上海交通大學
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Air Electrode Design and Preparation for Lithium Air Battery Application

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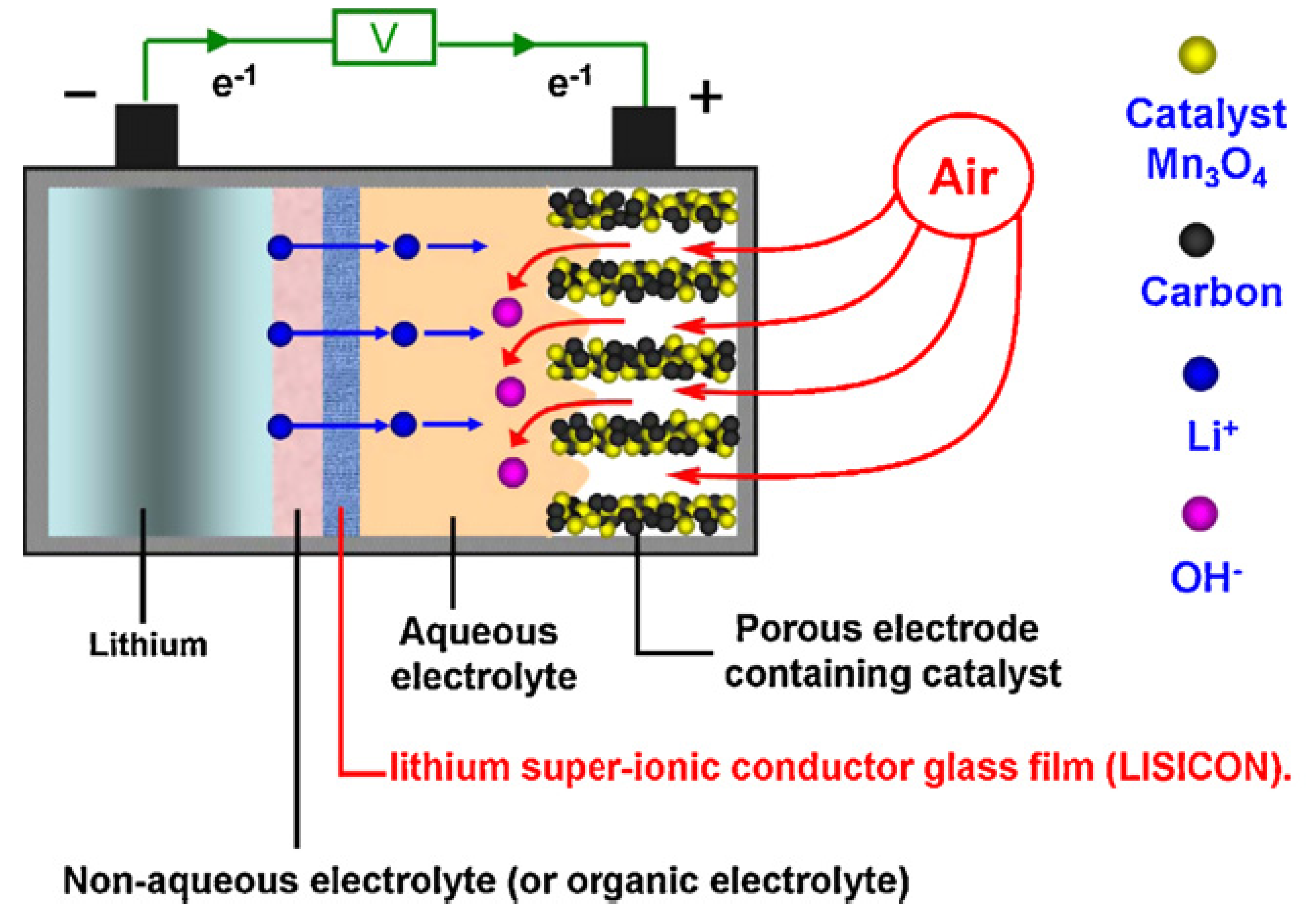
Principle of Li-air battery



Positive (cathode) : $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Negative (anode) : $Li \rightarrow Li^+ + e^-$

Battery reaction: $4Li + O_2 + 2H_2O \rightarrow 4Li^+ + 4OH^-$

$$4Li(s) + O_2(g) \rightarrow 2Li_2O(s) \quad V = 2.91V$$

$$2Li(s) + O_2(g) \rightarrow Li_2O_2(s) \quad V = 3.10V$$

Challenges of Li-air battery

High theoretical energy density is about **11972 Wh/kg**

Low practical capacity → **Low practical energy density**

Low round trip efficiency

- **Poor high-rate dischargeability**
- **Short cycle life** (Fast degradation under ambient conditions)
- **Safety issues**
- **Waterproof (**Isolated from water and oxygen permeating **)**
- **Unclear reaction mechanism at cathode electrode**

Objectives of SJTU-UM Projects on Li-Air battery

- Characterization of the catalyst microstructure and morphology during charge/discharge cycles
- Identification of the rate limiting mechanisms for decomposition of Li_2O_2 (the primary discharge product) during recharge in order to understand the origin of the high charging potential
- Identification of mechanisms by which cathode catalysts facilitate discharge and recharge
- Based on identified mechanisms, screen for optimal catalyst compositions and morphologies

Deliverables

- A comprehensive and computational model for creation and analysis of Li-air batteries
- Novel materials and structure for high capacity Li-air batteries
- Prototype of Li-air batteries

Critical Path

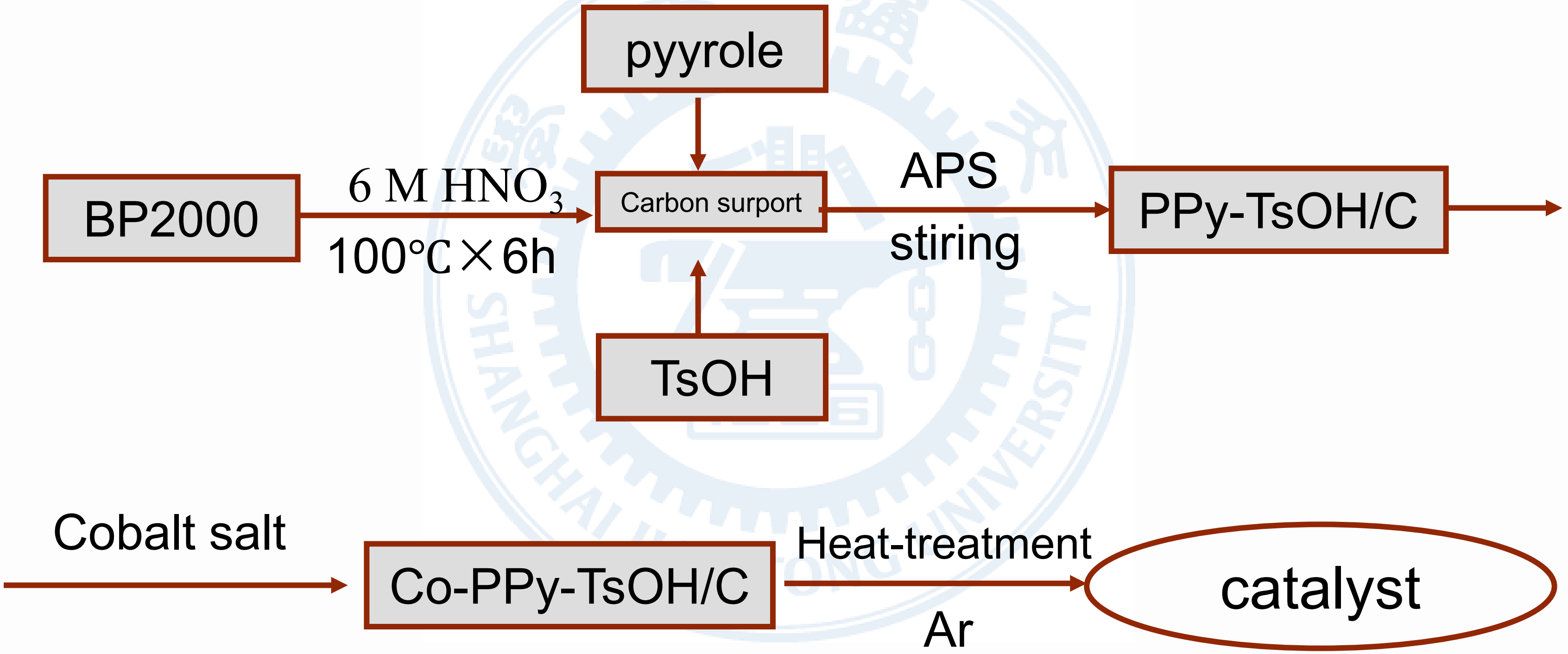
- Complete calculation of concentrations and diffusivities of all relevant neutral and charged intrinsic defects in Li_2O_2 at fixed oxygen chemical potential and consistent with the "bulk" morphology of catalytic decomposition.
- Prepare various catalysts and evaluate their structure-related catalytic performance and characteristics; Identify impact of transition metal catalysts on defect formation energies through "extrinsic dopant" approach.
- Prepare prototype Li-air batteries with various components. Determine the effect of electrodes and electrolytes on the electrochemical profoemance.

Research progress at SJTU side

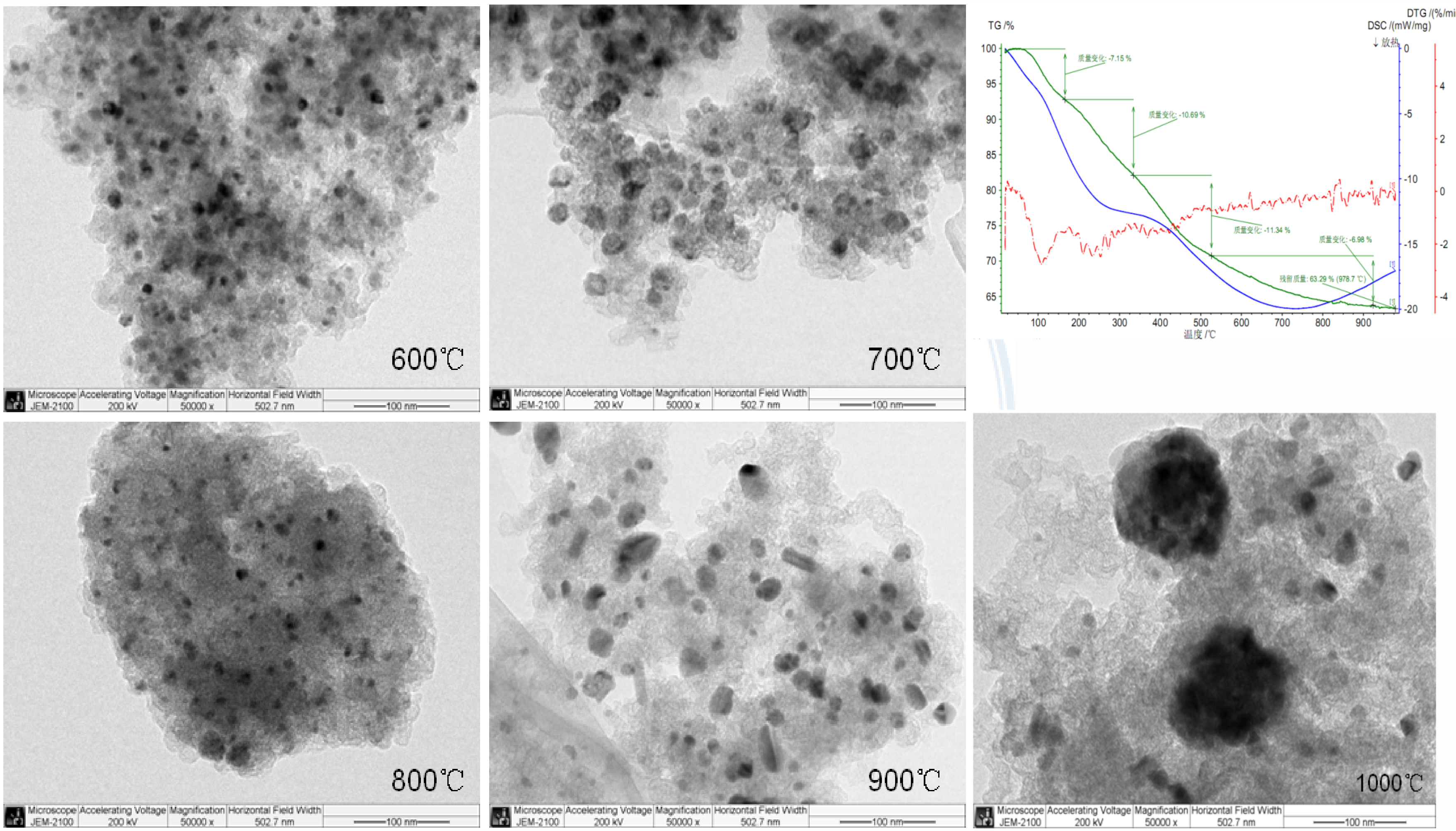
- ◆Cathode catalyst design and development
- ✓Co-PPy-TsOH/C
- ✓Co-N/C
- ✓MnO_x based catalysts
- ✓1.0 M LiTFSI-DMMP based electrolyte
- ◆Prototype Li-air battery design and development

Cathode catalysts development

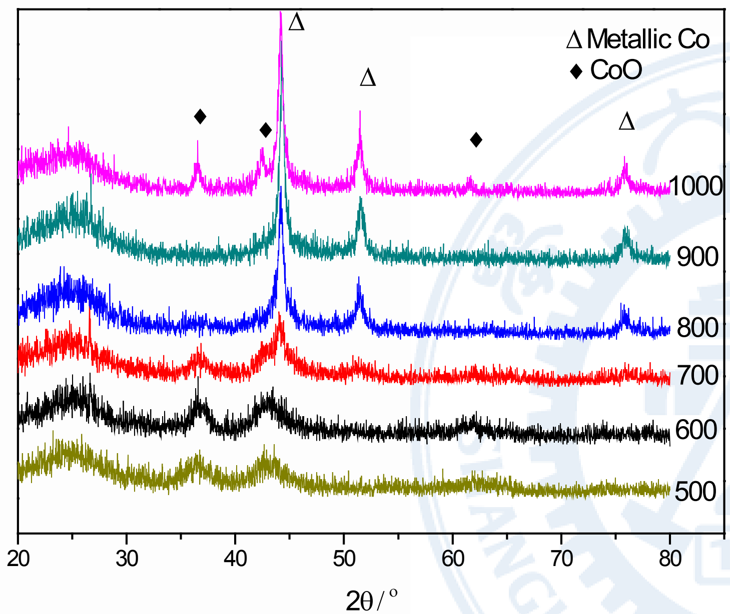
Effect of heat-treatment conditions on catalytic performance of Co-PPy-TsOH/C toward oxygen reduction reaction

