Lithium-Air Batteries

P.I.: Khalil Amine

Larry Curtiss, Jun Lu

Argonne National Laboratory

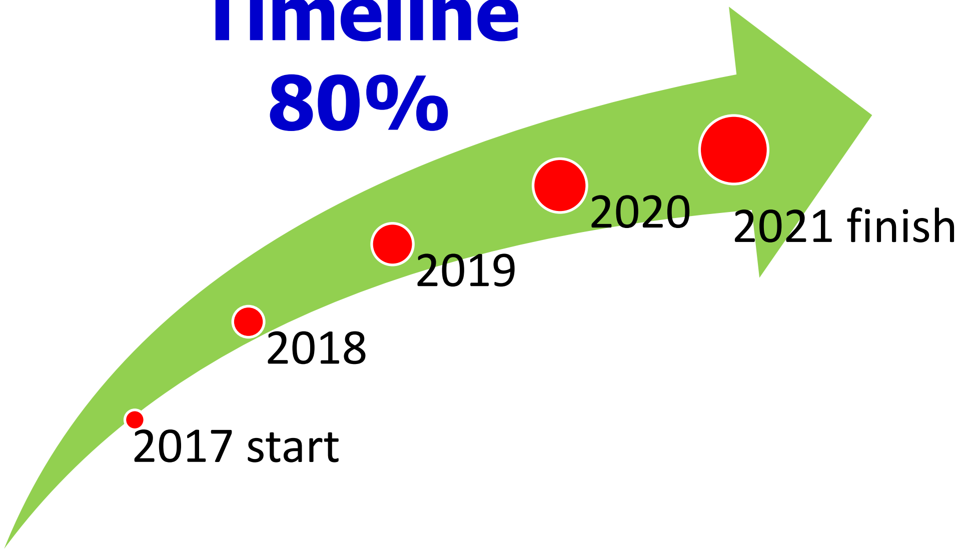
DOE merit review

June 25 , 2021

Project ID# ES-066

Overview

Timeline
80%



Barriers

- ❑ Barriers addressed
  - Unstable electrolytes
  - Electro-catalyst poisoning
  - Reversibility of the reaction

Budget

- ❑ Total project funding
  - DOE share: 1440
  - Contractor 0
- FY 17: $ 500 K
- FY 18: $ 500 K
- FY 19: $ 440 K

Partners

- ❑ Interactions/ collaborations
  - C. Liu, ANL
  - R. Shahbazian-Yassa, UIC
  - F. Wu, BIT

Project Objectives and Relevance

1. Developing new cathode materials and electrolytes for lithium oxygen ($Li-O_2$) batteries with high energy efficiency and long cycle life.

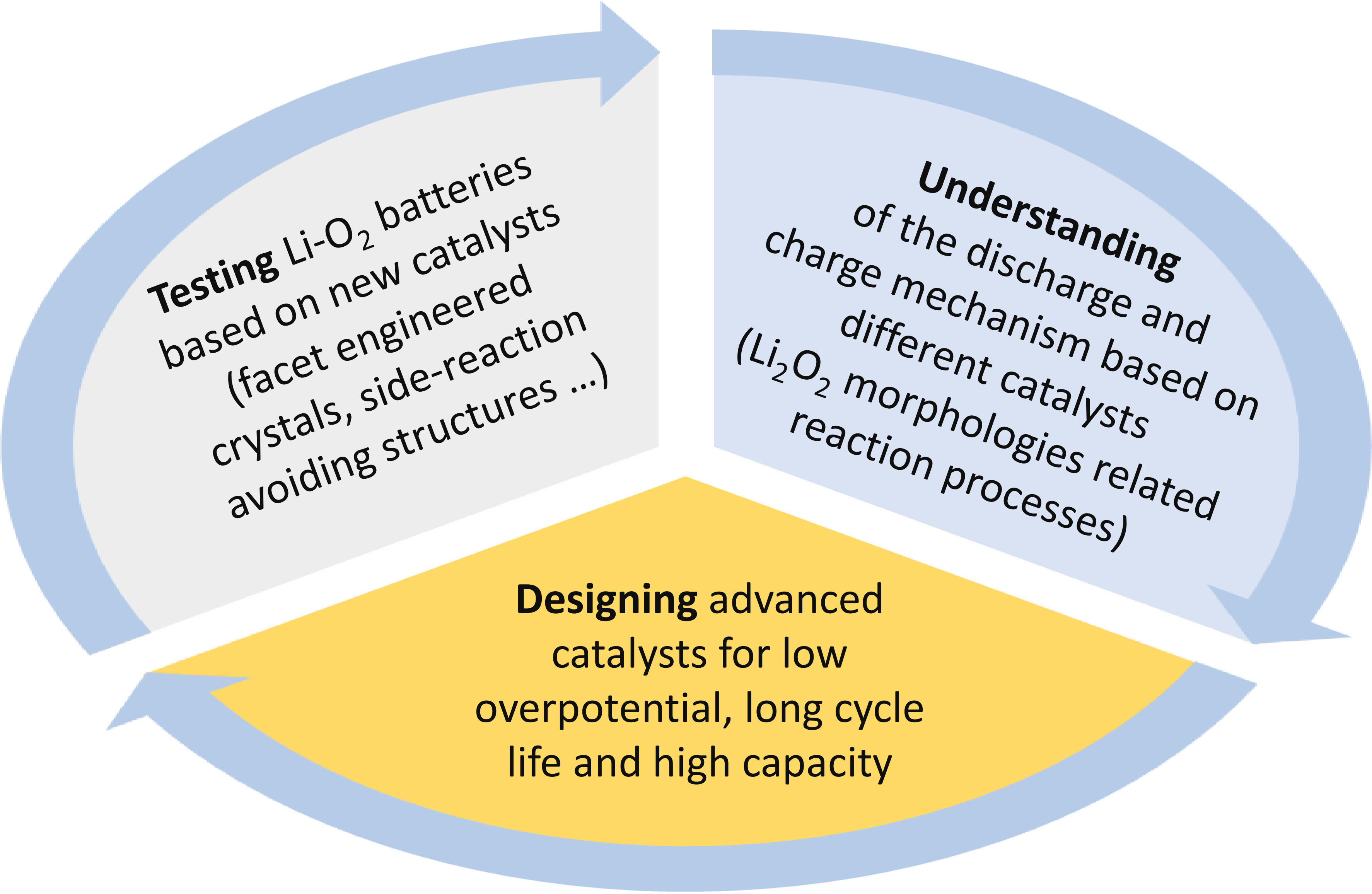
2. Obtaining critical insights into the electrochemical processes in $Li-O_2$ batteries via in-situ/ex-situ methods.

3. Using an integrated approach based on experimental synthesis and state-of-the-art characterization combined with high level computational studies focused on materials design and understanding.

Milestones

Month/ Year	Milestones
Jun/20	Design functionalized cathodes to achieve high electrochemical performance of Li-O2 batteries. (**Completed**)
Sep/20	Characterizing the cathode materials and investigating the electrochemical behaviors. (**Completed**).
Dec/21	Understanding the processes of ORR and OER of these materials and reveal the possible parasitic reactions. (**Completed**)
Mar/21	By understanding the effects, engineering new catalysts with improved catalytic performance and suppressed side reactions. (**Initiated**)

Strategies



An integrated experiment/theory approach that combines testing, understanding and designing to develop advanced catalysts for Li-O_2 batteries

Technical Accomplishments

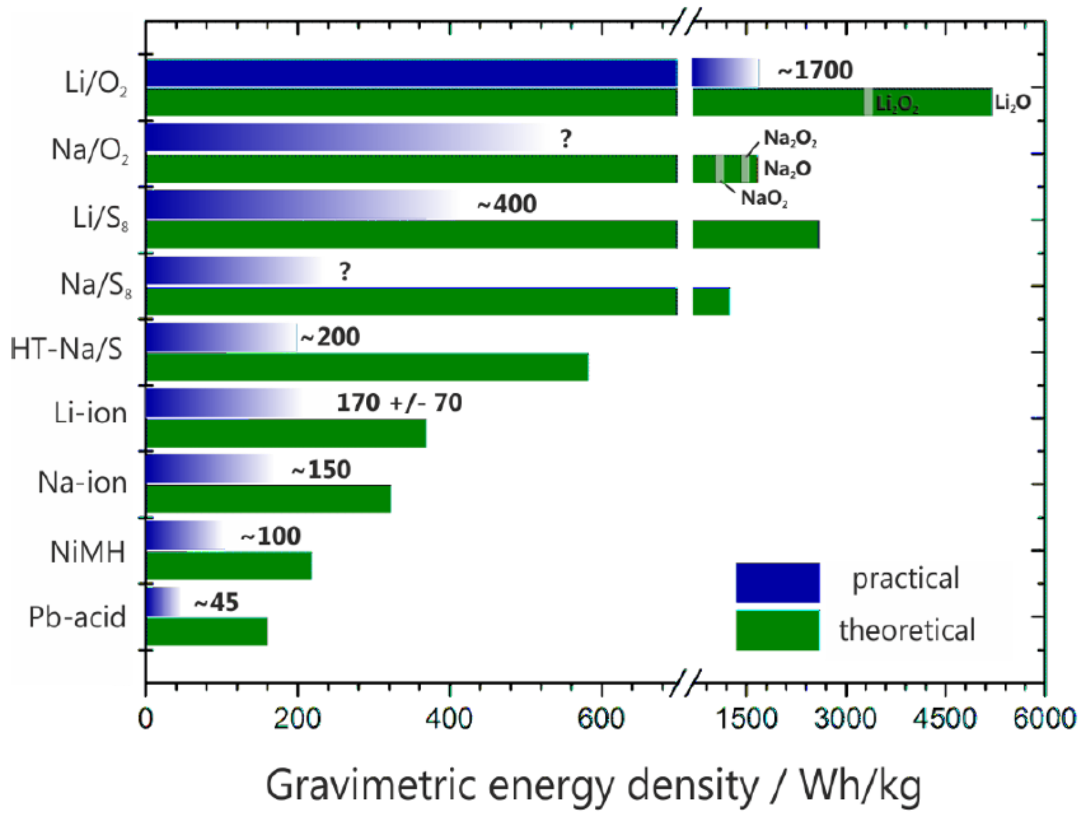
1. Achieved a rechargeable LiOH-based Li-O_2 battery by using a cation electrolyte additive

- Cation additive Na^+ was used, and LiOH-based rechargeable Li-O2 battery with low overpotential and long cycle life was achieved

2. Synergistically enhanced the electrochemical performance by combining optimized porous carbon cathodes and anion electrolyte additives

- Porous carbon materials with optimized pore structure were fabricated via a universal method, and increased capacity and long cycle life were achieved for Li-O_2 battery.
- Combing optimized porous carbon and anion additives, the electrochemical performance was further enhanced due to the synergistic effect.

