High Energy Density Battery of Li-air and Li-CF_x: some hints from mechanism study

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Scalable energy storage beyond Li ion battery – Material Aspect, USA, Oct.7-8, 2010

Outline

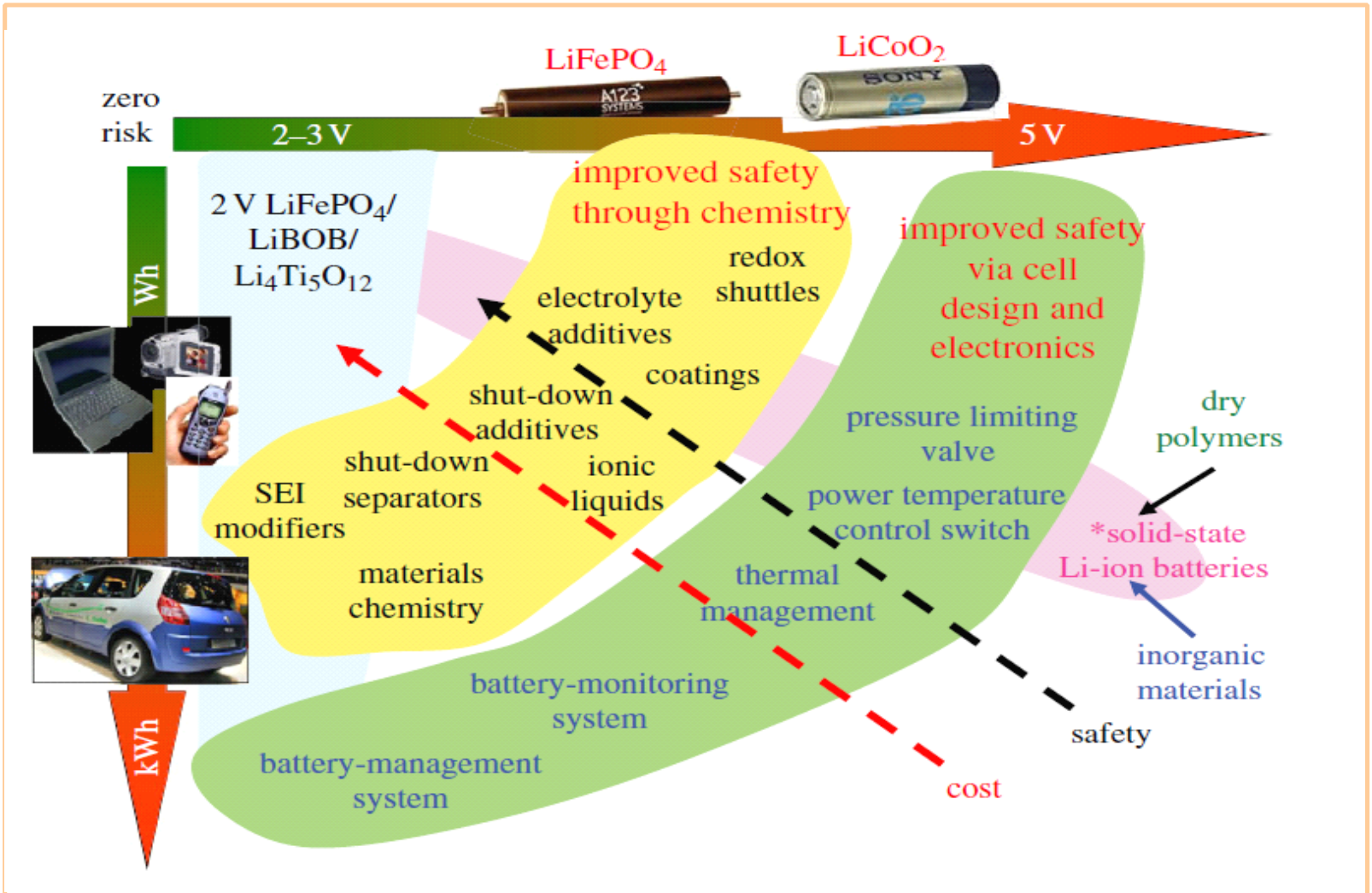
- Research Background (EV and Grid application)