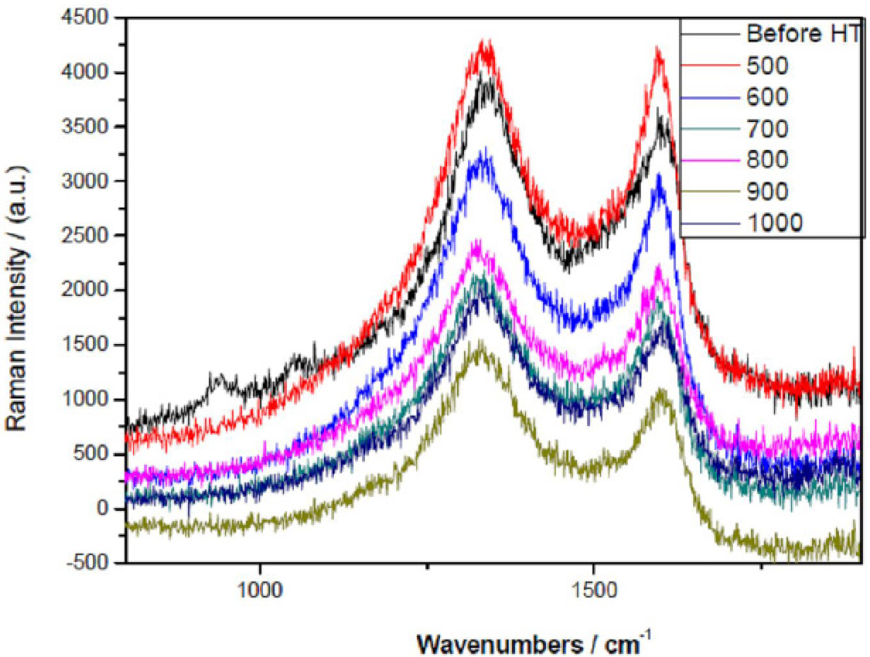


Xianxia Yuan, et al Improved Performance of Proton Exchange Membrane Fuel Cells with p-Toluenesulfonic Acid-Doped Co-PPy/C as Cathode Electrocatalyst. *Journal of the American Chemical Society*. 132(2010)6:1754- 1755

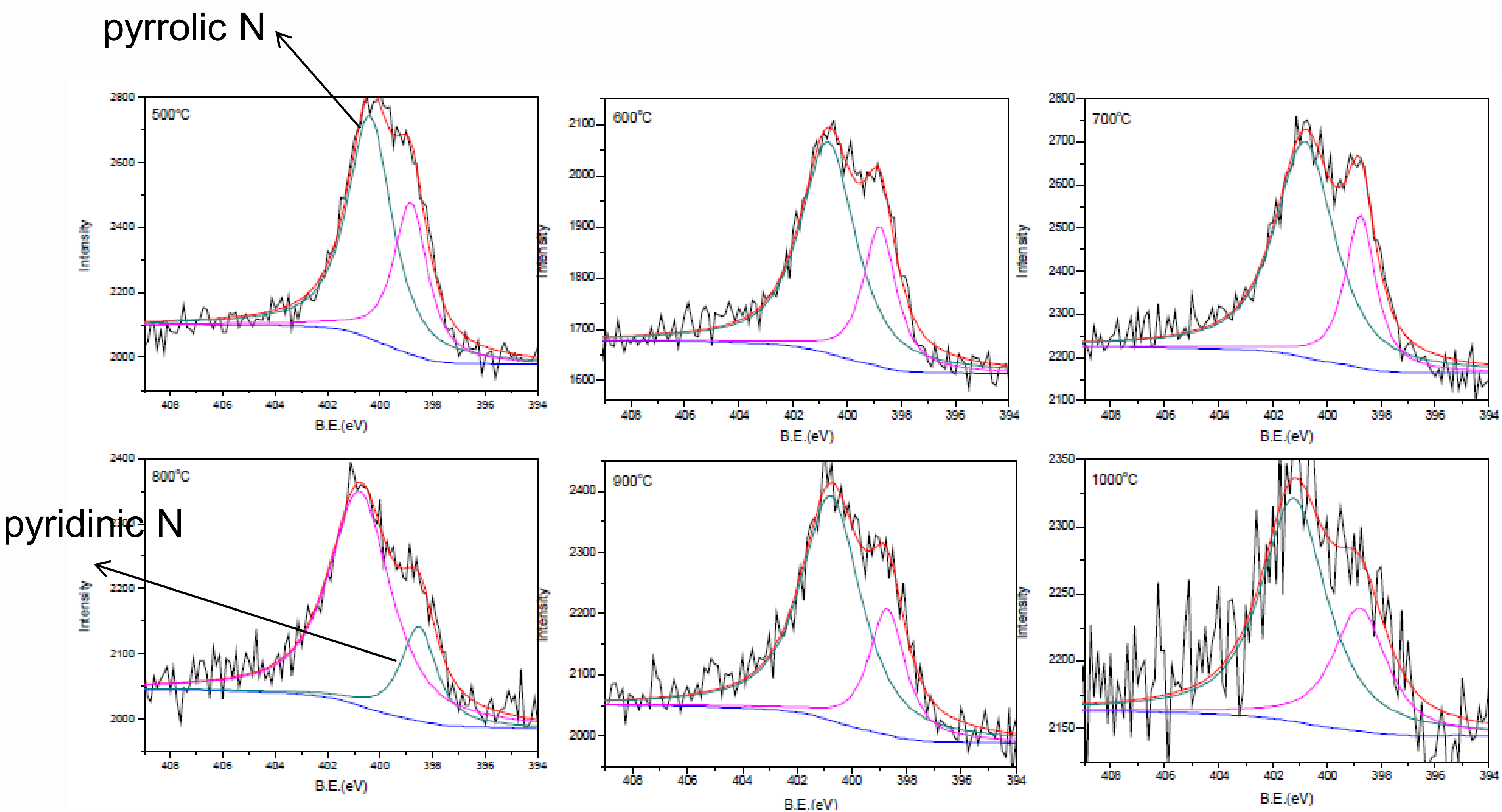


TEM images of Co-PPy-TsOH/C heat-treated at various temperatures





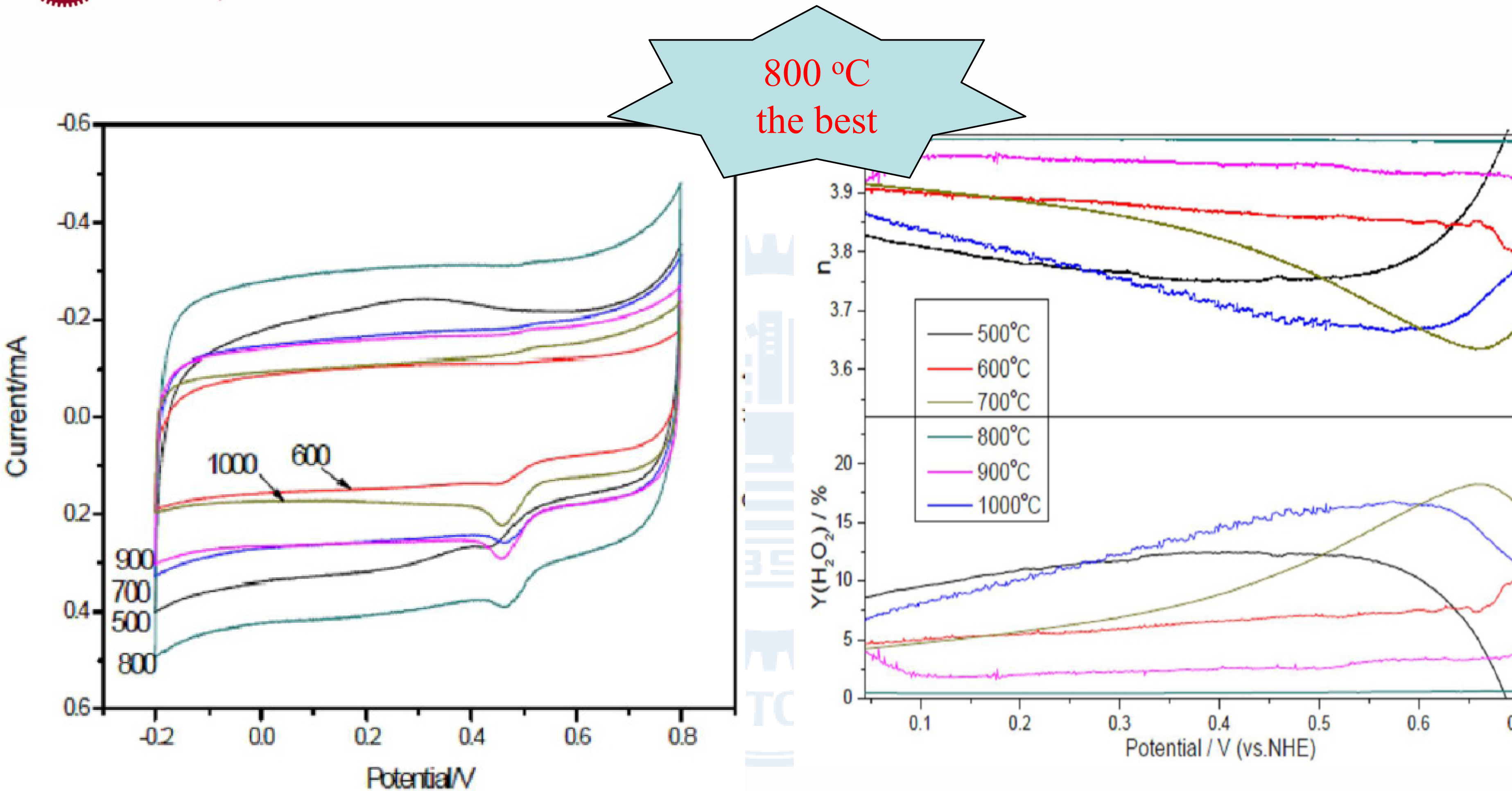
XRD patterns and Raman spectra of Co-PPy-TsOH/C catalysts heat-treated at various temperatures



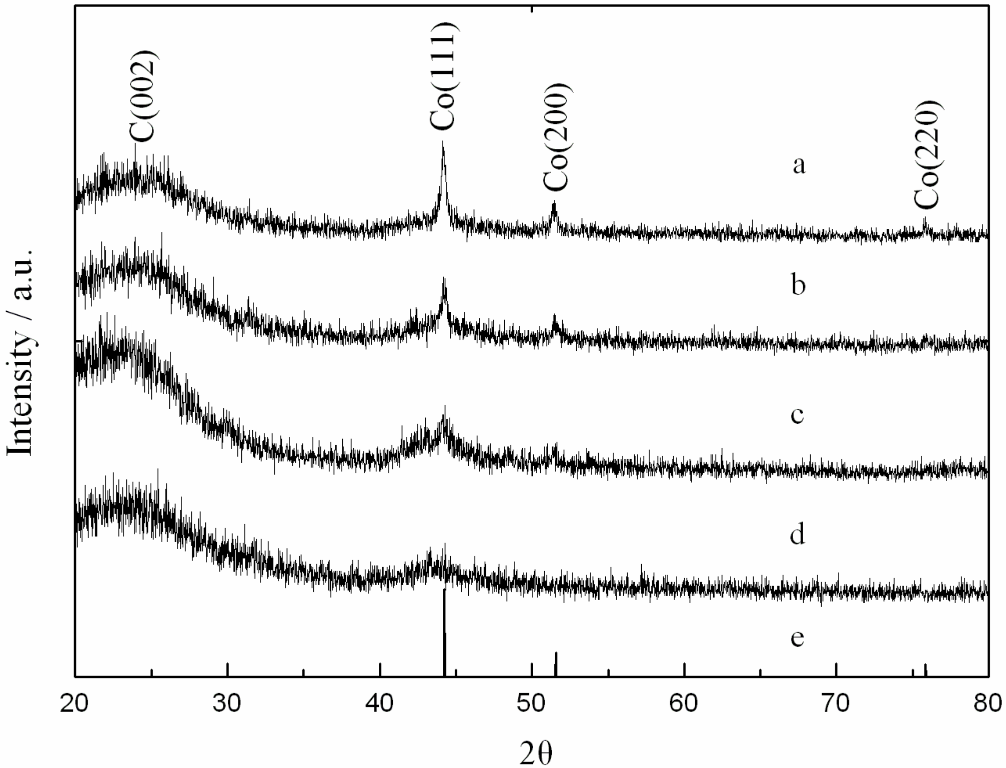
XPS $_{N1s}$ curves of catalyst Co-PPy-TsOH/C heat-treated at various temperatures

Area ratio of pyrrolic N/pyridinic N for of catalyst Co-PPy-TsOH/C heat-treated at various temperatures

Heat treatment temperature / ℃	Peak position of pyridinic N /ev	Peak position of pyrrolic N /ev	Area ratio of pyrrolic N/pyridinic N
500℃	398.837	400.399	1.9
600℃	398.792	400.706	2.5
700℃	398.761	400.814	2.7
800℃	398.526	400.814	3.9
900℃	398.702	400.759	2.9
1000℃	398.788	401.255	2.2