Background: *lithium oxygen batteries*



$2Li + O_2 \leftrightarrow Li_2O_2$ $E^0 = 2.96$ V (vs. Li^+/Li)

Theoretical Specific Energy Density:

3500 $Wh{\cdot}kg^{-1}$ based on the mass of Li_2O_2

J. Phys. Chem. Lett. 2010, 1, 2193

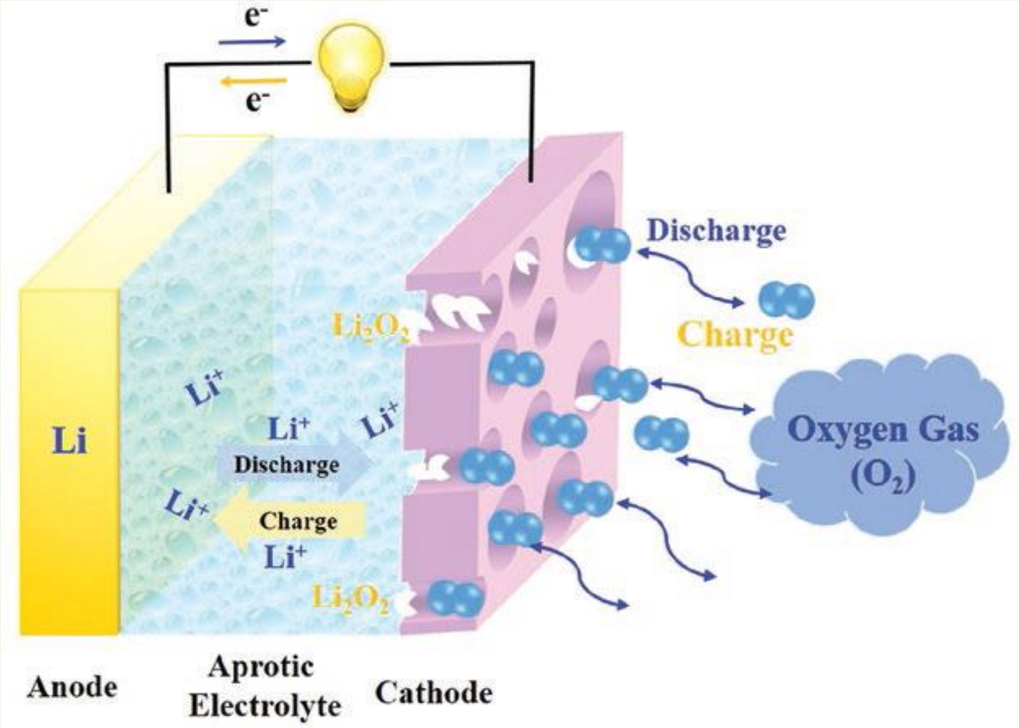
Typical Materials in Aprotic Li-O_2 Batteries:

Anode --- Lithium Metal

Cathode --- Porous Carbon

Separator --- Glass Fiber Paper

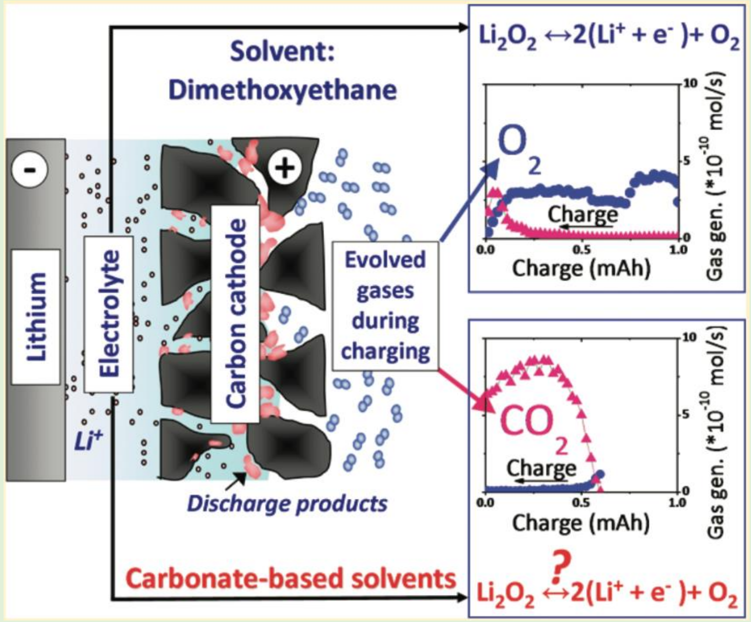
Electrolyte --- Ether-based Solvent



Adv. Energy Mater. 2016, 1502303.

