attention