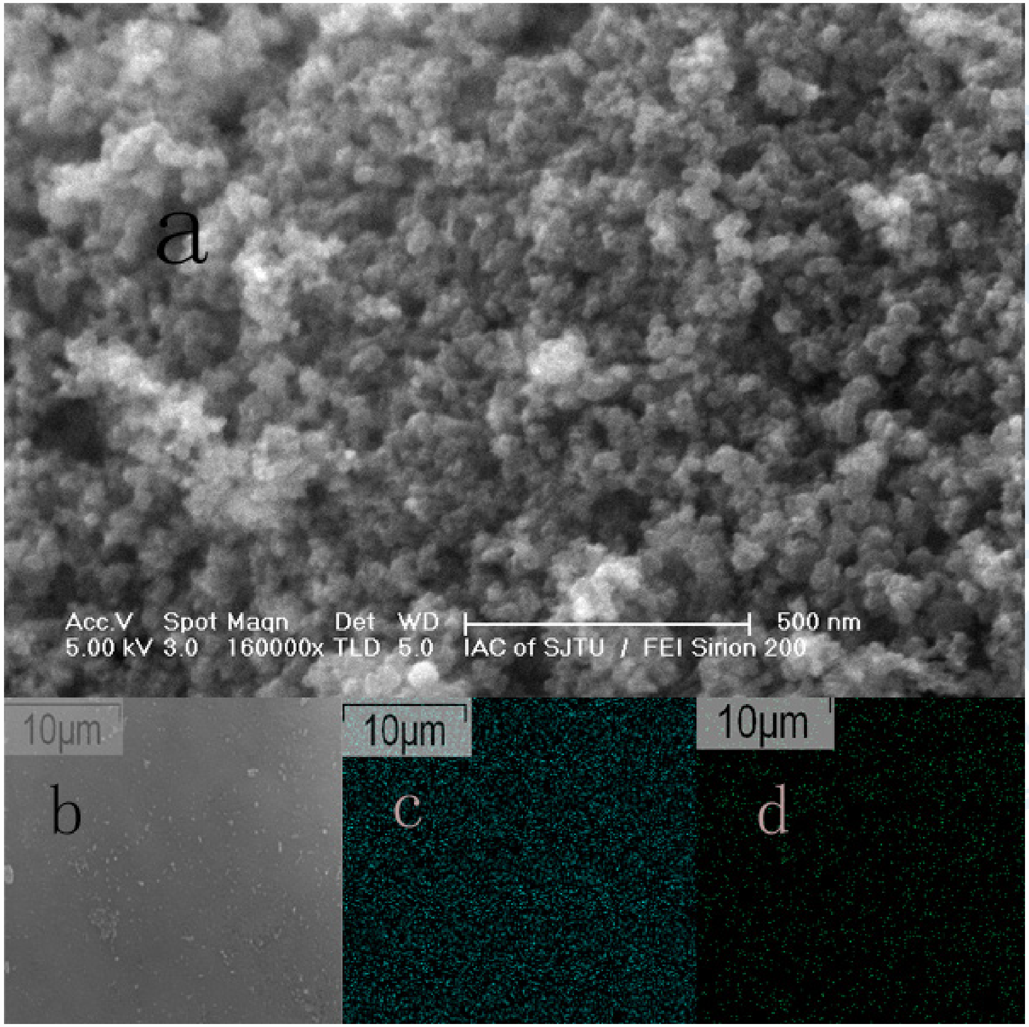
Electro-catalytic performance of catalyst Co-PPy-TsOH/C heat-treated at various temperatures



- a: 6%Co载量
- b: 3%Co载量
- c: 1%Co载量
- d: BP2000
- e: PDF89-4307

A simple and cheap Phenanthroline (phen) was used as a ligand to prepare Co(phen)2 complexes. The prepared Co(phen)2 complexes were coated on BP2000 then heat-treated to obtain carbon-supported Co-N/C catalyst).

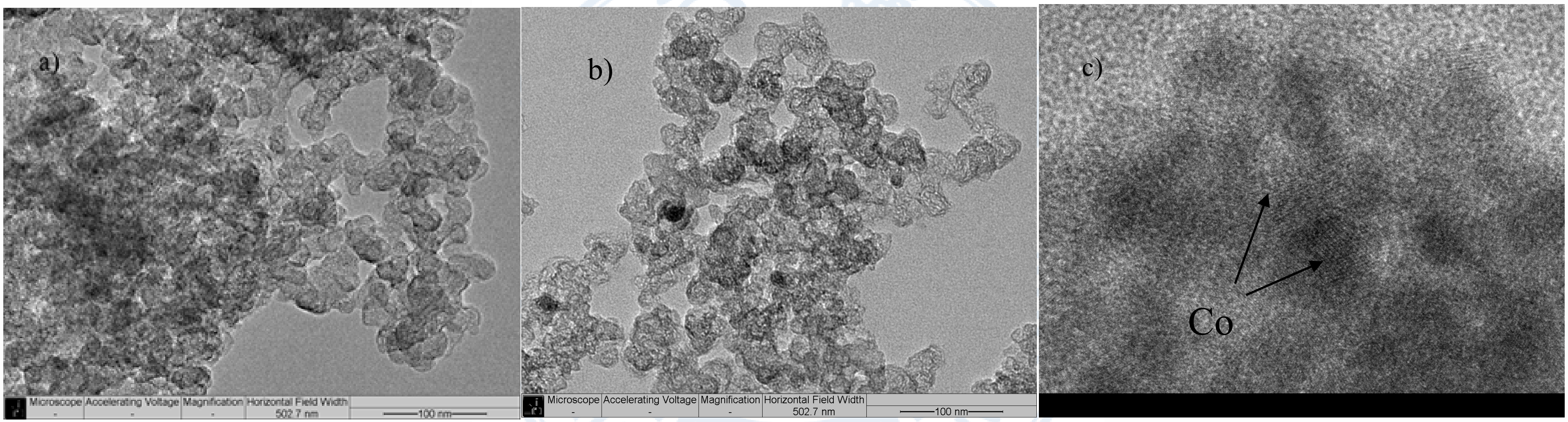
Hong Wang, Xiao-Zhen Liao, Zi-Feng Ma, J.Electrochem. Soc. 2012, in press



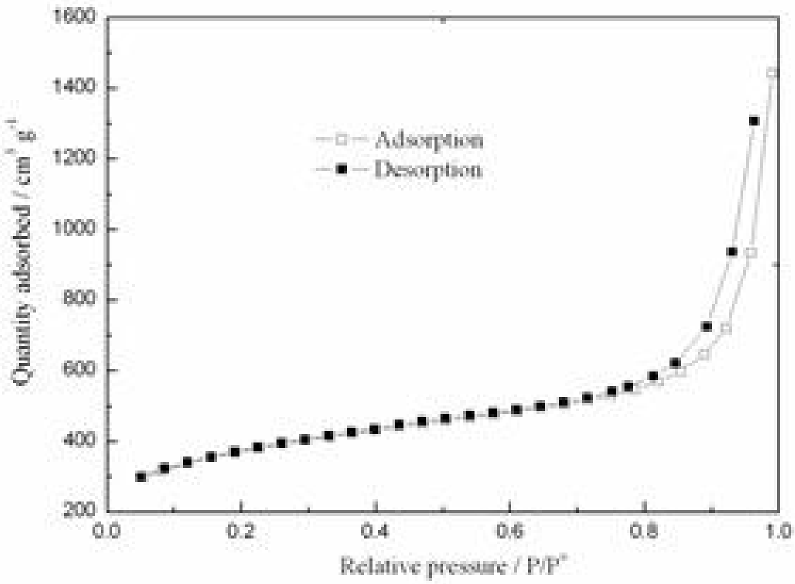
Most of the particles are distributed in the range of 20-40 nm. EDS mapping results corresponding to CoKα and NKα on Co-N show fairly uniform distribution of these elements, indicating that the Co-N composite in carbon surpport were well dispersed. It has the beneficial effect of promoting the reversibility of discharge product formation and decomposition.

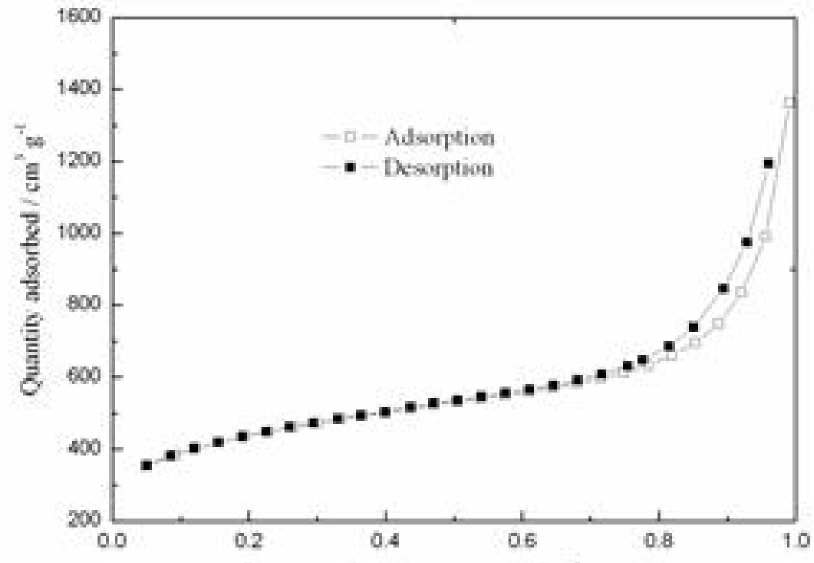
C: Co elements

D: N elements



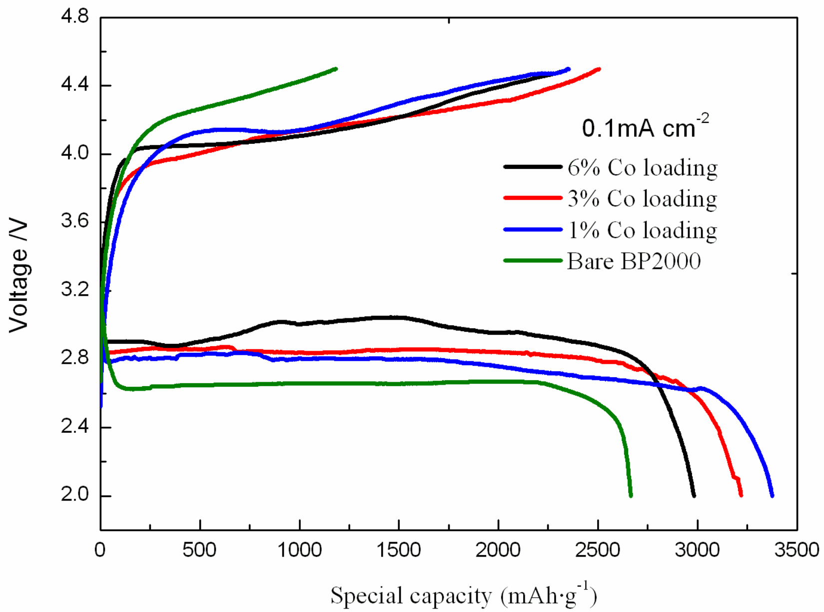
TEM a&b: Co-N/C catalyst c: BP2000

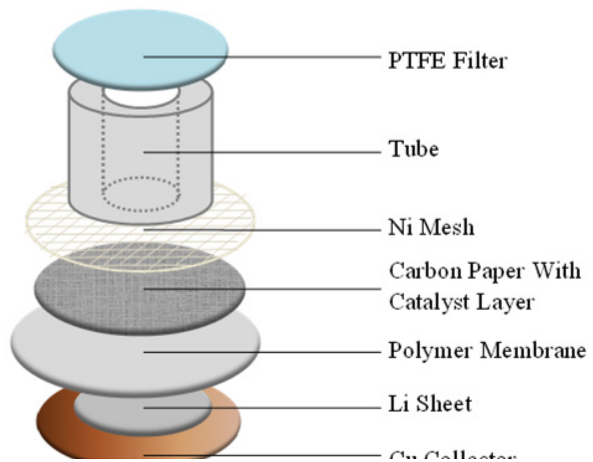




a: Co-N/C catalyst（3%Co coating） **b: BP2000**

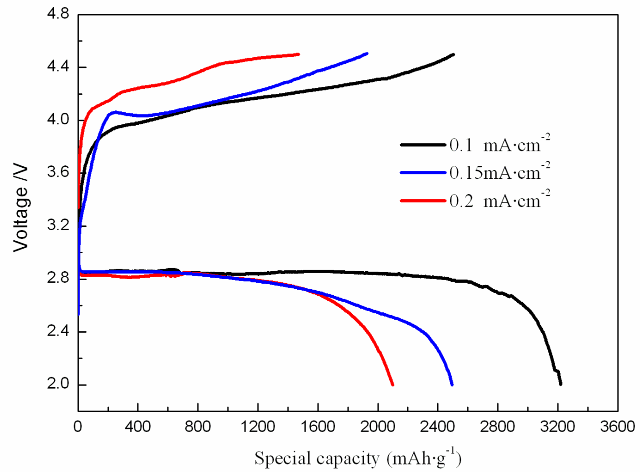
	BET surface area	Pore volume
BP2000	1491m^2/g	2.1cm^3/g
1%Co coating	1276m^2/g	2.0cm^3/g
3%Co coating	864m^2/g	1.8cm^3/g
6%Co coating	396m^2/g	1.1cm^3/g



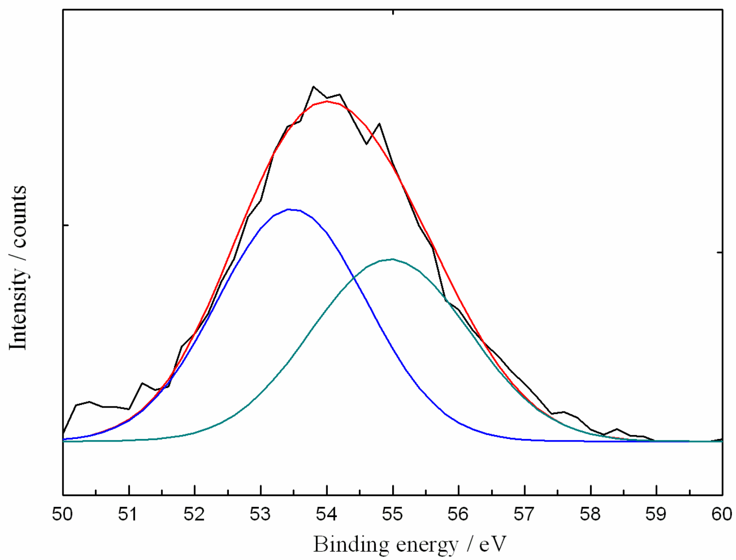


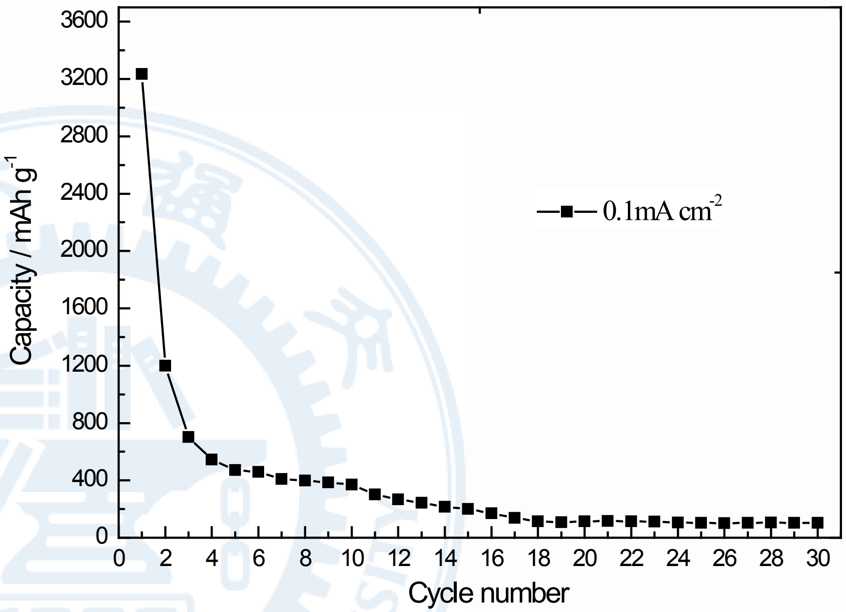
Higher capacity (based on catalysts)

Lower charge potential which tested in 1 atm oxygen atmosphere



3%Co loading with different current densities





XPS spectra of Li1s was analysized from oxygen electrode of disassembled cell after cycles. The Li 1s signal can be deconvoluted into two components. The component at 55.2 eV can be attributed to lithium peroxide. The another signal at 54 eV can be attributed to Li2CO3.