Background: *lithium oxygen batteries*

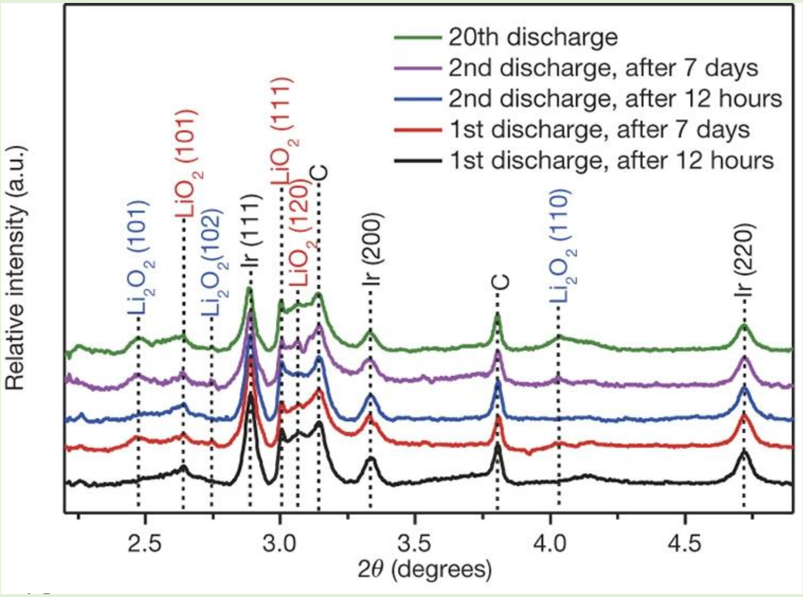
With carbonate electrolyte



Discharge product:
Li_2CO_3

J. Phys. Chem. Lett. 2011, 2, 1161

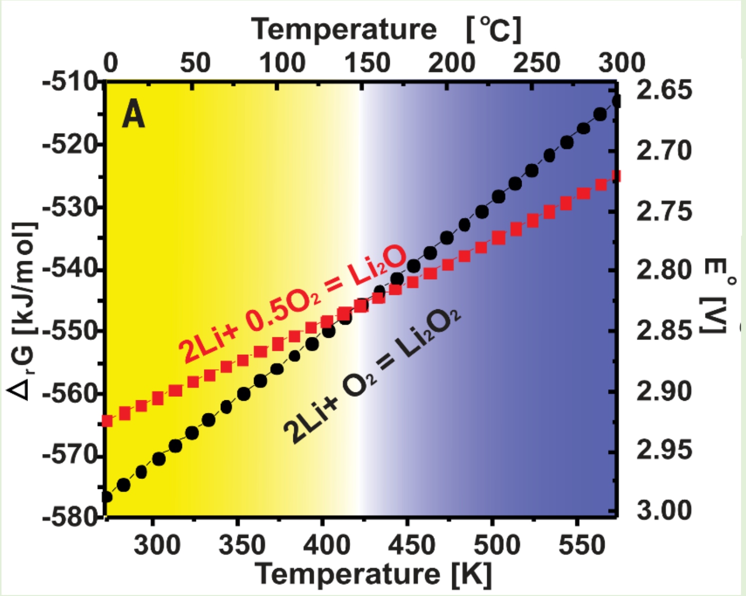
With Ir/rGO electro-catalyst



$Li + O_2 \leftrightarrow LiO_2$

Nature 2016, 529, 377

At higher temperature

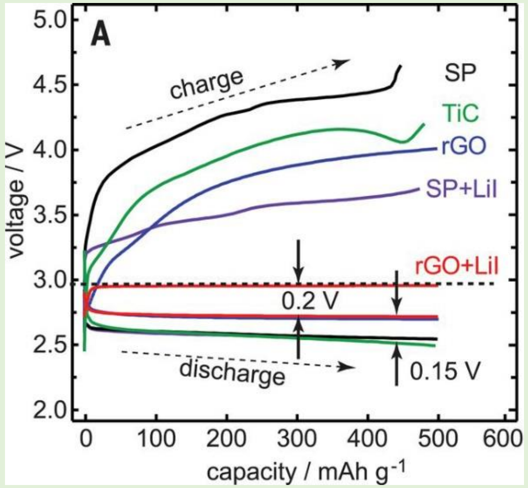


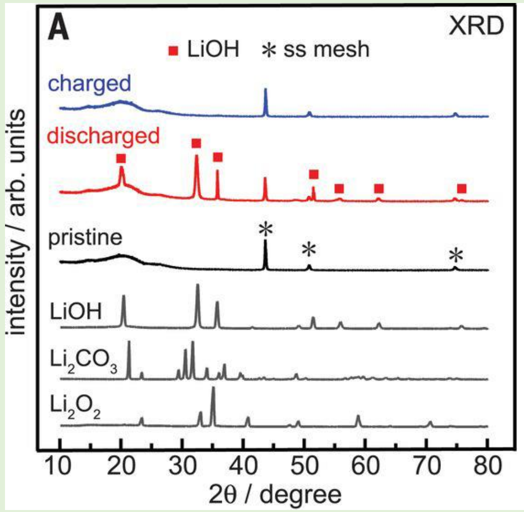
$4Li + O_2 \leftrightarrow 2Li_2O$

Science 2018, 361, 777

Background: *lithium oxygen batteries*

With LiI & H_2O

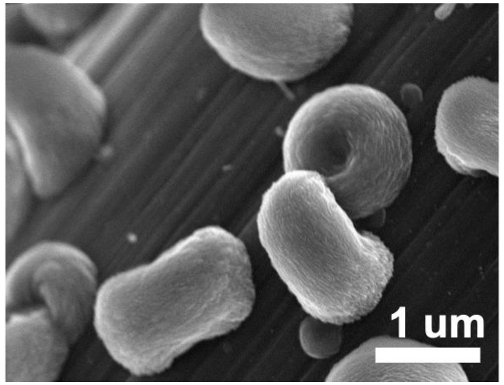


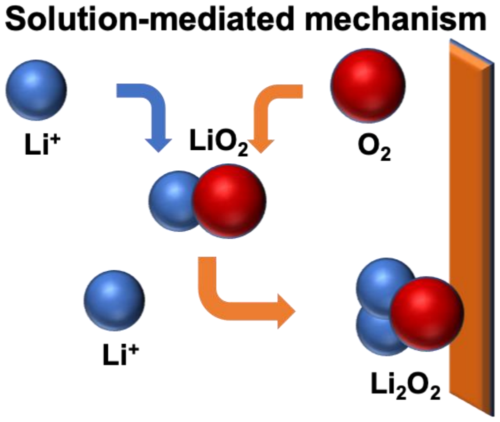


$4Li + 2H_2O + O_2 \rightarrow 4LiOH$

Science 2015, 350, 530

Electrolyte additives change reaction pathway





Discharge: $2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$

1st step: $O_2 + e^- \leftrightarrow O_2^-$

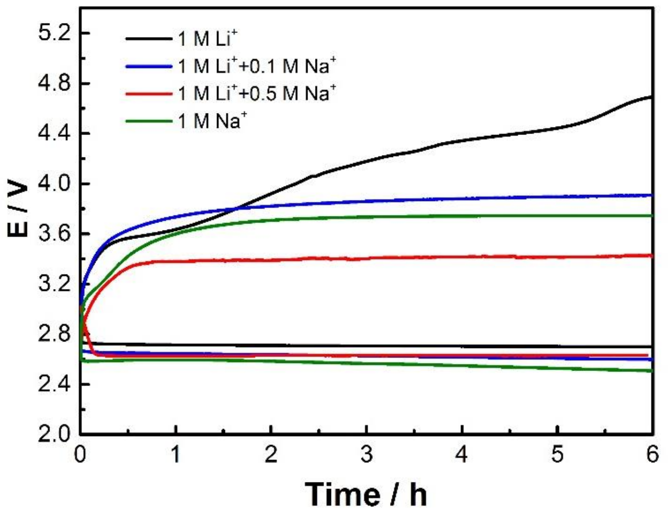
2nd step: $Li^+ + O_2^- \leftrightarrow LiO_2$

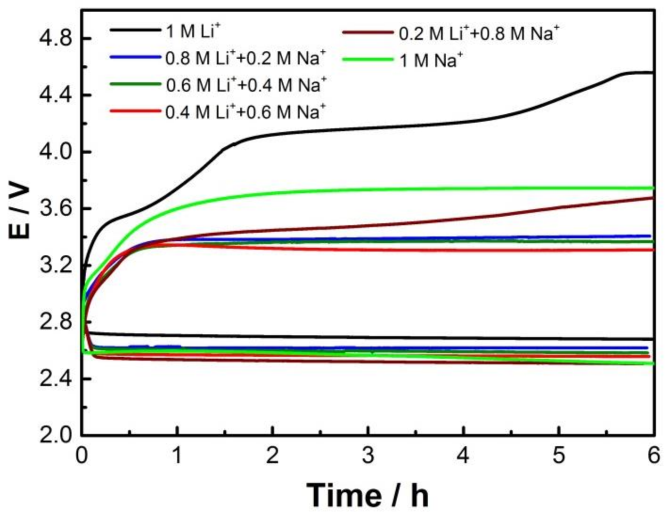
3rd step: $LiO_2 + Li^+ + e^- \leftrightarrow Li_2O_2$

Anion: I^-

Cation: Na^+ (same valance state)

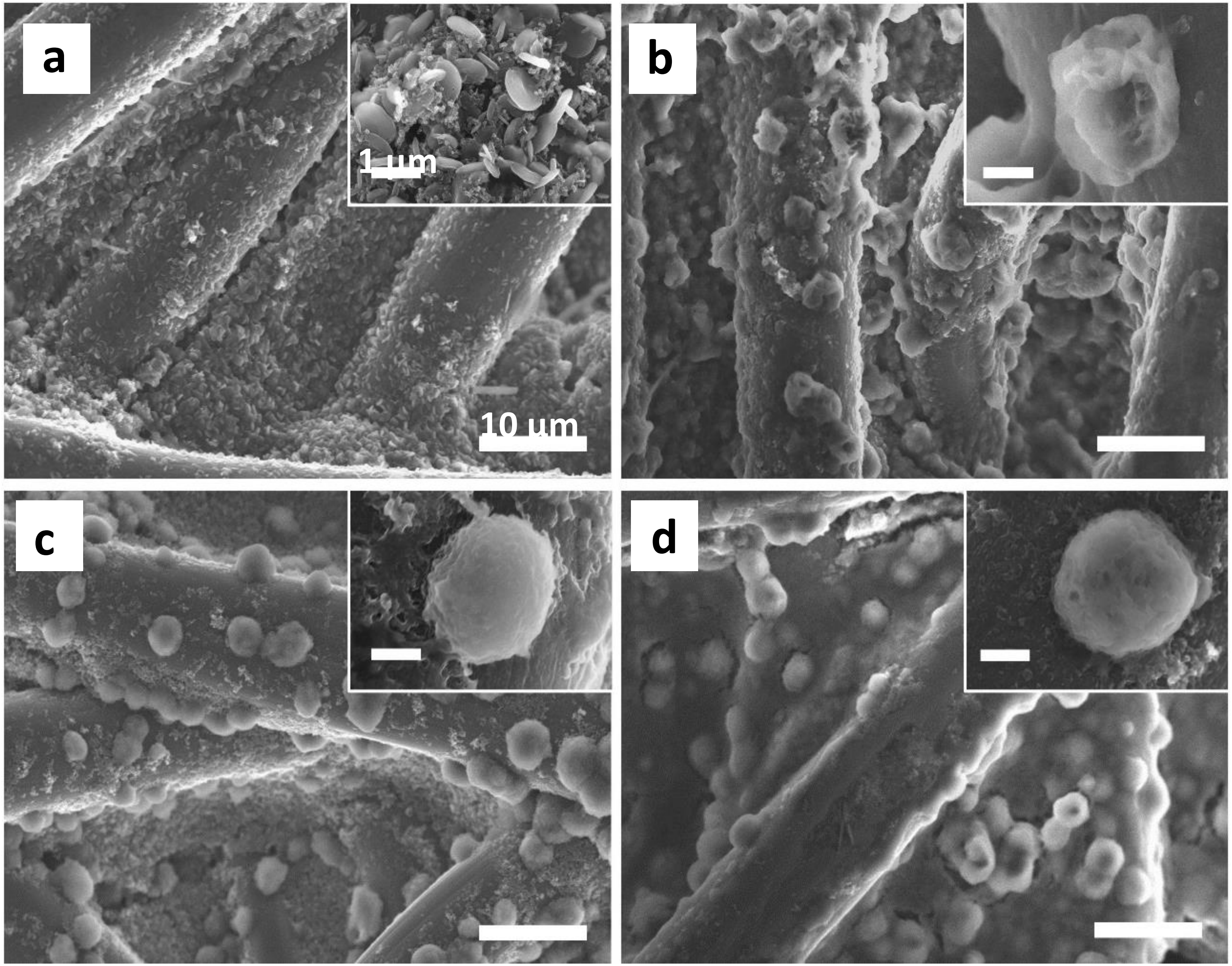
With Na^+





Angew. Chem. 2020, 59, 22801

Cation additive: *Characterization*



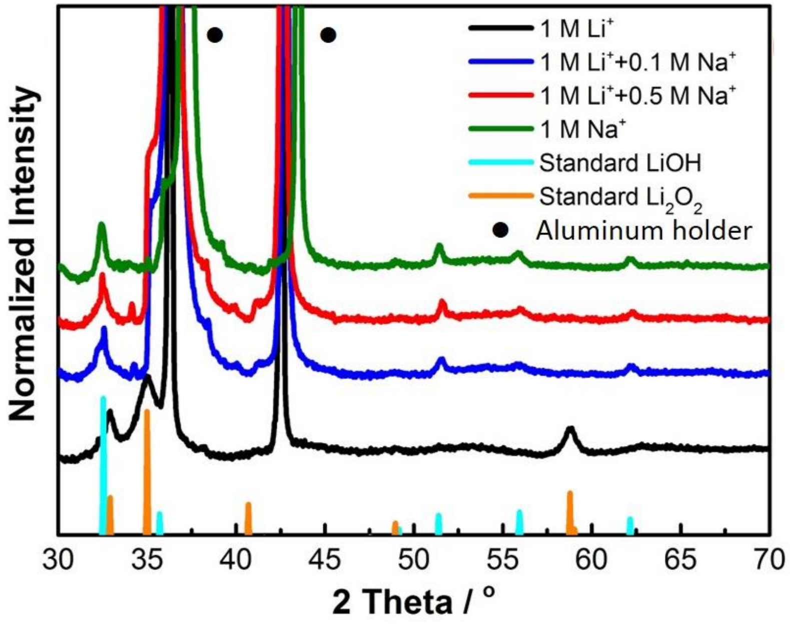
SEM of discharged air electrodes in:

