How initial nucleation influences discharge capacities of Li-O$_2$ cells

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Li-O$_2$ battery has high theoretical energy density.

High expectations, ....

A lot of fundamental scientific challenges to be addressed for discharge and charge of Li-O$_2$ battery:

- Solvent stability
- O$_2$ solubility
- Catalysis &/or mediator for Li$_2$O$_2$ oxidation
- Li Anode stability

Various power demands within applications.
Introduction

• General Battery: Various power demands within applications.

• Li-ion Battery shows no history effect.
  - At different sequences of varying (high) C-rate the total capacity can be retained when returned to lower C-rate.

• How is it the case for Li-O$_2$ Battery?
Various power demands within applications.

Li-ion Battery shows no **history effect**.
- At different sequences of varying C-rate the total capacity can be preserve when used at lower C-rate.

How is it the case for Li-O₂ Battery?
Introduction

**Li$_2$O$_2$ Nucleation**  →  **Growth**  →  **sudden death**

Motivation:

The questions raised are:

1. Is there a history effect for Li-O$_2$ battery?

2. How does the initial discharging profile influence the electrochemical behavior?
Experiments

i. Nucleate (pre-discharge) cathode at varying Overpotentials.

ii. Subsequent Discharge at low current density (50 mAh/g).
Experiments

- Fresh
- Pre-discharge (Nucleation)
- Fully discharged

Investigation with electron microscopy & Impedance Spectroscopy.
The Li-O₂ Battery Cell

Cathode: Graphitized Acetylene Black + 20 wt% PVDF (~1 mg, 10um, coated on Celgard)
Electrolyte: 90 uL 0.1M LiClO₄ in DME (1,2 Dimethoxy ethane).

El-Cell GmbH ECC-air setup.
Experiments: Impedance Spectroscopy

100kHz-10mHz, AC 10mV, DC 2.6V (vs Li/Li+).
Experiments: Impedance Spectroscopy

Argon

\[
\begin{align*}
Z_{\text{Re}} / \Omega &\quad Z_{\text{Im}} / \Omega \\
0 &\quad 0 \\
200 &\quad 200 \\
400 &\quad 400 \\
600 &\quad 600 \\
800 &\quad 800 \\
1000 &\quad 1000 \\
1200 &\quad 1200 \\
1400 &\quad 1400
\end{align*}
\]

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\end{align*}
\]

\[
\begin{align*}
\text{Argon}_{-\text{OCV}} \\
\text{Argon}_{-2600\text{mV}}
\end{align*}
\]

\[
\begin{align*}
\text{O}_2_{-\text{OCV}} \\
\text{O}_2_{-2600\text{mV}}
\end{align*}
\]

O₂
The 2nd semicircle correspond to the formation of Li$_2$O$_2$. 
Results: History effect in Li-O$_2$ cathode (i)

- **Graph 1**: Time vs. $E$ (vs Li/Li$^+$) / V
  - i. constant voltage discharge to 400 mAh/g
  - ii. constant current 50 mA/g

- **Graph 2**: Discharge capacity vs. voltage
  - Initial discharge
  - Discharge at various voltages: 1.7 V, 1.9 V, 2.1 V, 2.3 V, 2.6 V

"nucleation"
Results: History effect in Li-O_2 cathode (i)

Slow initial growth

Fast initial growth
Extended discharge of cathode at low & high Overpotentials

\[ E_{\text{eq}} = \sim 2.85 \text{ V} \]

\[ E_{\text{app}} \]

2000 mAh/g_c

\sim 40 \text{ monolayers of Li}_2\text{O}_2

Capacity / mAh/g_c
Extended discharge of cathode at different Overpotentials

XRD measurements show that the deposits in both cases (the film & flakes) are Li₂O₂.

- Different morphology of Li₂O₂ deposited at different Overpotentials.
- The history effect is therefore dependent on the nucleation step.

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Results: Impedance Spectroscopy measurements

\[ E_{\text{Eeq}} = \sim 2.85 \text{ V} \]

\[ E_{\text{EIS}} = 2.6 \text{ V} \]

\[ E_{\text{app}} \]
Results: Impedance Spectroscopy measurements

![Graph showing impedance spectroscopy results with discharge capacity in mAh/g_c on the x-axis and R_{ct} in ohm.m^2 on the y-axis.]

- Fresh
- 1.7 V
- 1.9 V
- 2.6 V

![Graph showing capacitance C_{dl} in F/g_c on the x-axis and discharge capacity in mAh/g_c on the y-axis.]

- Fresh
- 1.7 V
- 1.9 V
- 2.6 V
Results: Impedance Spectroscopy measurements

- $R_{ct}$ / ohm.m^2
- $C_{dl}$ / F/g_c

Discharge Capacity / mAh/g_c

Fresh

1.7 V

1.9 V

2.6 V

E (vs. Li/Li^+) / V

Initial discharge
at 1.7 V
1.9 V
2.1 V
None
2.3 V

Discharge capacity / (mAh/g)
Results: History effect in Li-O$_2$ cathode (ii)

Fresh Carbon vs low $\eta_{dis}$ Li$_2$O$_2$-coated Carbon

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Results: History effect in Li-O$_2$ cathode (ii)

1.7 V on fresh carbon

1.7 V on Li$_2$O$_2$ (2.6 V)

Discharge Capacity / mAh/g$_c$

$R_{ct}$ / ohm.m$^2$

$C_{dl}$ / F/g$_c$

Impedance Spec (Rct, Cdl)

Fresh Carbon

VS

“seed”

2.6 V

1.7 V

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Results: History effect in Li-O₂ cathode (iii)

- With Li₂O₂ seed layer deposited at low Overpotential: higher capacity in the subsequent step.
- For fast discharge, pre-conditioning of the cathode is necessary.

<table>
<thead>
<tr>
<th>Step</th>
<th>1st step (mAh/g)</th>
<th>2nd step (mAh/g)</th>
<th>3rd step (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 (fresh carbon)</td>
<td>400</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td>400 (8 monolayer)</td>
<td>400</td>
<td>1100</td>
<td></td>
</tr>
</tbody>
</table>
Proposed mechanism:

\[ \text{Li}^{+} + e^- + O_2 + * \rightleftharpoons \text{LiO}_2^*, \quad \text{Li}^{+} + e^- \quad \text{on Carbon surface} \]

\[ \text{Li}^{+} + e^- + \text{LiO}_2^* \rightleftharpoons \text{Li}_2\text{O}_2^*, \quad \text{Li}^{+} + e^- \quad \text{on Li}_2\text{O}_2 \text{ surface} \]

- Kinetic Overpotential + Crystallization overpotential
- Kinetic Overpotential = Charge transfer at different available sites.
- Kinks and steps have the lowest \( \eta_{dis} \)
1. Li-O₂ Battery shows a history effect.

2. The “nucleation” at different overpotential resulted in different Li₂O₂ morphology.

3. The “nucleation” (initial Li₂O₂ deposits) on carbon alter the electrochemical performance of the cathode.

4. Higher impedance of the cathode at higher Overpotential.

5. Initial Li₂O₂ from high overpotential, impede the subsequent discharge.

6. Initial Li₂O₂ from low overpotential “stabilizes” the subsequent (high overpotential) discharge.
Thank you