- The poor cyclability of the Li/O2 cell could be attributed to the ecomposition of PC-based solvent.

1M LITFSI in propylene carbonate (PC) and diethyl carbonate (DEC), 1:1 in volume

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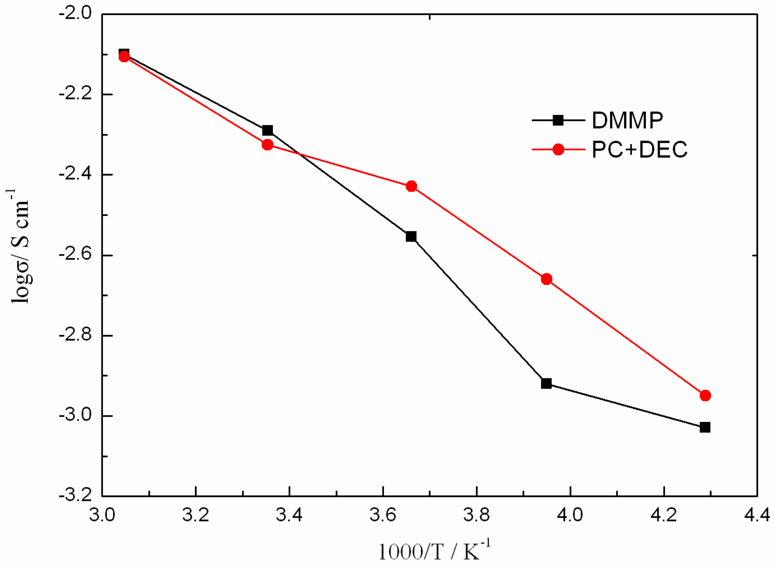
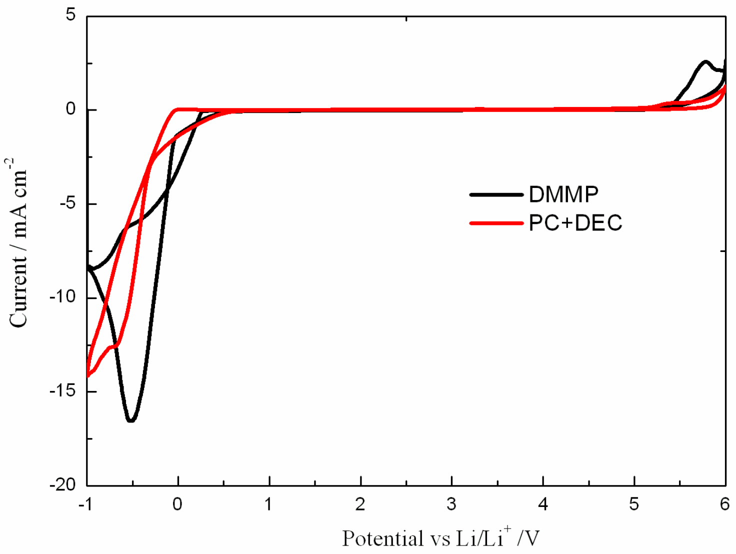
1.0 M LiTFSI-DMMP based electrolyte

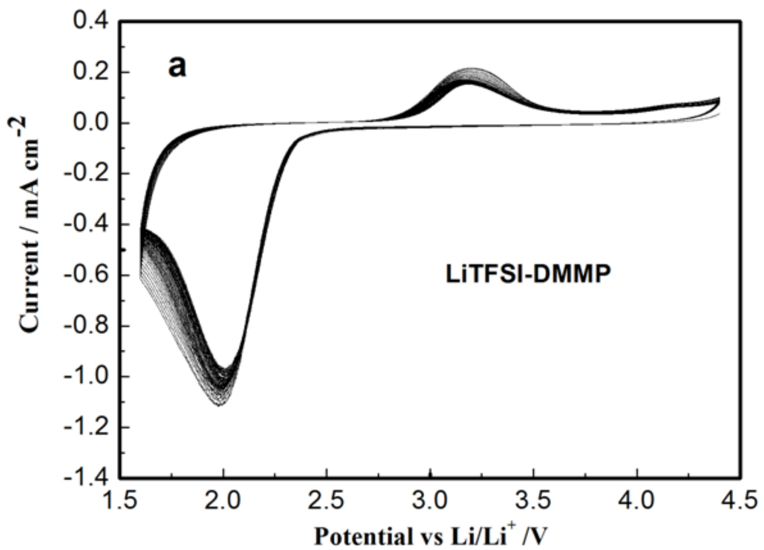
1.0 M LiTFSI-DMMP solution displayed high ionic conductivity of ~5.12 mS cm^{-1} at 25 ℃



wide electrochemical stability windows of the 1.0 M LiTFSI-DMMP electrolyte as well as that of 1.0 M LiTFSI-PC+DEC electrolyte.

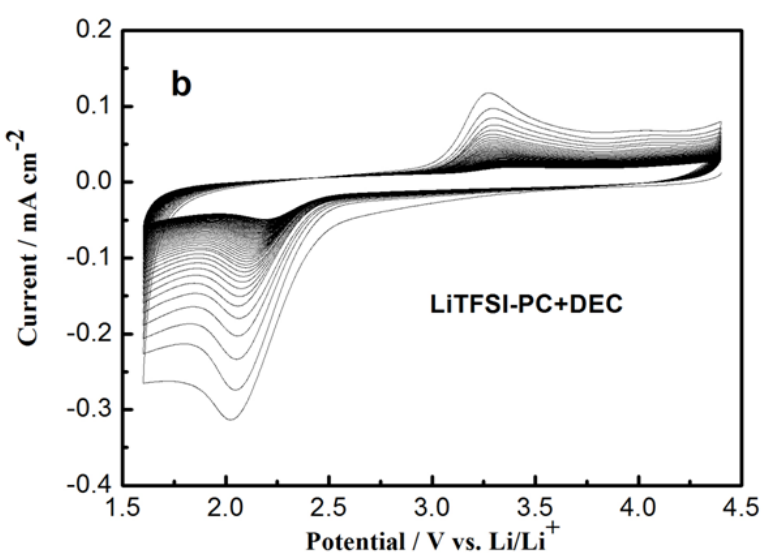


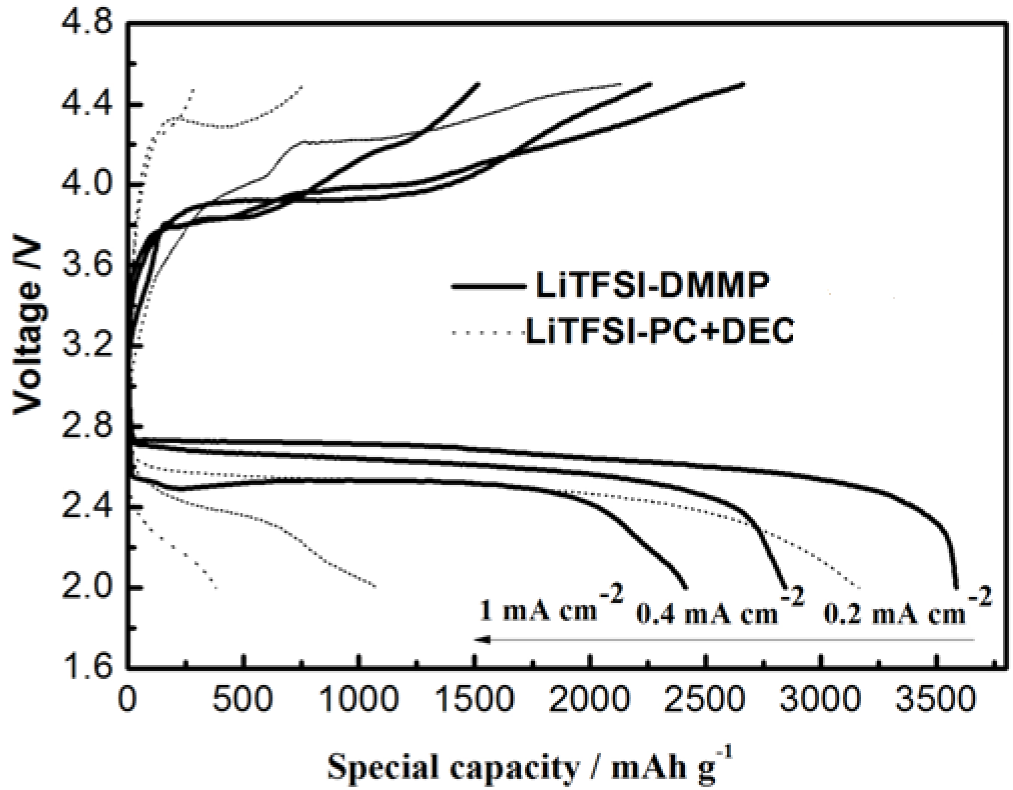
The CV test was performed under O2 atmosphere (O2 purged) at 100 mV s-1 up to 50 cycles
a: LiTFSI-DMMP electrolyte
b: LiTFSI-PC/DEC electrolyte



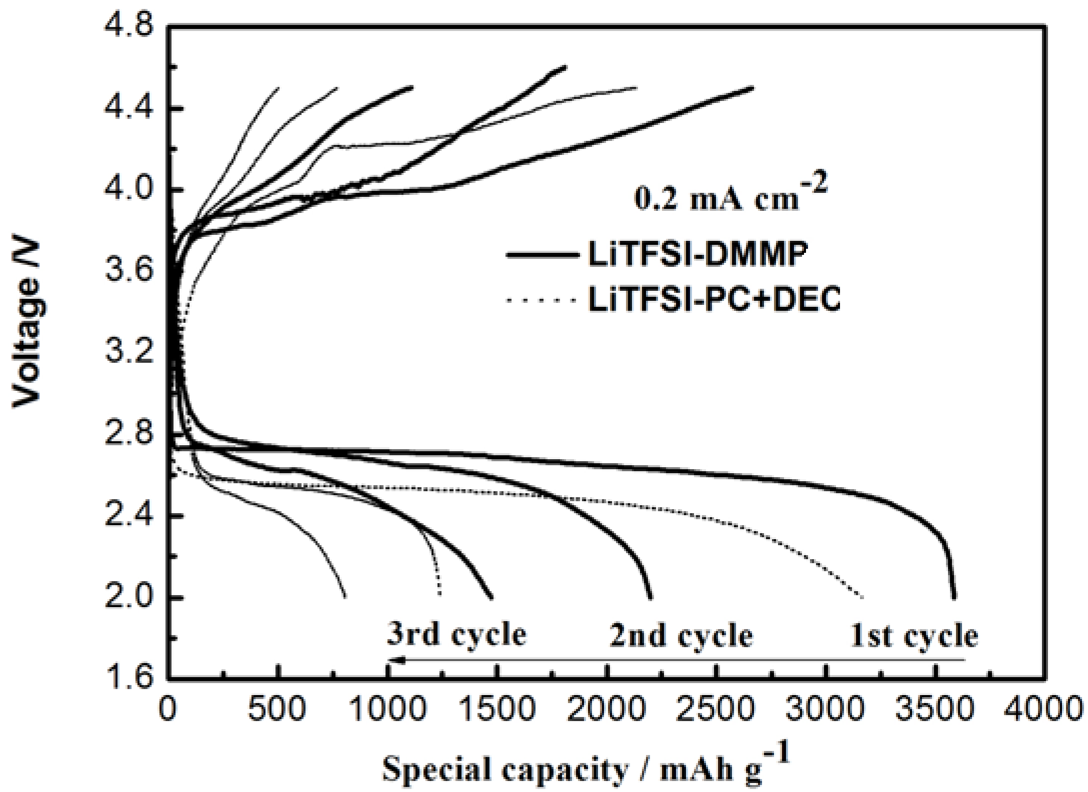
Higher reduction currents were observed in DMMP-based electrolyte than those in PC-DEC based electrolytes, which is probably due to a better O2 solubility and diffusion in the DMMP-based solution.

Oxidation current peak appeared at ~3.2 V_{Li} in DMMP-based electrolyte, while the other showed oxidation peaks at ~3.28 V_{Li}.