(a) 1 M Li^+

(b) 1 M Li^+ + 0.1 M Na^+

(c) 1 M Li^+ + 0.5 M Na^+

(d) 1 M Na^+

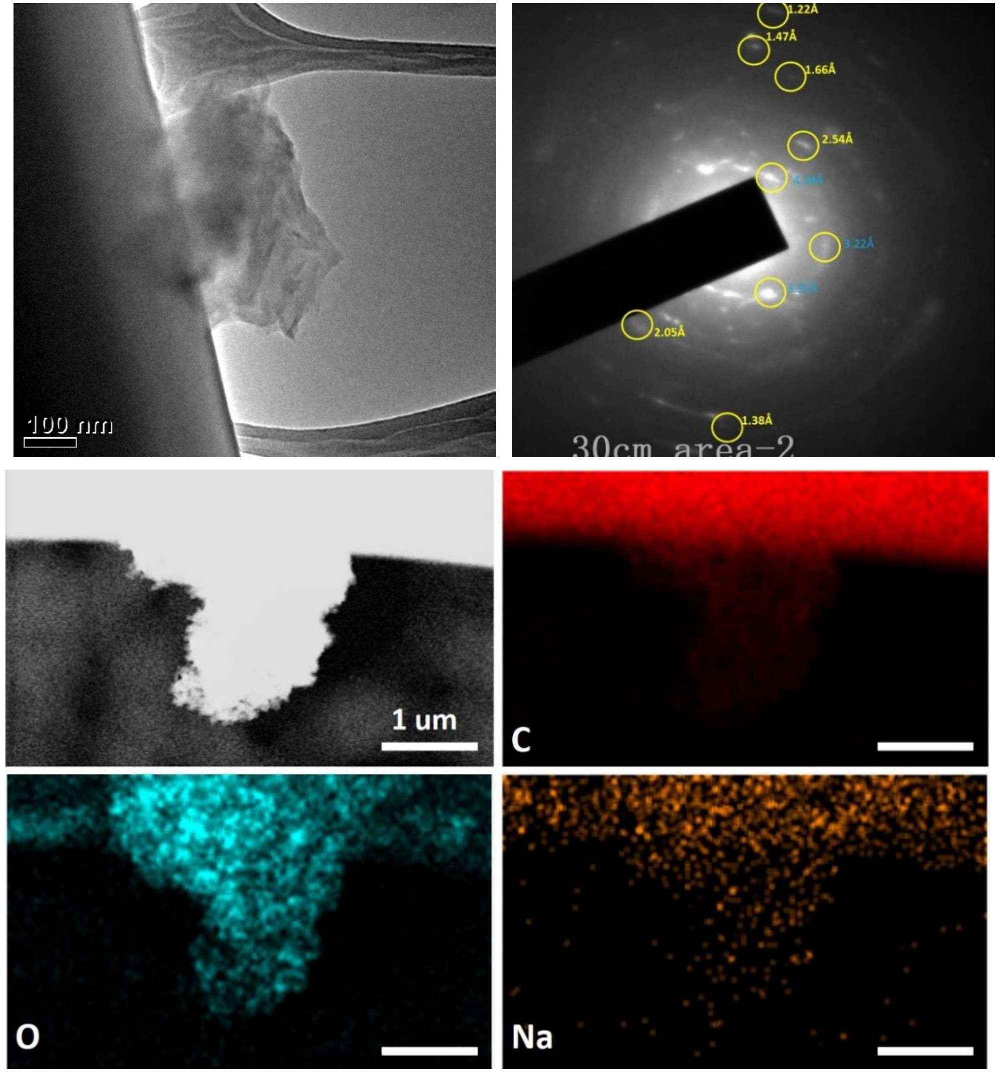


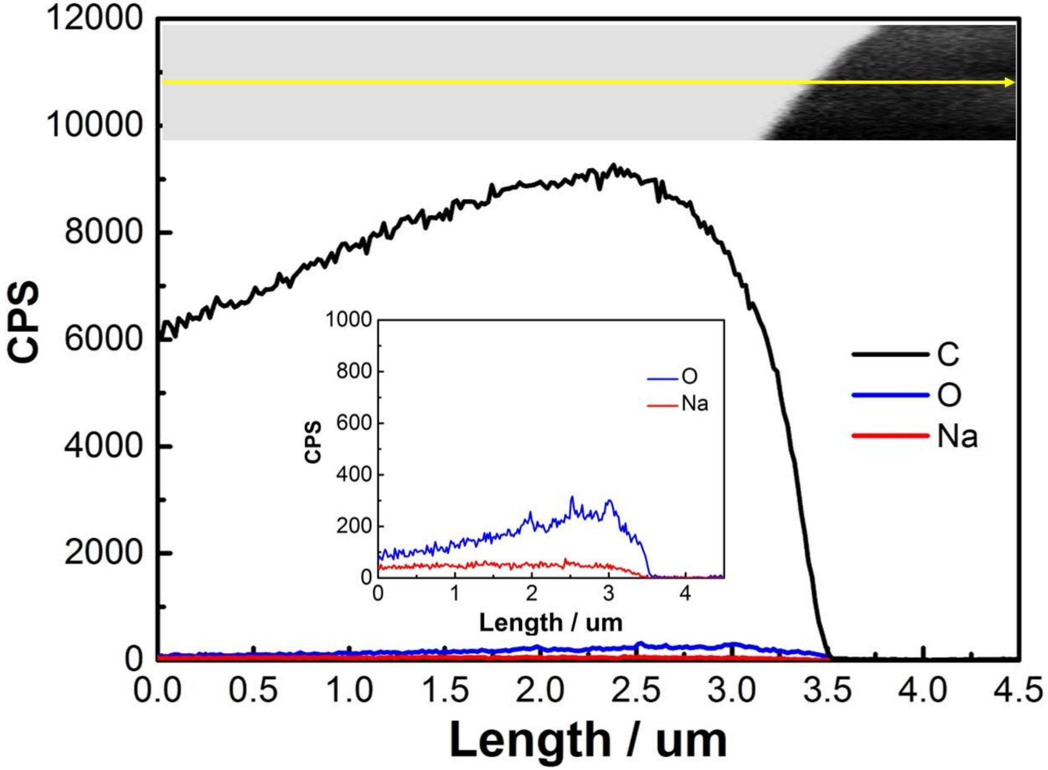
The results confirm that LiOH is the main discharge product.

Angew. Chem. 2020, 59, 22801

Cation additive: *Na^+*

TEM and SAED of the discharge product in 1 M Li^+ + 0.5 M Na^+





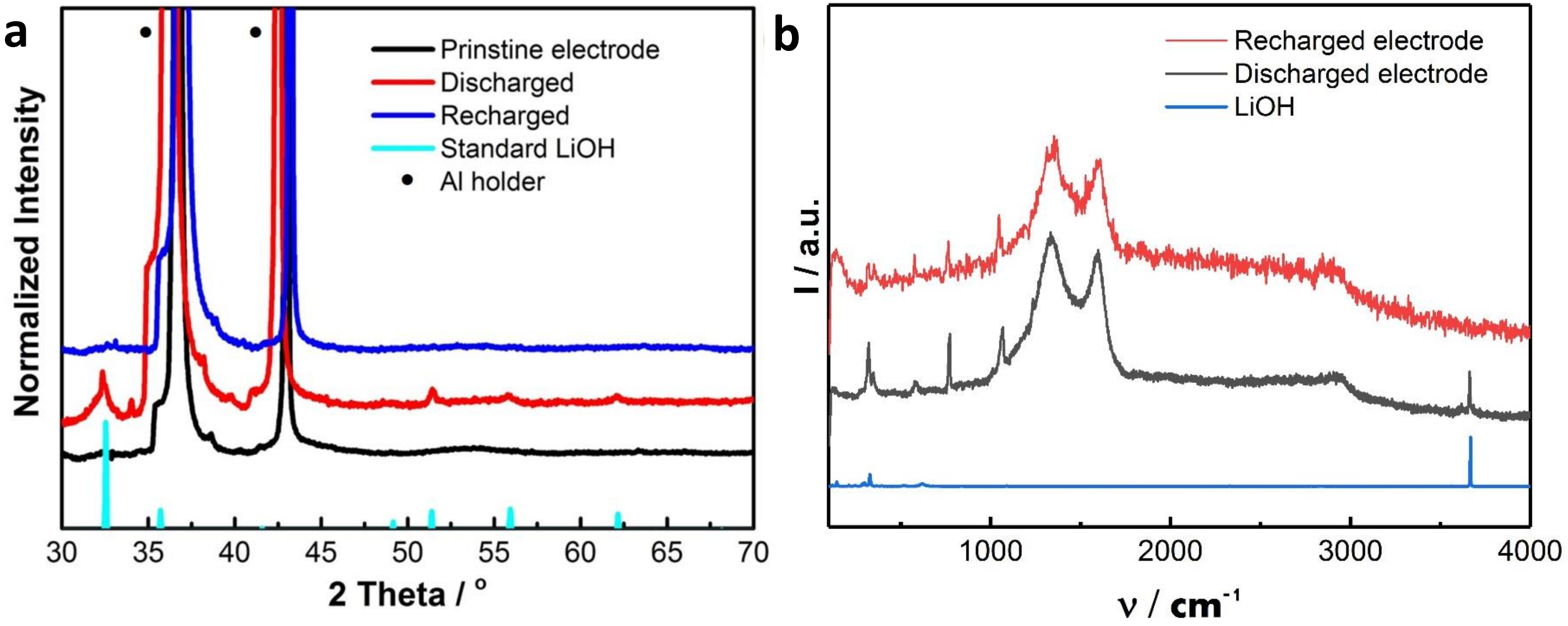
Element	Content
C	97.0%
O	2.9%
Na	0.1%

The results further confirm that LiOH is the main discharge product.

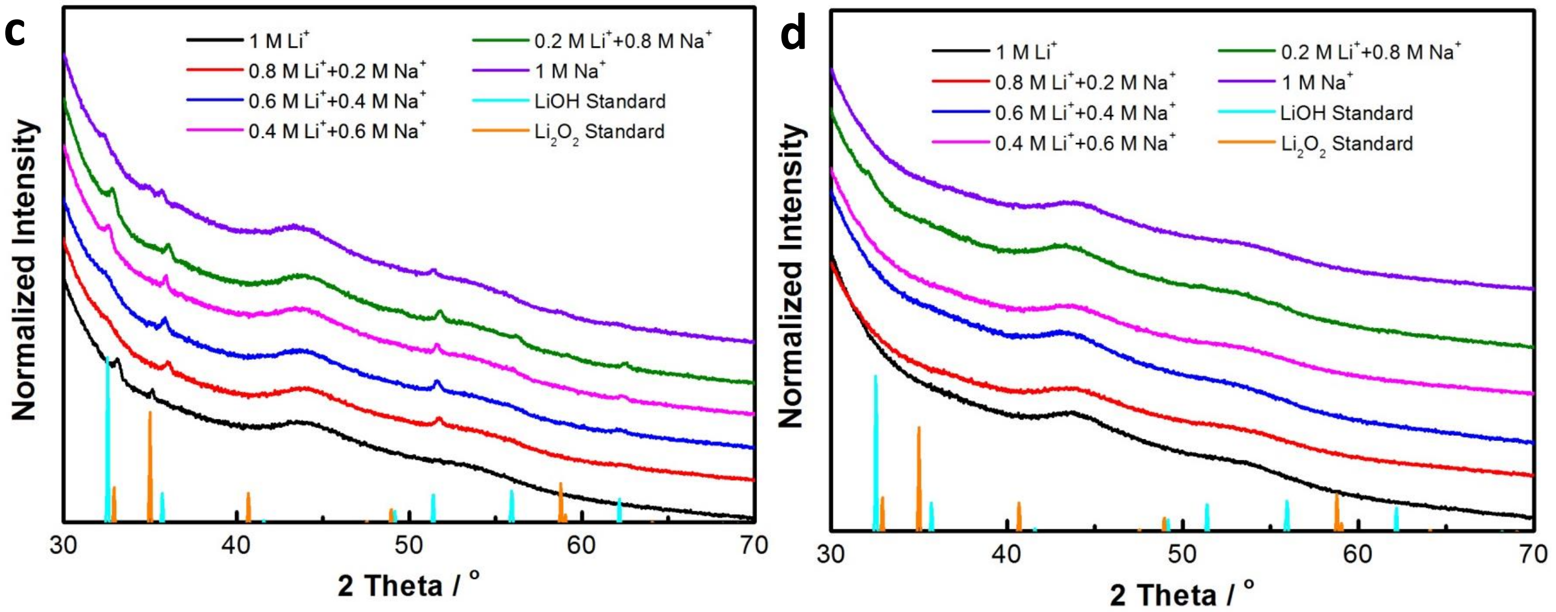
Angew. Chem. 2020, 59, 22801

Cation additive: *LiOH is reversible*

(a) XRD and (b) Raman of discharged and recharged air electrodes in 1 M Li^+ + 0.5 M Na^+.



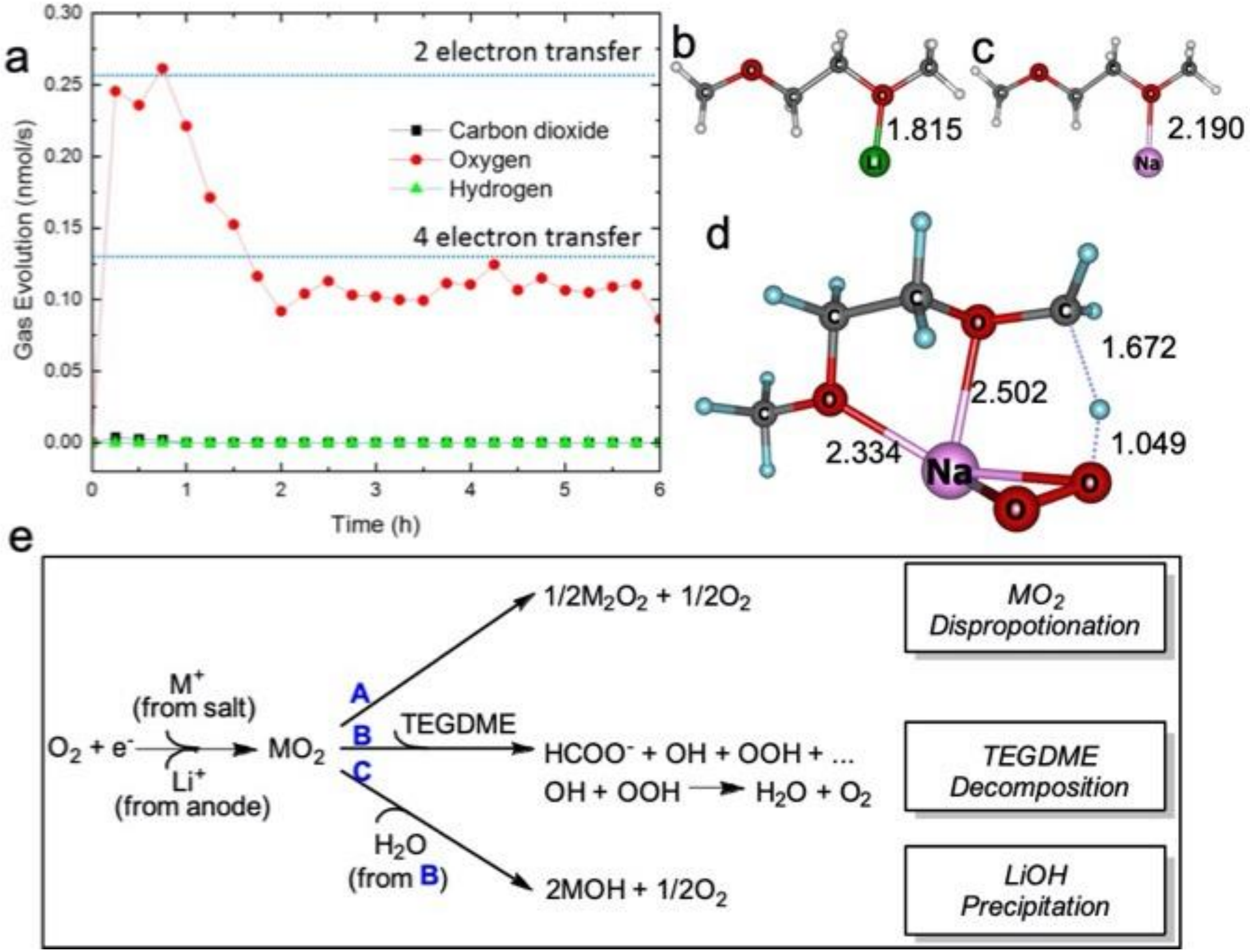
XRD of the (c) discharged air electrodes , and (d) recharged electrodes



Angew. Chem. 2020, 59, 22801

Cation additive: *Reaction pathway*

$4Li + 2H_2O + O_2 \leftrightarrow 4LiOH$



$Li^+ + NaOH \rightarrow LiOH + Na^+$, $\Delta H_{298K, sol} = -0.59$ eV

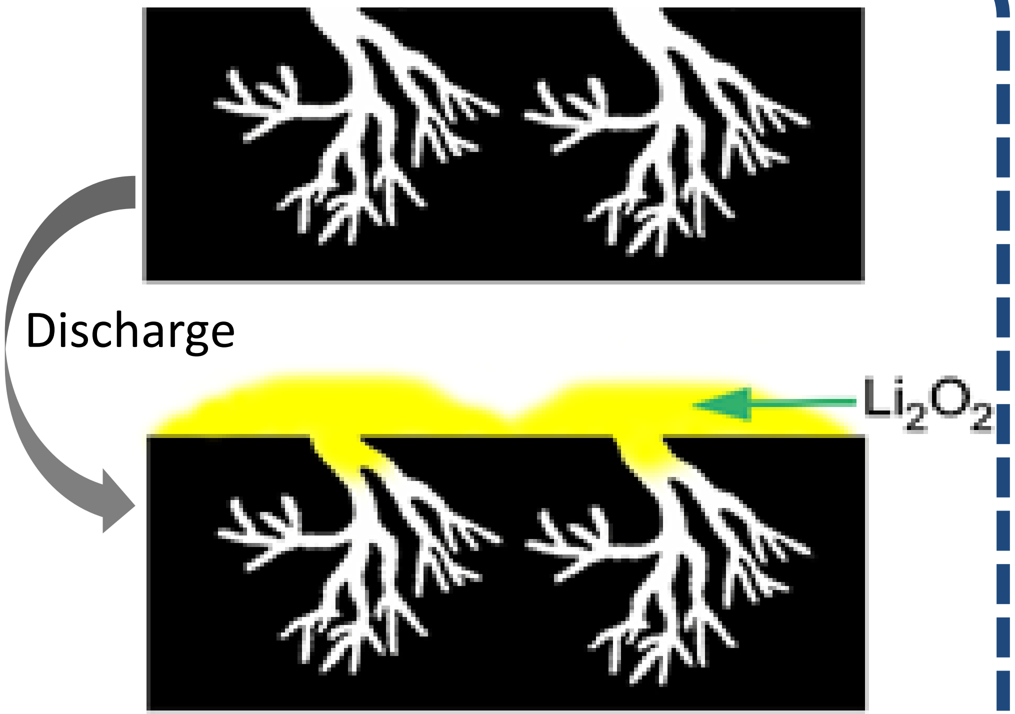
The formation of LiOH is thermodynamically favorable.