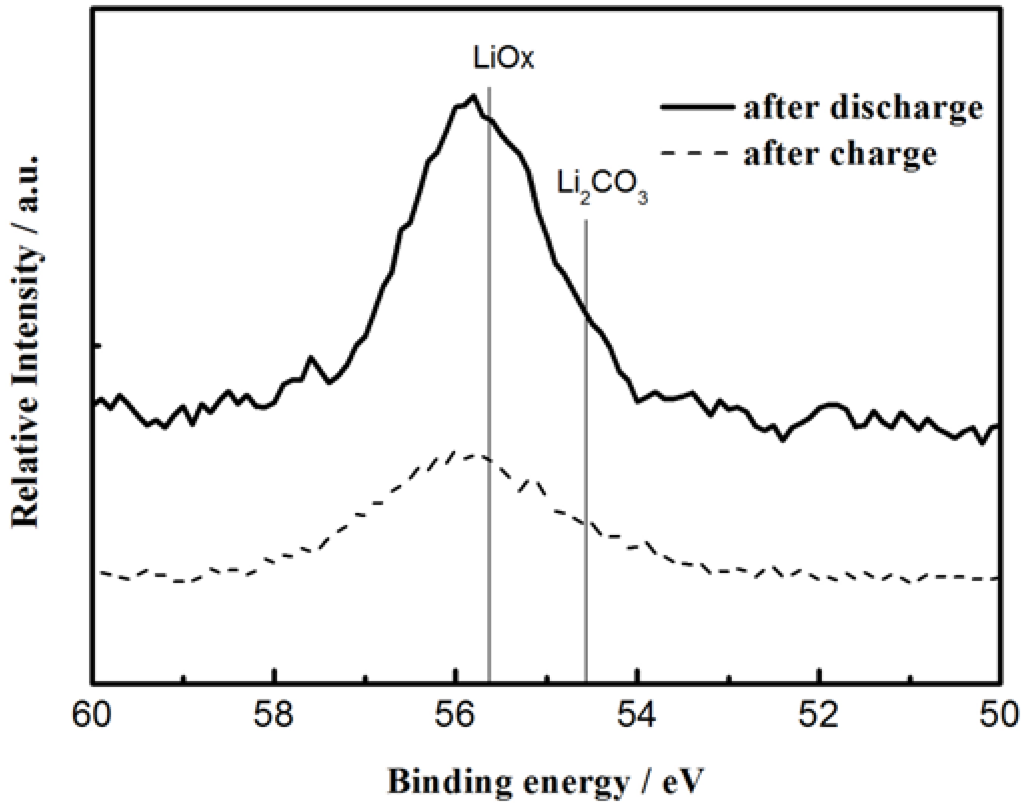




The cell exhibited reasonably high capacities at rates (0.2, 0.4 and 1mA cm-2) with flat discharge potential plateaus. The capacities were 3585 mAh g−1 (0.2 mA cm-2, average voltage plateau of 2.70 V), 2845 mAh g−1 (0.4 mA cm-2 , average voltage plateau of 2.65 V) and 2413 mAh g−1 (1 mA cm-2, average voltage plateau of 2.53 V), respectively. The high capacities of the Li/O2 cell can be attributed to the good O2 solubility and diffusion in the DMMP-based electrolyte



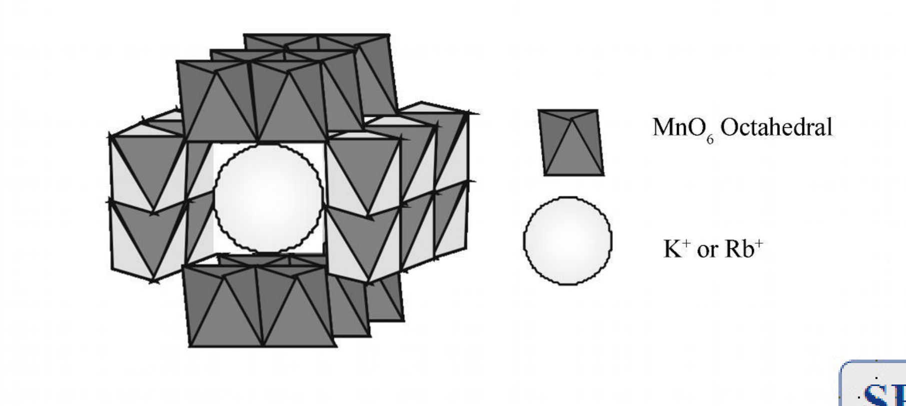
The first three cycle performance of the Li/O2 cells at 0.2 mA cm-2. The cell with DMMP delivered capacities of 3585 mAh g-1 (1st cycle), 2199 mAh g-1 (2nd cycle) and 1472 mAh g-1 (3rd cycle), while the another cell with PC electrolyte showed capacities of 3154 mAh g-1 (1st cycle), 1241 mAh g-1 (2nd cycle) and 807 mAh g-1 (3rd cycle).



The Li 1s XPS spectra of the product samples

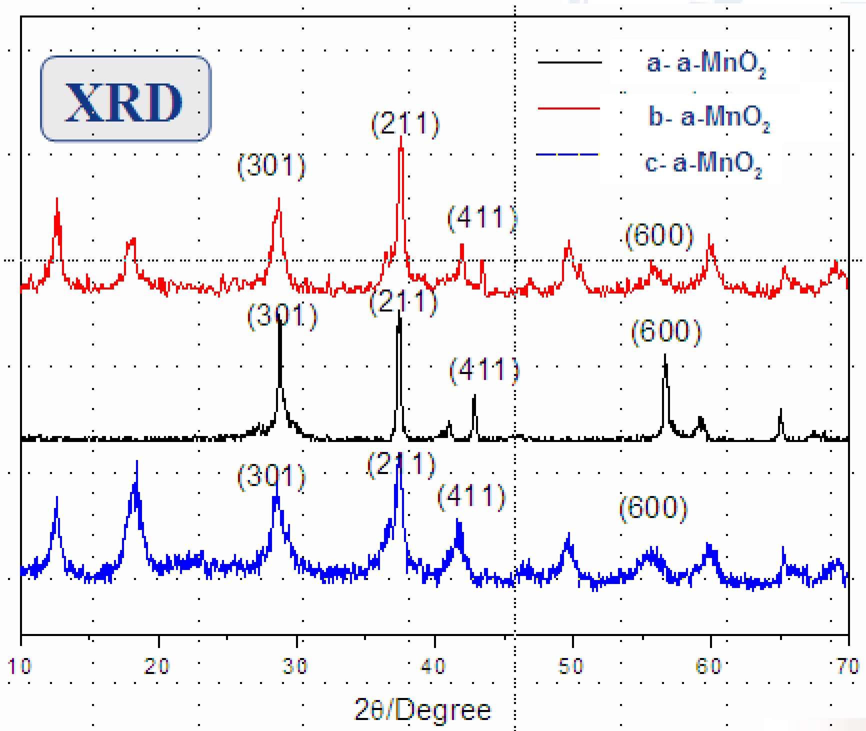
the major oxygen reduction products in DMMP-based electrolyte are lithium oxides. The XPS spectrum of the charged sample shows that the reduction product can not be completely decomposed during charge.

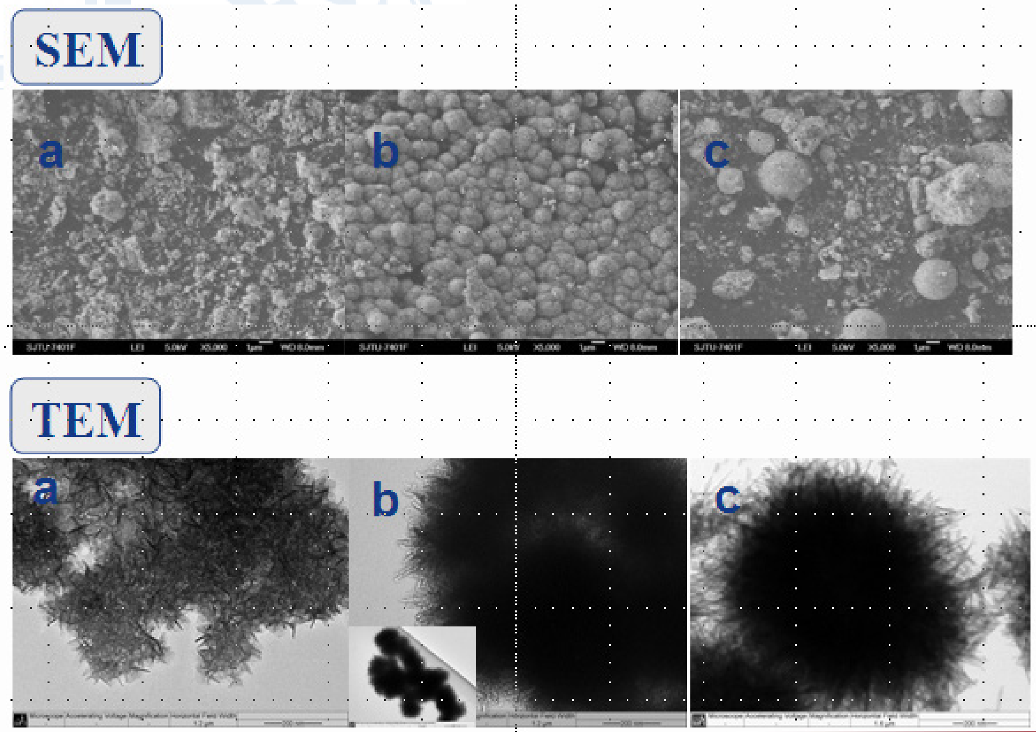
MnO_x based catalysts



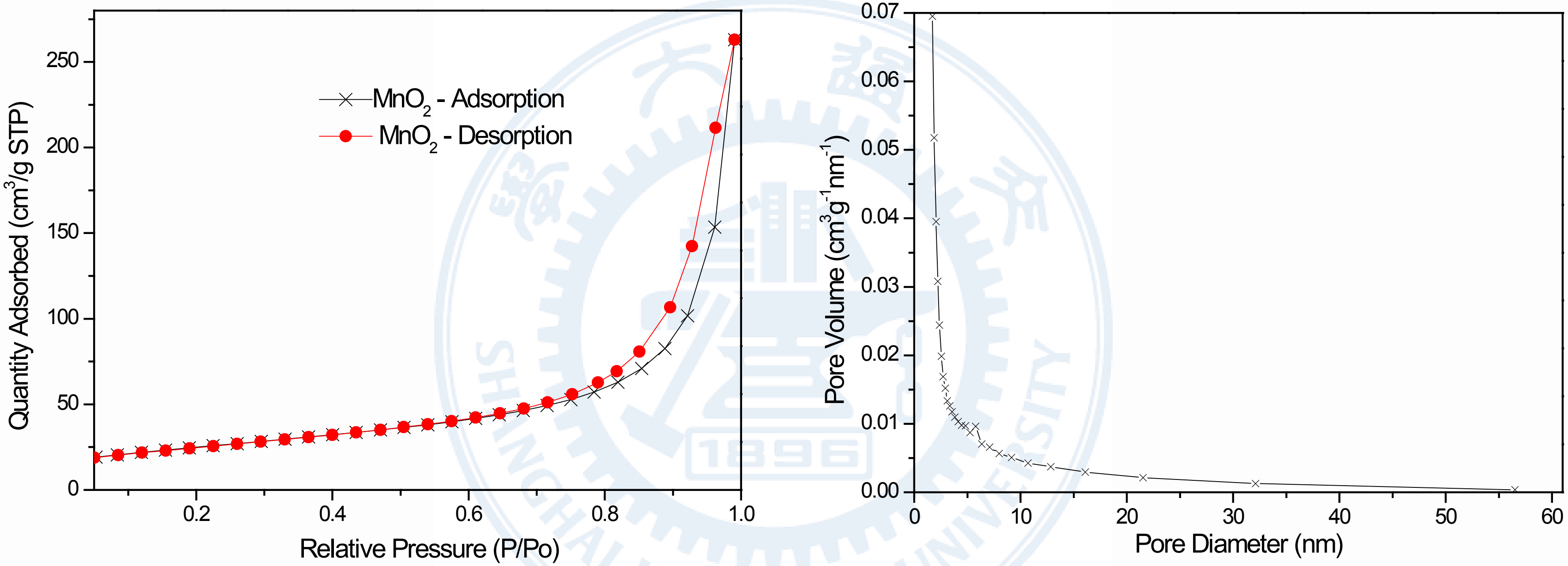
Why a-MnO_2?

1. The structure of a-MnO_2 ([2x2],or[1x1]) contains large tunnels or holes, which help in the transfer of the products after discharge/charge
2. low cost, and easy to be prepared

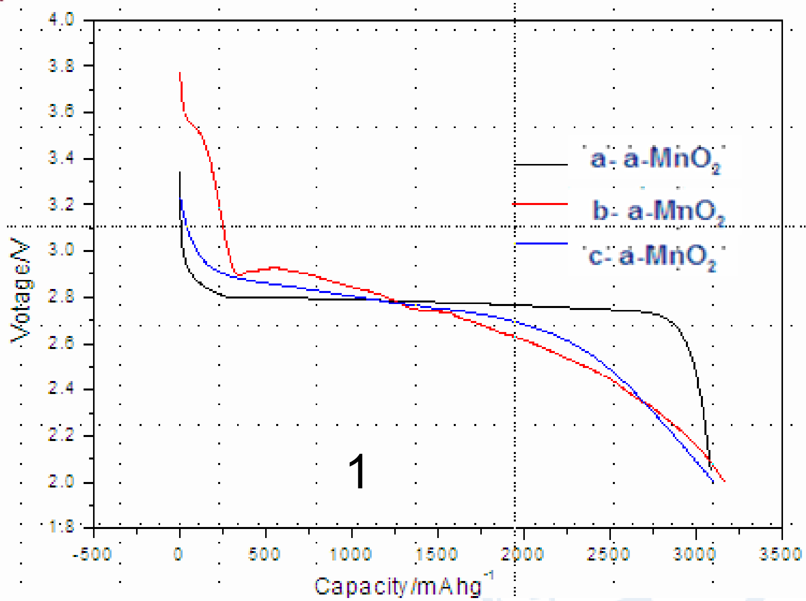




SEM and TEM of different a-MnO2 prepared in our experiment



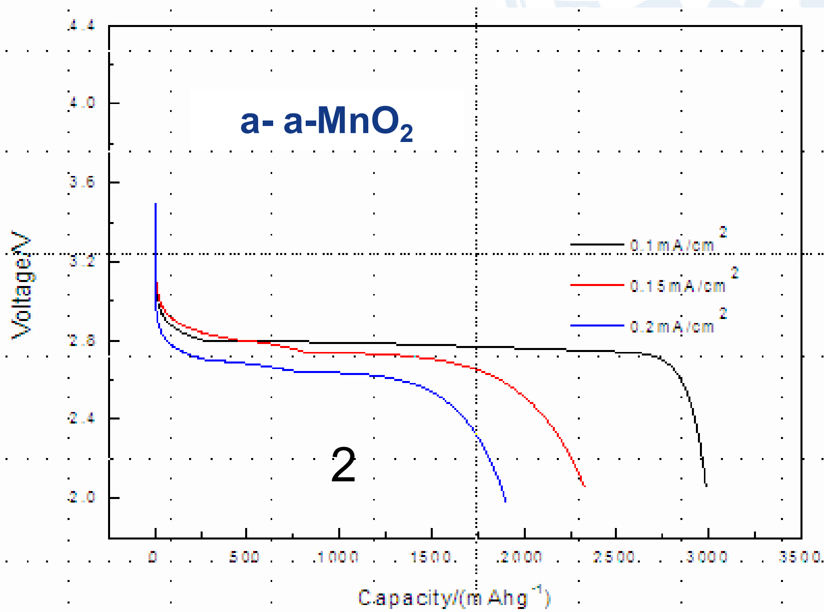
The specific surface area (BET) and pore size and pore distribution of a-MnO2 nanowires catalyst