- LiOH is the discharge product in the addition of Na^+ to the electrolyte.
- LiOH is reversibly charged at a low voltage, leading to a high energy efficient $Li\text{-}O_2$ battery.
- The mechanism is proposed through the function of NaO_2, which reacts with H_2O to form the hydroxide.

Angew. Chem. 2020, 59, 22801

Porous carbon cathodes: *why and how to optimize the pore structure?*

Motivation

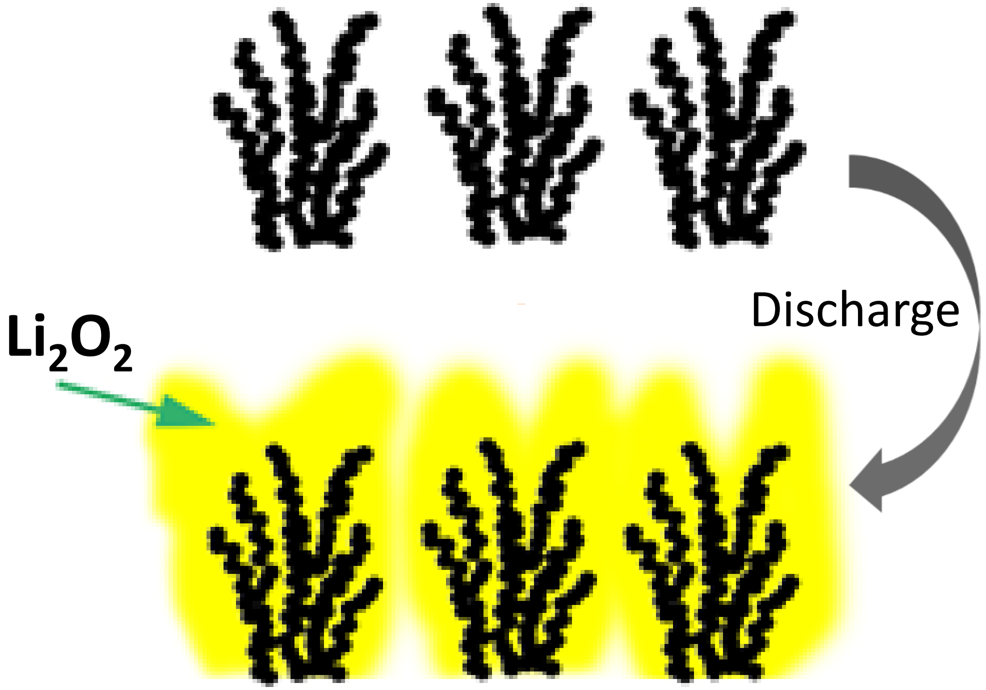


Conventional porous carbon cathodes with concave cylindrical pores:

easily blocked by discharge products, resulting in **degraded reaction kinetics** and **shortened cycle life**

VS

Strategy



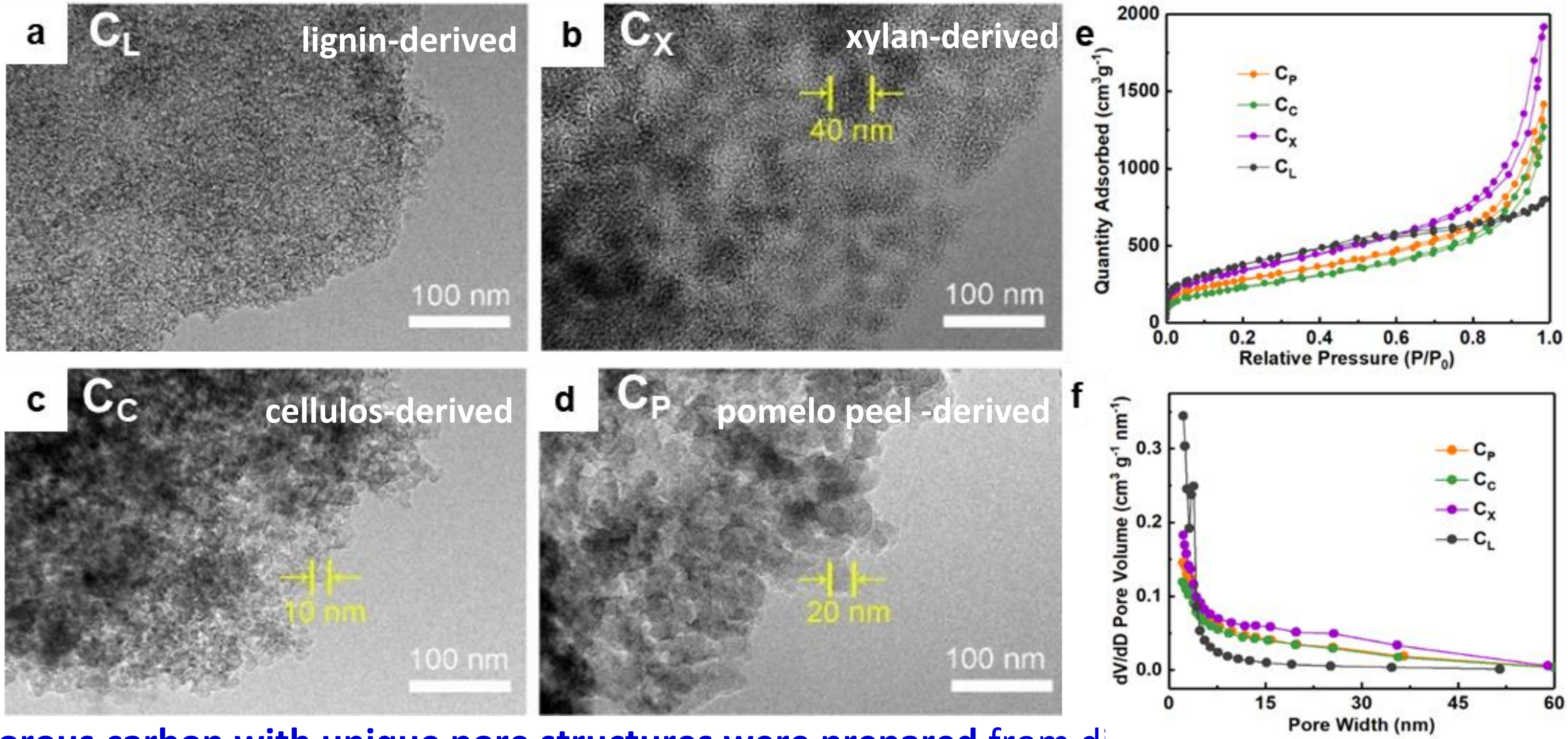
Optimized porous carbon cathodes with open slit-shaped pores:

fully exposed sites and **enhanced mass transport**, resulting in **fast reaction kinetics** and **ultra-high capacity**

Nano Energy 2021, 82, 105782

Porous carbon cathodes: *universal fabrication*

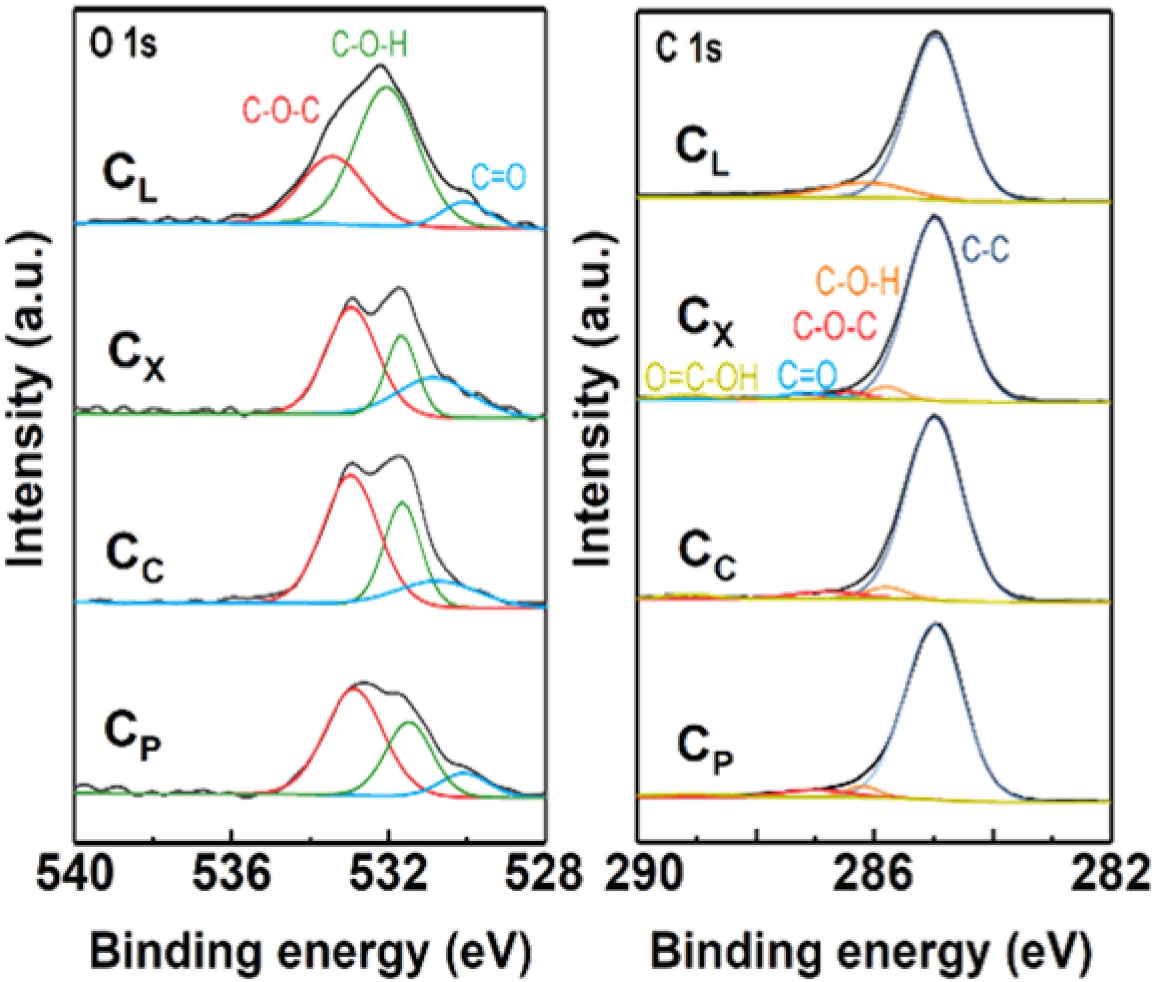
Mechanism for the porous structure formation: $2H_4P_2O_7+5C=5CO_{2\,(g)}+4H_2O_{\,(g)}+P_4$

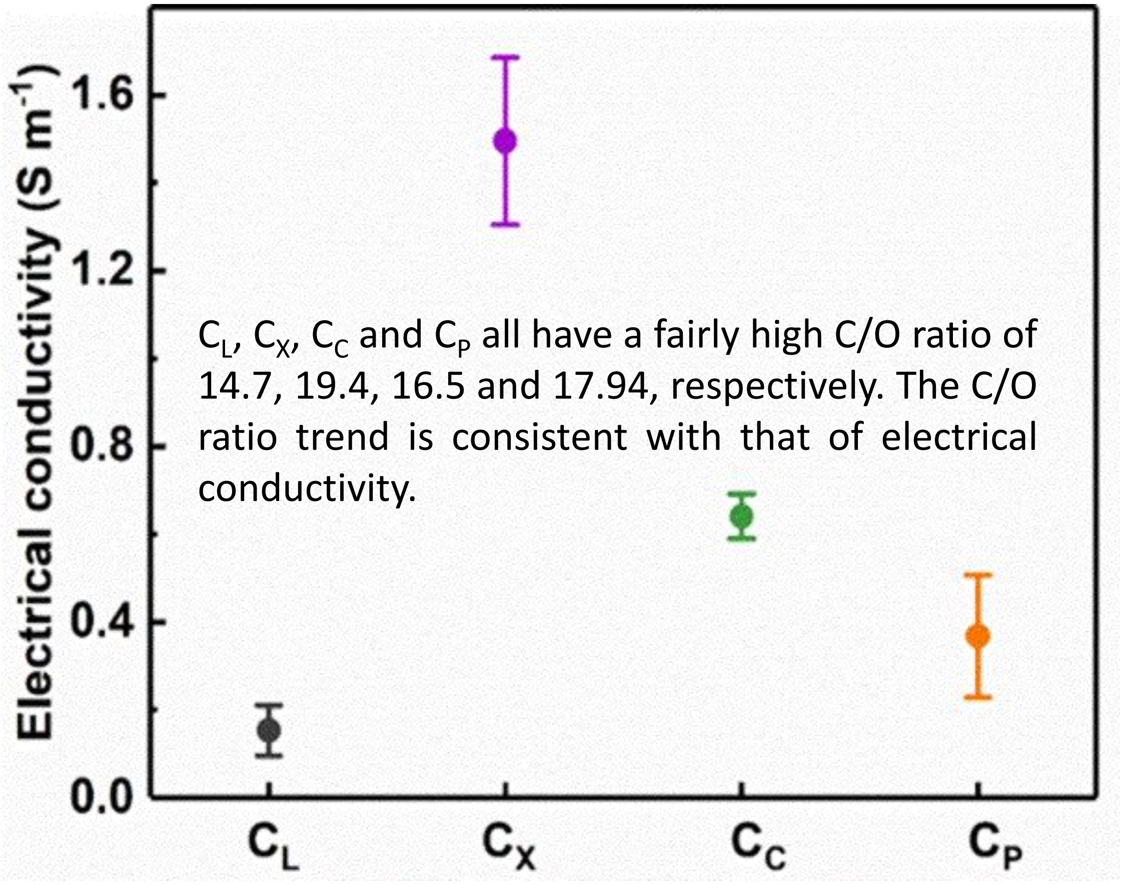


- **Porous carbon with unique pore structures were prepared** from different raw materials
- **C_L** shows **concave cylindrical pores**, while **C_X, C_C and C_P** possess **open slit-shaped pores**

Nano Energy 2021, 82, 105782

Porous carbon cathodes: ***surface structure related properties***



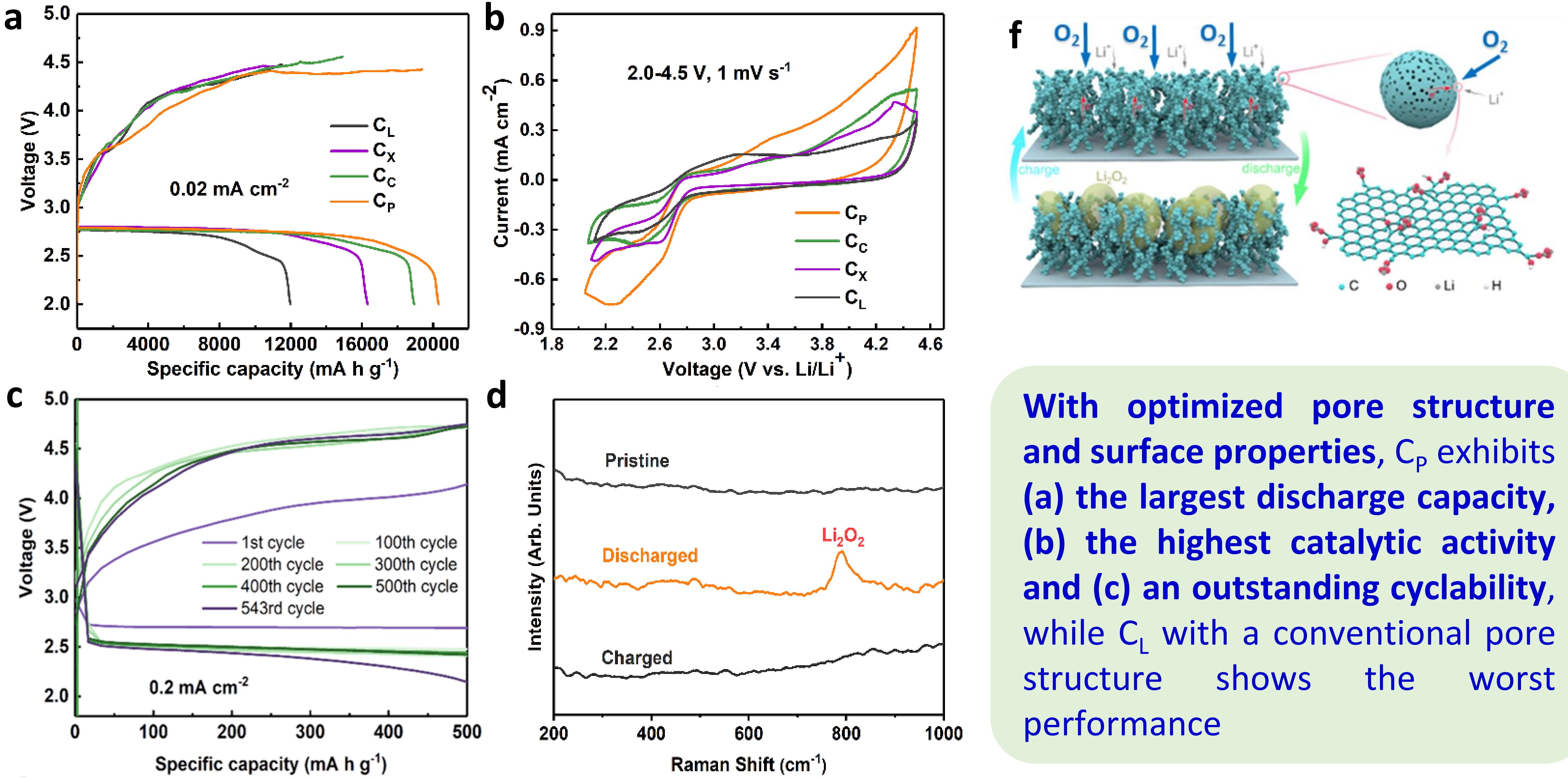


C_L, C_X, C_C and C_P all have a fairly high C/O ratio of 14.7, 19.4, 16.5 and 17.94, respectively. The C/O ratio trend is consistent with that of electrical conductivity.

- All samples have a **fairly low concentration of oxygen-containing groups and defect structures**: (1) the **side reactions** associated with carbon decomposition **can be minimized**, and (2) the **reaction kinetics** can be **enhanced** due to the **good conductivity**.