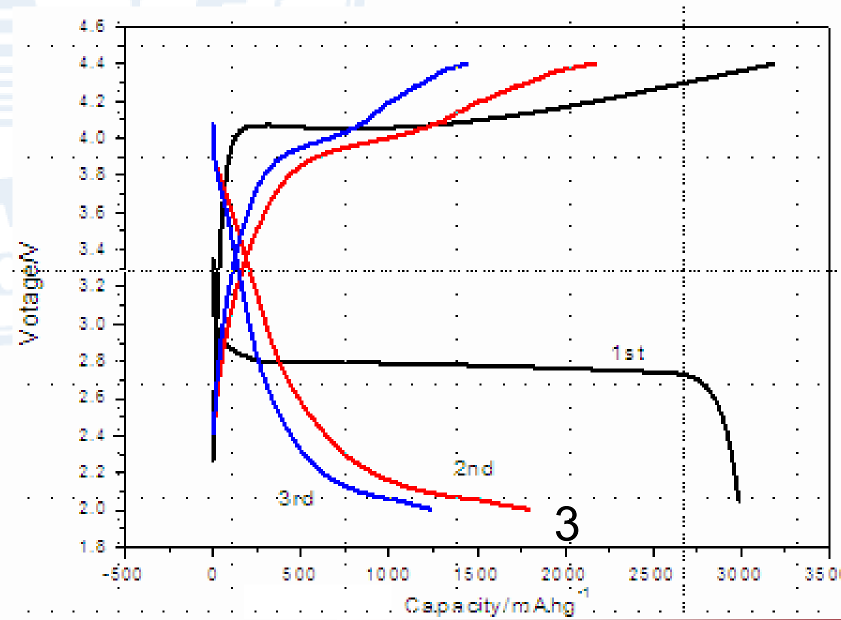


1: Discharge curves of different a-MnO2 under current 0.1mA/cm2

2: Discharge curves of type a a-MnO2 under current 0.1,0.15,0.2mA/cm2,respectively

3: Cycle performance of type a a-MnO2 under current 0.1mA/cm2





MnO_2

1. Improve the Rate performance
2. Improve the discharge voltage and reduce the charging voltage

Poor Cycle performance

Cocatalyst

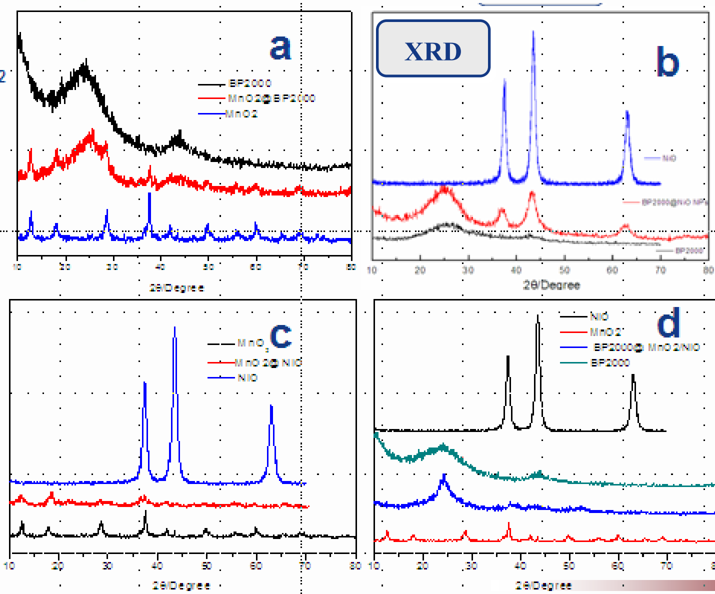
→ **MnO_2@NiO**

a-BP2000@MnO_2

b-BP2000@NiO

c-MnO_2@NiO

d-BP2000@ MnO_2/NiO



Why MnO_2-based catalyst?

1.Insulation material, apt to increase the Lithium-air battery's internal resistance
2.Cocatalyst, such as NiO, CeO2, can can effectively improve the Catalytic properties.

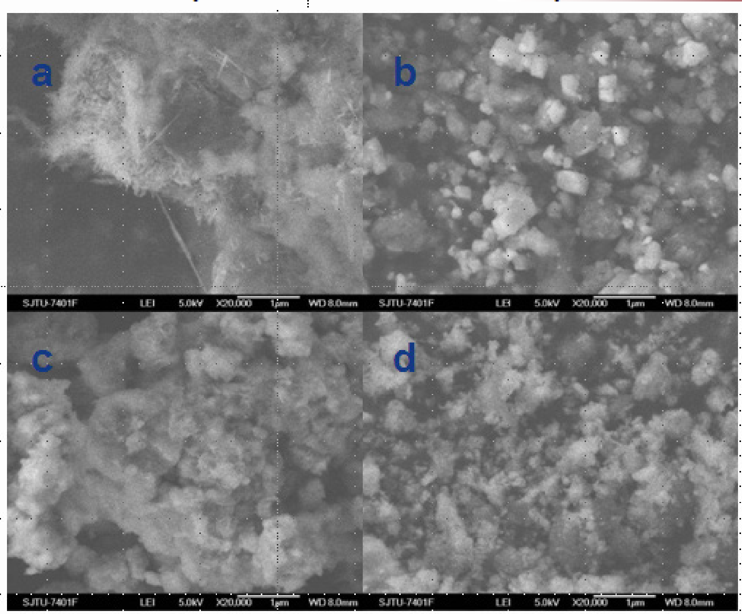
SEM

a-BP2000@MnO_2

b-BP2000@NiO

c-MnO_2@NiO

d-BP2000@ MnO_2/NiO



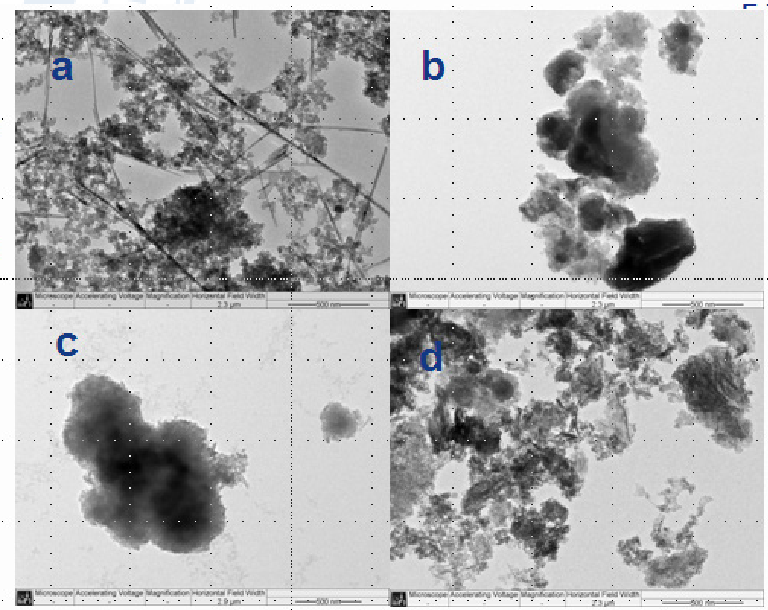
TEM

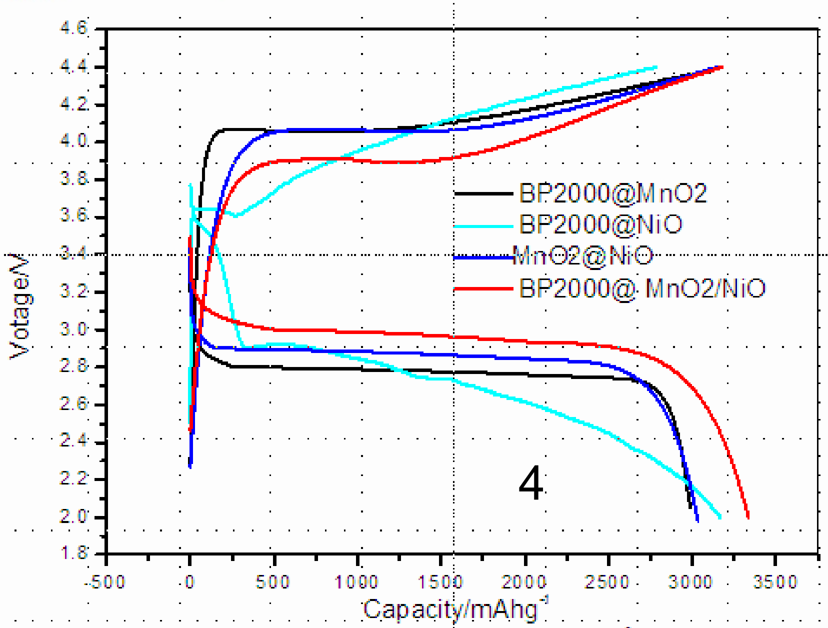
a-BP2000@MnO_2

b-BP2000@NiO

c-MnO_2@NiO

d-BP2000@ MnO_2/NiO

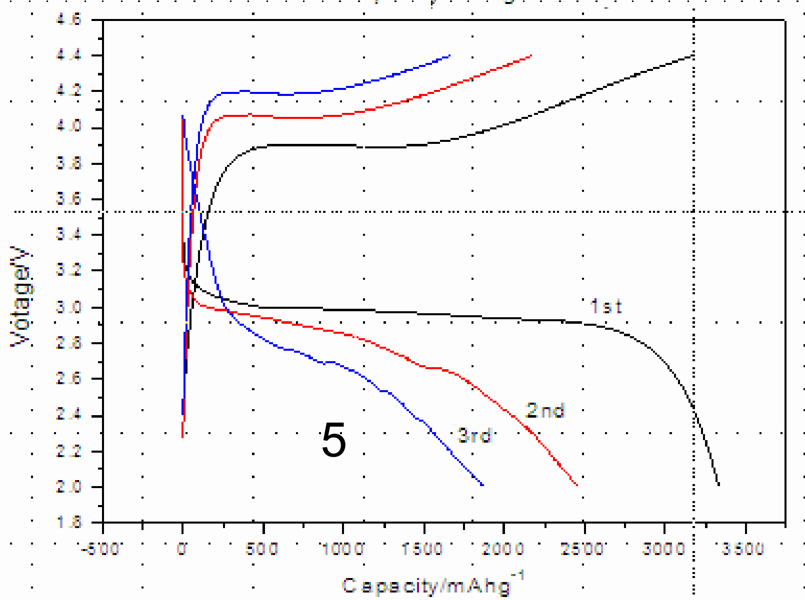


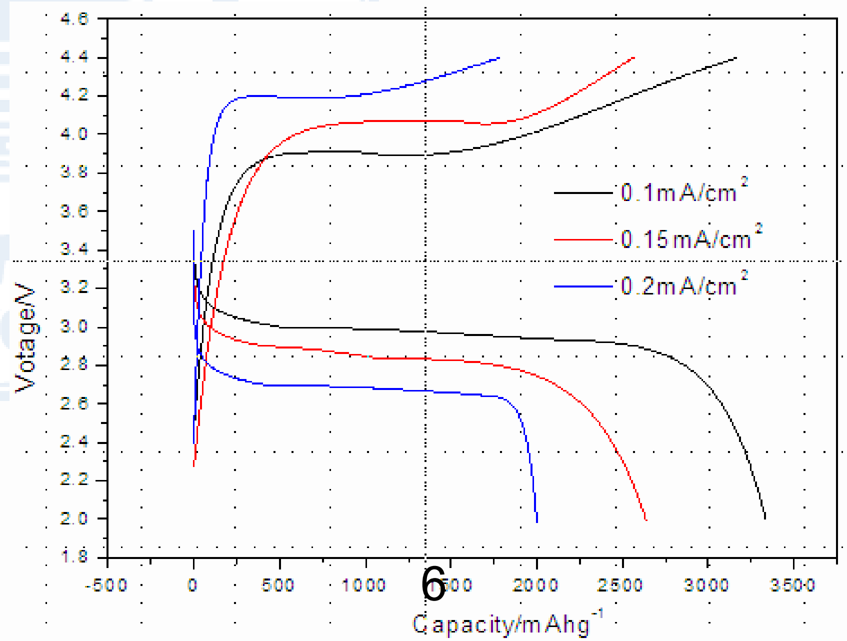


4: Discharge curves of different a-MnO2 under current 0.1mA/cm2

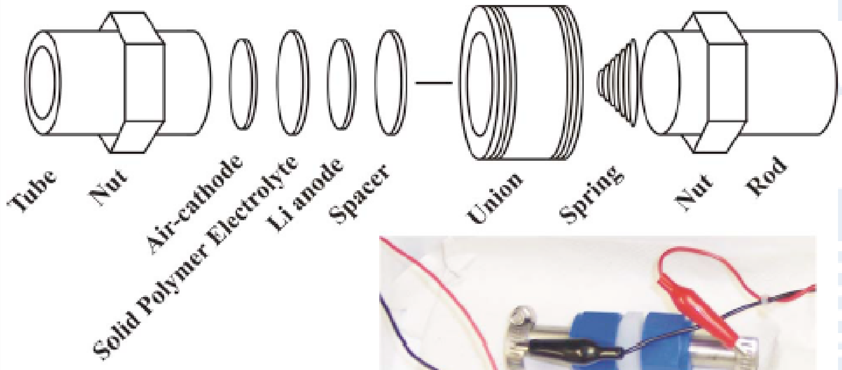
5: Discharge curves of type a a-MnO2 under current 0.1,0.15,0.2mA/cm2,respectively

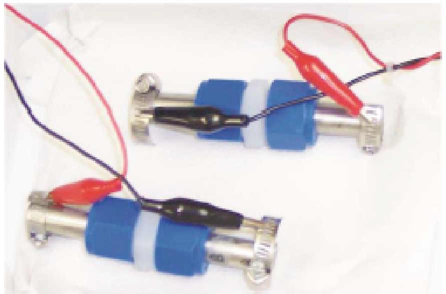
6: Cycle performance of type a a-MnO2 under current 0.1mA/cm2