Nano Energy 2021, 82, 105782

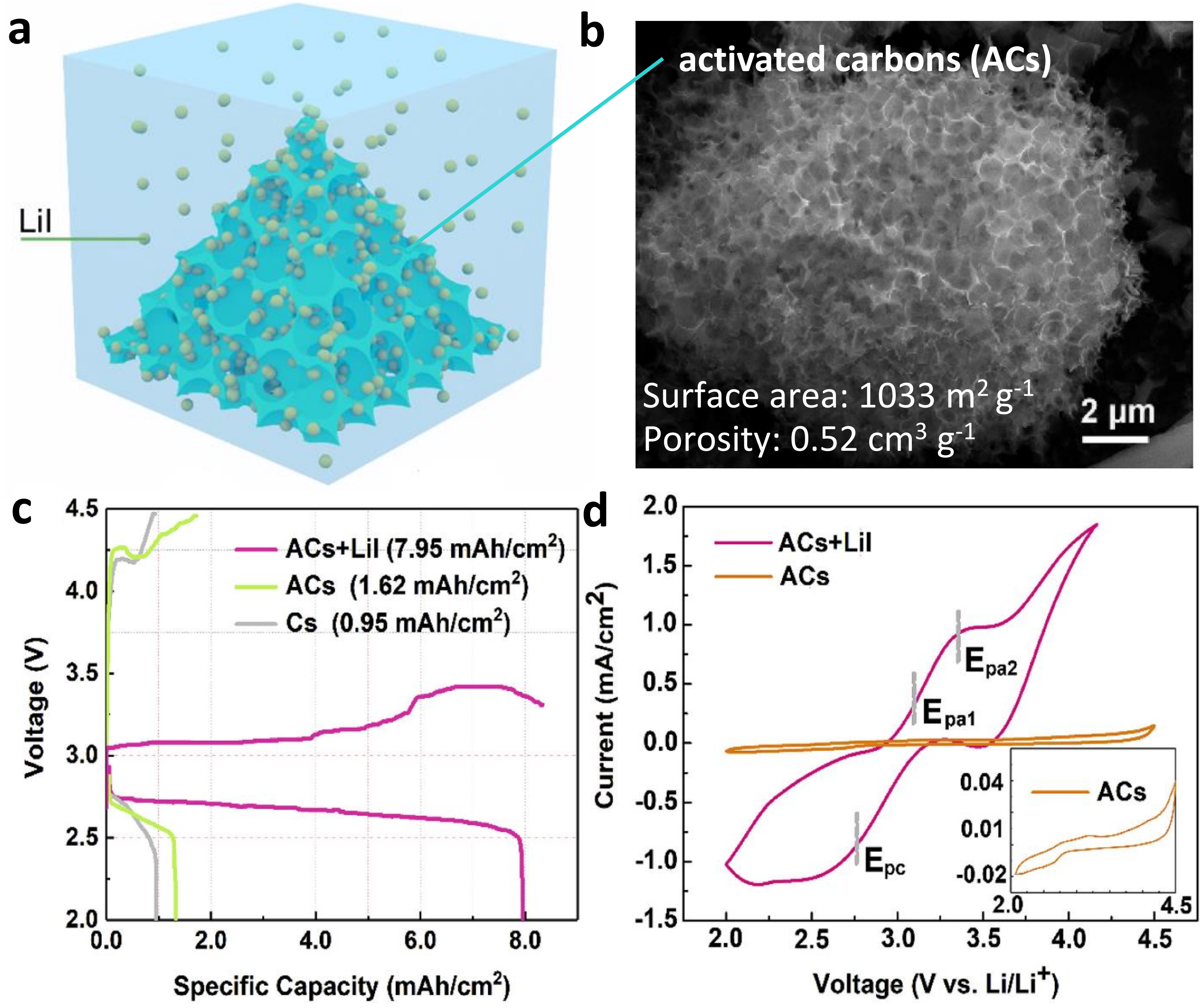
Porous carbon cathodes: *increased capacity and reduced overpotential*



With optimized pore structure and surface properties, C_P exhibits **(a) the largest discharge capacity, (b) the highest catalytic activity and (c) an outstanding cyclability**, while C_L with a conventional pore structure shows the worst performance

Nano Energy 2021, 82, 105782

The synergy of anion additive and optimized carbon: *design motivation*



Energy Storage Mater. 2020, *28*, 73

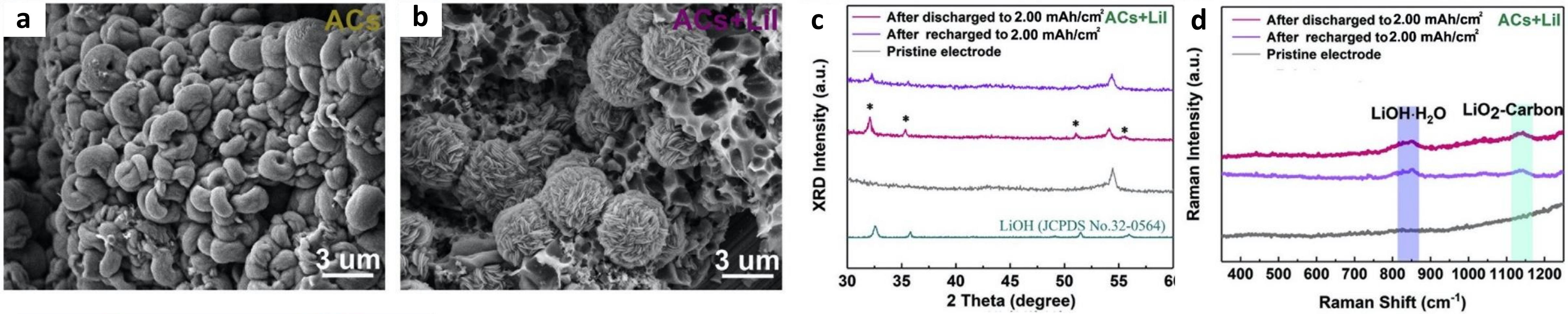
Motivation:

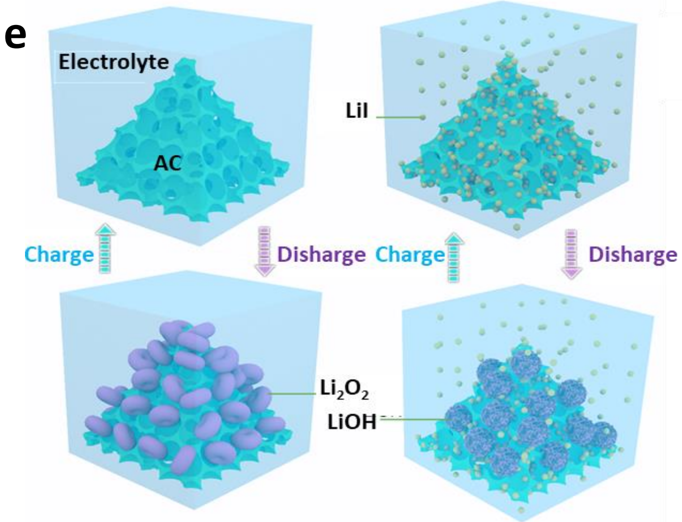
To further enhance the battery performance by taking advantage of electrolyte additive and optimized cathode

Methods and Results:

- ACs with high specific surface area and optimized porosity are combined with LiI in the Li-O_2 system.
- The Li-O_2 battery with ACs and LiI delivers a high areal discharge capacity of 7.95 mAh cm^{-2} and shows a reduced overpotential.

The synergy of anion additive and optimized carbon: *reaction mechanism*





Overall reaction with ACs+LiI: $4Li^+ + O_2 + 4e^- + 2H_2O \leftrightharpoons 4LiOH$

Discharge:

$4Li^+ + 4O_2 + 4e^- \rightarrow 4LiO_2$

$4LiO_2 + 2H_2O \xrightarrow{LiI} 4LiOH + 3O_2$

$4Li^+ + O_2 + 4e^- + 2H_2O \xrightarrow{LiI} 4LiOH$

Charge:

$6I^- \rightarrow 2I_3^- + 4e^-$

$4LiOH + 2I_3^- \rightarrow 4Li^+ + 6I^- + 2H_2O + O_2$

$4LiOH \rightarrow 4Li^+ + 2H_2O + O_2\uparrow$

With ACs and LiI together in the Li-O_2 system, **four electron transfer reactions with LiOH as the main discharge product were detected**. **Low overpotential and long cycle life are achieved** based on the reversible formation and decomposition of LiOH.

Energy Storage Mater. 2020, *28*, 73

Response to last year reviewer's comments

N/A

Collaborations with other institutions and companies

Cong Liu (ANL, USA)

- Complement on Density functional calculations

Reza Shahbazian-Yassar (UIC, USA)

- Conducting TEM for material characterization

Ying Yao/Feng Wu (Beijing Institute of Technology, China)

- Development of new cathode materials: optimized biomass derived active carbon materials

Summary

1. **A rechargeable LiOH-based Li-O_2 battery was achieved by using a cation additive**
   - LiOH is formed after adding sodium ions into the lithium electrolyte.
   - LiOH is rechargeable in the presence of the sodium ions and the charge overpotential is low, resulting in a high energy efficiency.

2. **Porous carbon cathodes with optimized pore structures were universally fabricated, resulting in increased discharge capacity and enhanced cyclability in Li-O_2 batteries**
   - A series of nano-carbon materials with unique pore structures were prepared via a low cost, facile and nanoscale controllable method.
   - A super-high specific capacity of 20,300 mAh g^{-1} and an extremely long cycle life (543 cycles at 0.2 mA cm^{-2} with limited 500 mAh g^{-1} capacity were achieved.

3. **The synergistic effect of anion additive and optimized porous carbon cathode was explored**
   - Rational design of biomass derived air electrode with 3D porous carbon architecture to achieve a high discharge capacity.
   - With synergetic effect of a soluble additive, LiI, a long cycle life of 1000 cycles was reached, and a suppressed polarization was obtained.

Proposed Future Work

- Developing new cathode materials for lithium oxygen (Li-O_2) batteries with high energy efficiency and long cycle life.
  - Our preliminary results show that low charge overpotential Li-O2 battery can be achieved without any electrocatalysts.
  - Investigate optimization of Li-O_2 cell cathode material to increase stability of the cell.
- Obtaining critical insights into the electrochemical processes in Li-O2 batteries via in-situ/ex-situ methods.
  - Investigate the discharge product using cryo-TEM
  - Examine the ORR and OER process using in-situ high-energy X-ray techniques.
- Using an integrated approach based on experimental synthesis and state-of-the-art characterization combined with high level computational studies focused on materials design and understanding.
  - Synthesize new alloy particles for testing in cathodes
  - Develop electrolyte blends for improving the OER and protecting Li-anode for longer cycle life.