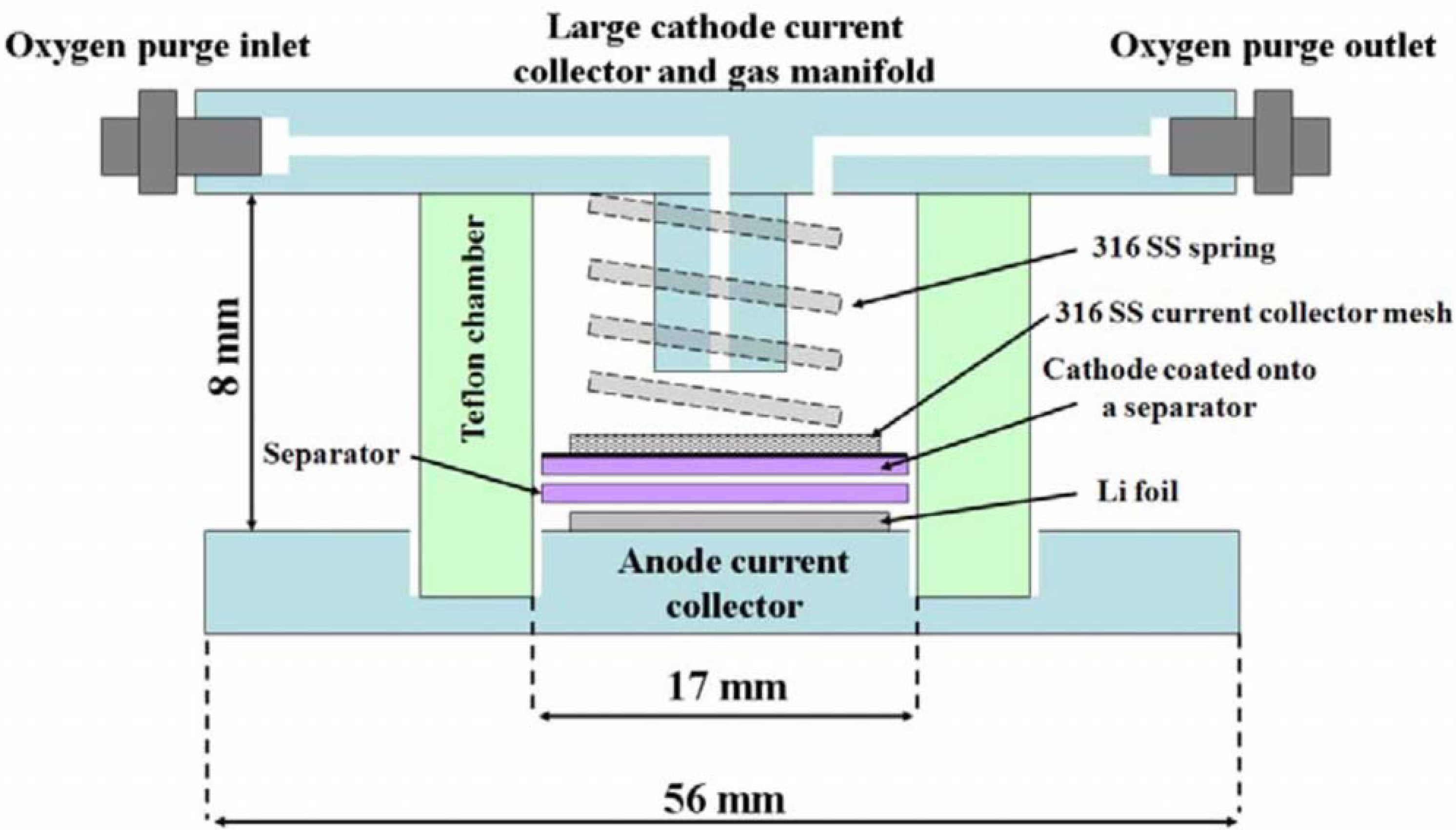
Battery Module





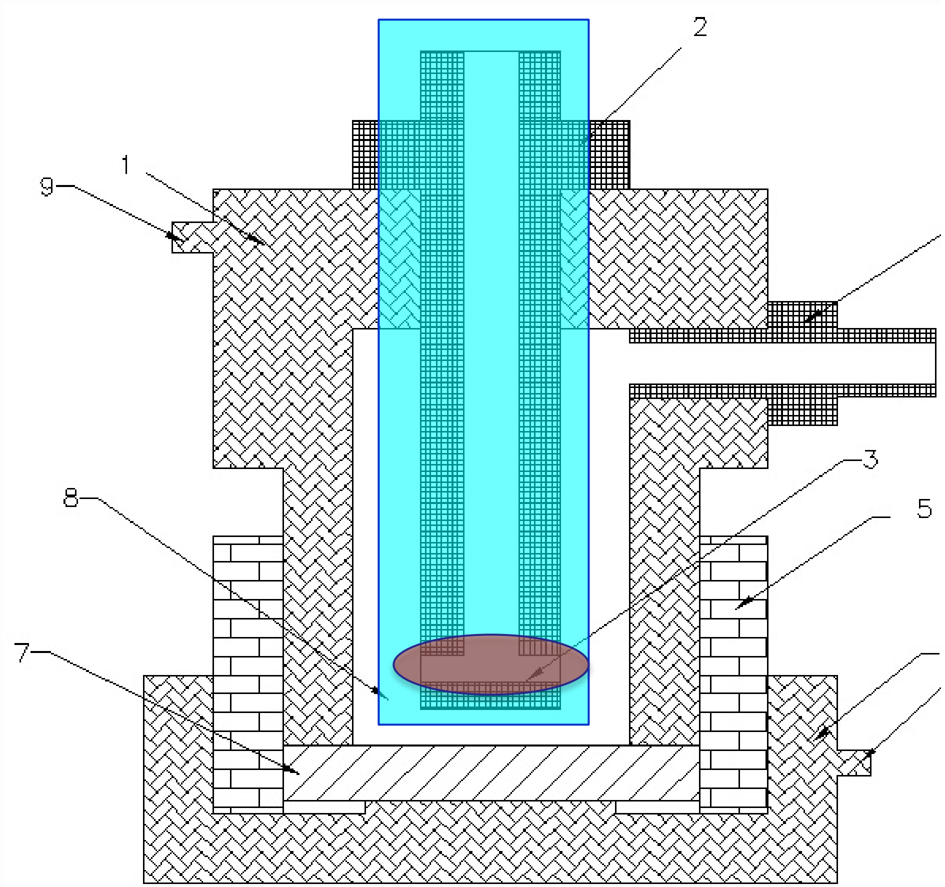
Swagelok Cell

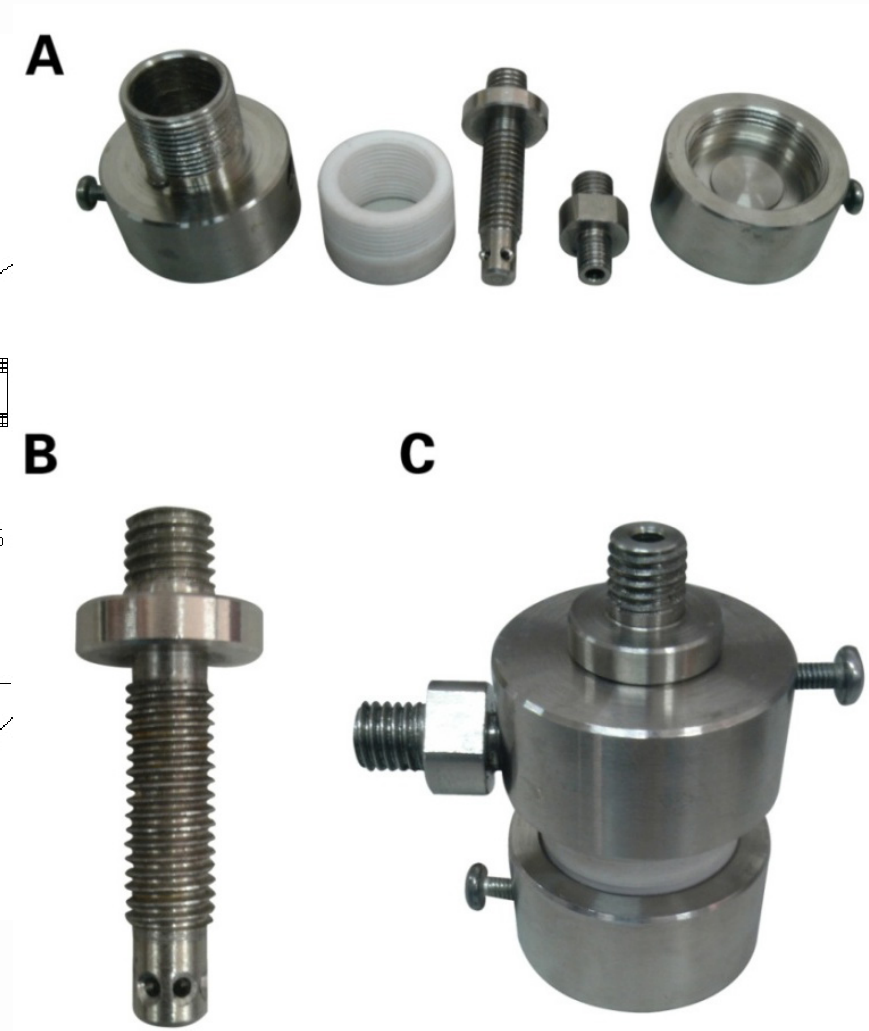
Journal of The Electrochemical Society, 1561 (2009)A44-A47



Yang Shao-Horn's Cell

Electrochemical and Solid-State Letters, 13(2010)A69-A72





SJTU Cell

Battery Module

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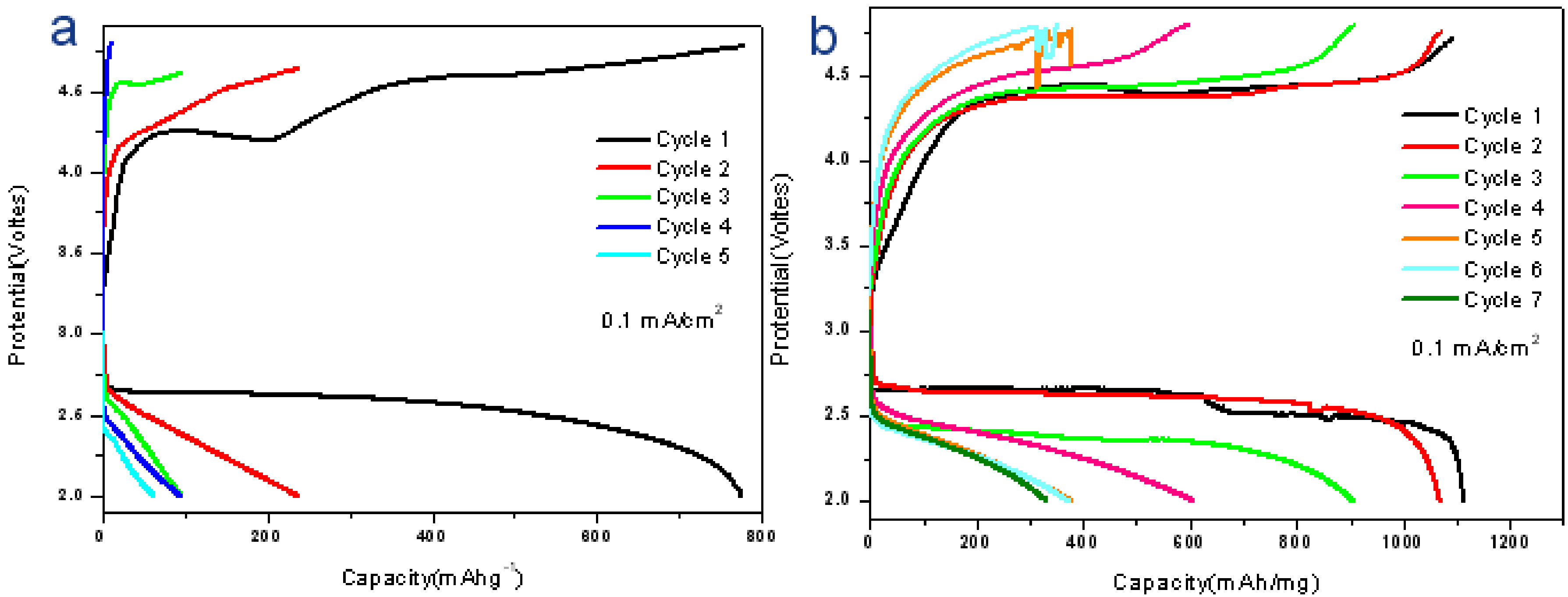
PC V.S TEGDME

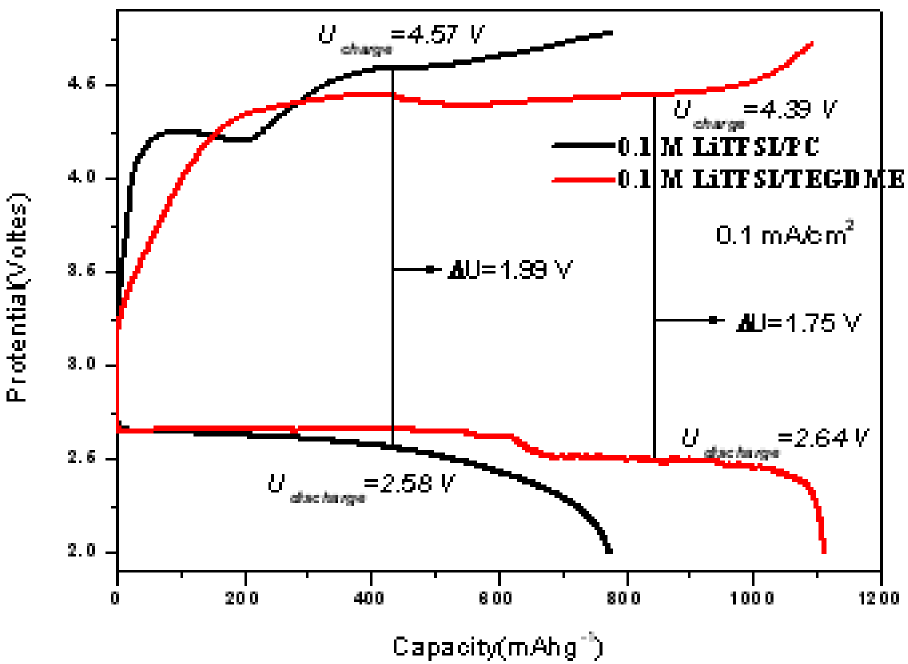
Effect of electrolyte on electrochemical performance



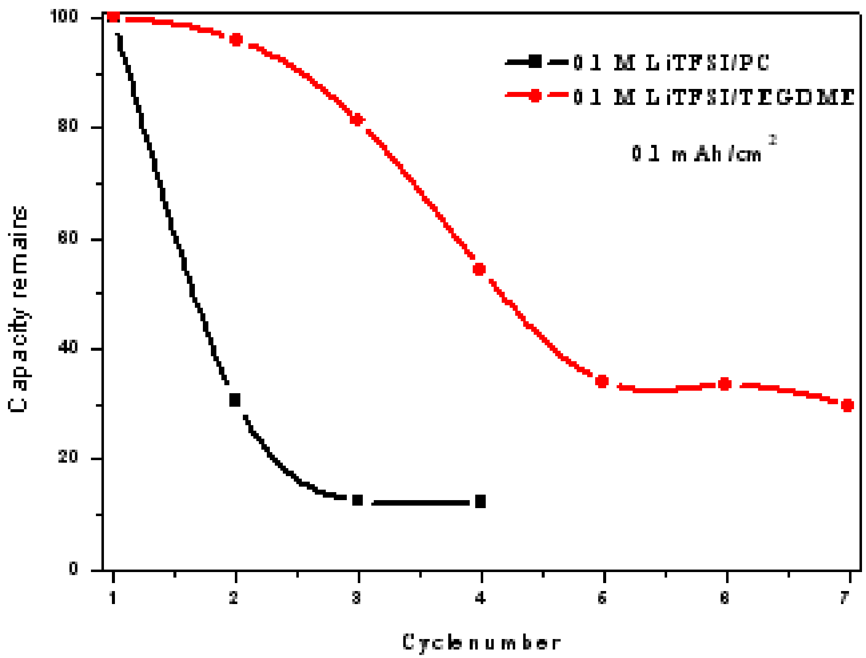
Discharge/charge curves using 0.1 M LiTFSI/ PC (a) and TEGDME (b) Li-O_2 cells at 0.1 mA cm^{-2} in oxygen

Notes: Specific capacities are based on per gram of the supports

PC V.S TEGDME



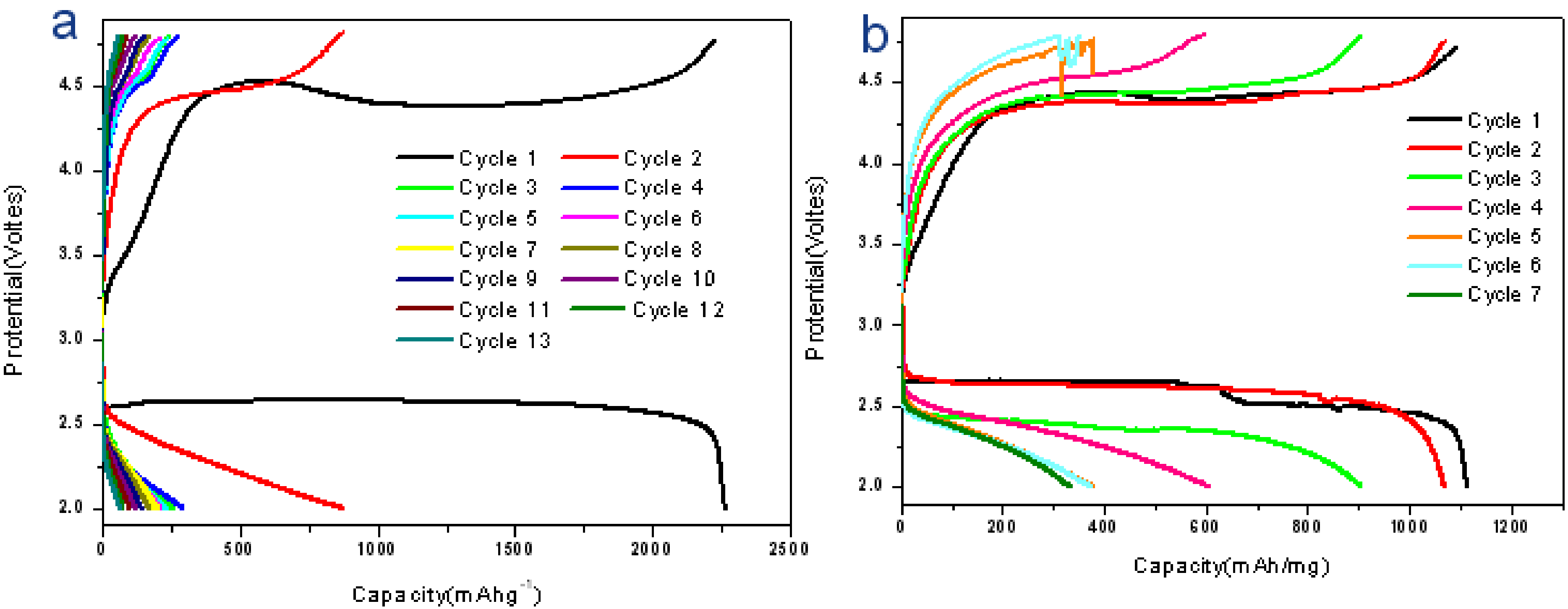
First discharge/charge curves of Li-O_2 cells using the 0.1 M LiTFSI/ PC and TEGDME as electrolyte at 0.1 mA cm^{-2} in oxygen



Discharge capacities remains versus cycle numbers using the 0.1 M LiTFSI/ PC and TEGDME as electrolyte at 0.1 mA cm^{-2} in oxygen

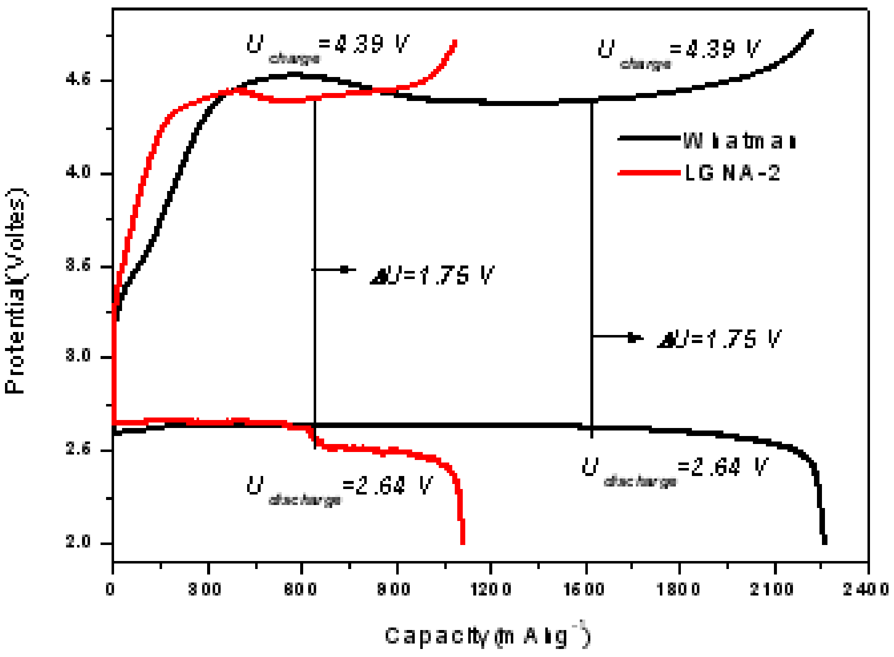
Whatman V.S LGNA-2

Effect of separator on electrochemical performance

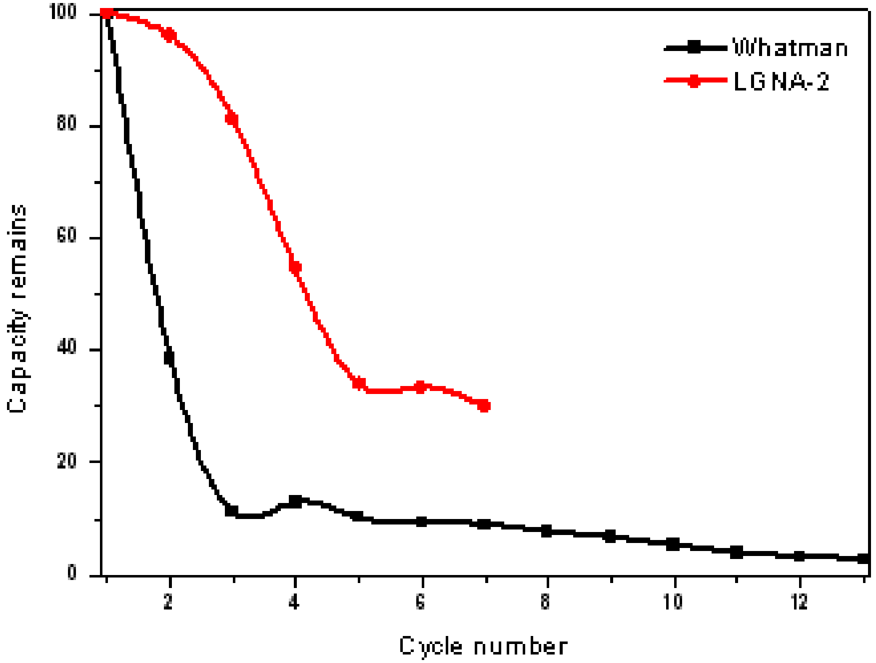


Discharge/charge curves using Whatman (a) and LGNA-2 (b) Li-O_2 cells at 0.1 mA cm^{-2} in oxygen

Whatman V.S LGNA-2



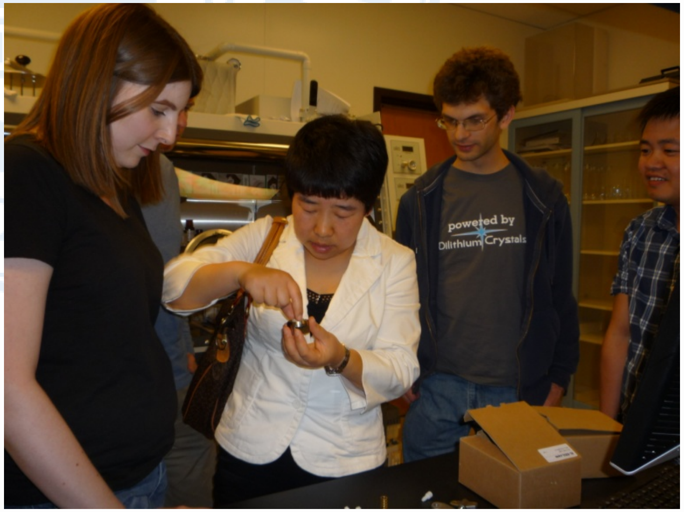
First discharge/charge curves of Li-O_2 cells using the Whatman and LGNA-2 as membrane at 0.1 mA cm^{-2} in oxygen



Discharge capacities remains versus cycle numbers using the Whatman and LGNA-2 as membrane at 0.1 mA cm^{-2} in oxygen

Collaborations

- ◆Prof Ma attended the U.S.–China Electric Vehicle and Battery Technology Workshop，August 1-6,2011,Chicago, USA
- ◆Prof Ma will attend the U.S.–China Electric Vehicle and Battery Technology Workshop on August 23-24, 2012,Boston, USA
- ◆Prof Xianxia Yuan visited UM on May 9-12, 2012
- ◆Dr. Max Radin and Dr.Feng Tian in Donald J. Siegel's group visited SJTU on October 17 to 26, 2011



Follow-on funding

Proposed Timeline for Major Tasks and Milestones

UM/Siegel:

A. (0-9 months)	Evaluate concentrations and diffusivities of intrinsic defects using "bulk morphology" of catalytic decomposition of Li_2O_2.
B. (9-12 months)	Dependence on temperature and pressure.
C. (12-21 months)	Metal catalyst screening.
D. (21-24 months)	Preliminary investigation of "interface morphology" of catalytic decomposition.

SJTU/Ma-Yuan:

E. (0-12 months)	Design, preparation, and characterization of catalyst structure and performance. Activation energy of Li_2O_2 decomposition.
F. (12-18 months)	Comparative study of experimental results and modeling analysis; Improvement and optimization of catalysts.
G. (19-24 months)	Evaluate dependence of battery performance on cathode structure.

Follow-on funding

Follow-on funding in China:

- ◆RBM 600,000, NSFC: Study on microstructure and key materials of cathode in lithium-air battery (21176155) (PI: Xianxia Yuan)
- ◆RMB 360,000, NSFC: Electrochemical basic study on the key materials for Li-air cell stack design (21073120) (PI: Xiaozhen Liao)
- ◆RMB300,000, NSF Shanghai: Oxygen reduction reaction Catalysts preparation and its fuel cell and Li-air battery application (10JC1406900) (PI: Xianxia Yuan)
- ◆RMB 8,000,000, Sinopoly Battery Research Center (SBRC,Hong Kong), Next generation battery development for electric vehicle application (2011.09-2015.08) (PI: Zi-Feng Ma)

Publications

◆**Yuan Xianxia, Jia Chao, Ding Xin-Long, Effects of heat-treatment temperature on properties of Cobalt-Manganese-Boride as efficient catalyst toward hydrolysis of alkaline sodium borohydride solution , *International Journal of Hydrogen Energy*, 2012,37(1):995-1001**

◆**Li He, Xiao-Zhen Liao, Ke Yang, Yu-Shi He, Wen Wen, Zi-Feng Ma, Electrochemical Characteristics and Intercalation mechanism of ZnS/C Composite as Anode Active Material for Lithium-ion Batteries, *Electrochim. Acta*, 2011，56（3）：1213-1218**

◆**Qiang Gong, Yu-Shi He, Yang Yang, Xiao-Zhen Liao, Jun Chen, Zi-Feng Ma, Synthesis and electrochemical characterization of $LiFePO_4$/C-Polypyrrole composite prepared by a simple chemical vapor deposition method, *Journal of Solid State Electrochemistry,*2012,16（4）：1383-1388**

◆**Hui-Juan Zhang, Hai-Chuan Kong, Xianxia Yuan, Qi-Zhong Jiang, Junhe Yang, Zi-Feng Ma, Influence of metal precursors on the catalytic activity and structure of non-precious metal electrocatalysts for oxygen reduction reaction, International Journal of Hydrogen Energy, DOI: 10.1016/j.ijhydene.2012.03.049**

- Hong Wang, Xiao-Zhen Liao, Zi-Feng Ma, A novel Co(phen)/C catalyst for Lithium air batteries, Chinese Science Bulletin, 2012, 57(16):1959-1963
- Hui-Juan Zhang, Xianxia Yuan, Zi-Feng Ma, Zongping Shao. Synthesis and characterization of binary non-precious metal electrocatalyst for oxygen reduction reaction in proton exchange membrane fuel cells. Electrochimica Acta. Doi: 10.1016/j.electacta.2012.06.011.
- Hai-Chuan Kong, Xianxia Yuan, Xiao-Yun Xia, Zi-Feng Ma. Effects of preparation on electrochemical properties of CoTMPP/C as catalyst for oxygen reduction reaction in acid media. International Journal of Hydrogen Energy. DOI: 10.1016/j.ijhydene.2012.03.025.
- Xianxia Yuan, Zi-Feng Ma, et al. Properties of Co-PPy-TsOH/C prepared from various cobalt precursors as catalyst towards oxygen reduction reaction. Applied catalysis B: environmental, revised

Patent application filed

1 Invention patent: Hao-Dong Sha, Xianxia Yuan, Zhong Ma, Zi-Feng Ma. A novel mould for lithium-air battery. Application number: 201210134349.5

2 Invention patent: Hong Wang, Xiao-Zhen Liao, Zi-Feng Ma, A novel cathode catalyst and preparation method for lithium air battery. Application number: 201110131455.3

3 Utility model patent: Zhong Ma, Xianxia Yuan, Hao-Dong Sha, Zi-Feng Ma. A novel mould for lithium-air battery. Application number: 201220197482.0

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