- The effects of solvents and salts on the electrochemical reduction of oxygen in organic solvents

- Some preliminary results about Li-CF_x battery

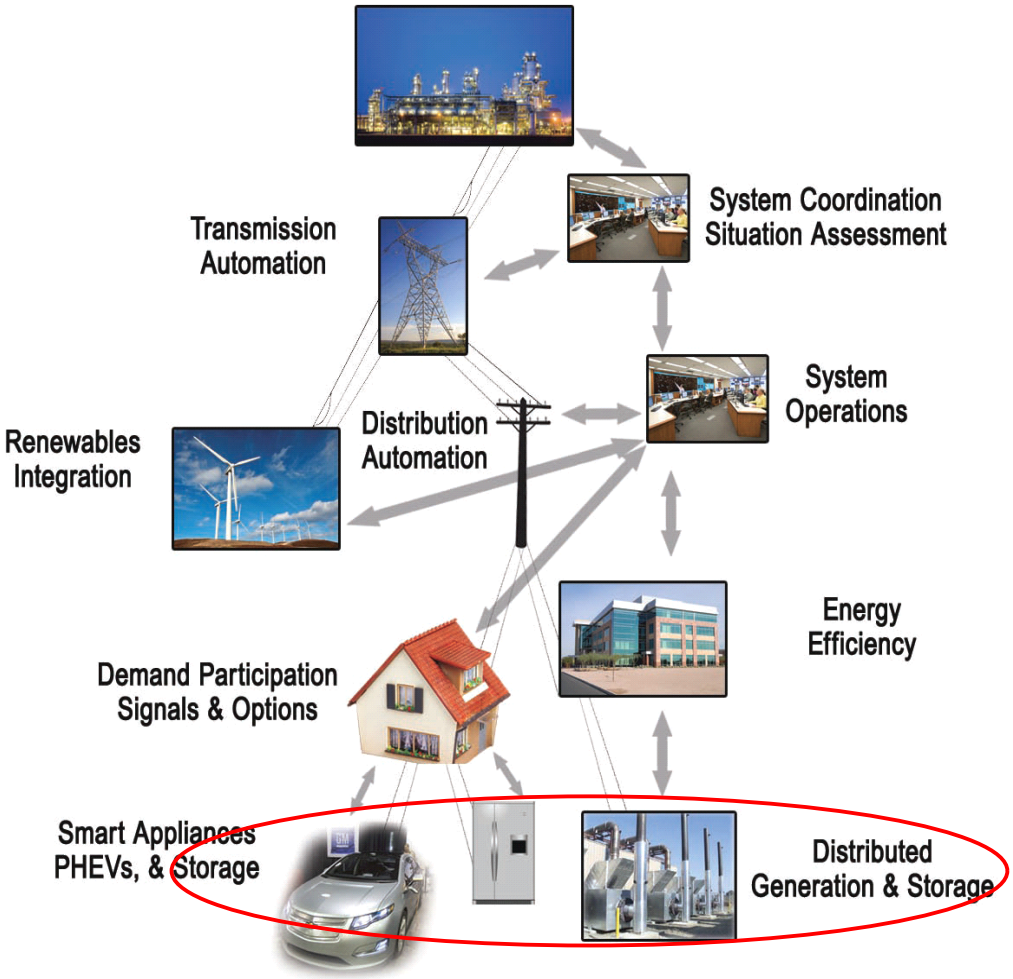
- Conclusions

Research Background: low-medium scale application



J.-M. Tarascon, *Phil. Trans. R. Soc. A 2010*, ***368, 3227-3241***

Research Background: Scope of Smart Grid Concerns



A smart grid uses digital technology to improve reliability, security, and efficiency (both economic and energy) of the electric system from large generation, through the delivery systems to electricity consumers and a growing number of distributed-generation and storage resources

Adapted from: Smart grid system report, DOE, 2009

Demonstration of Li-ion battery in electricity storage

http://www.altairnano.com

Altairnano 1 MW,

Single cell: $LiMn_2O_4/Li_4Ti_5O_{12}$
Voltage: 2.5 V
Capacity: 50 Ah
Weight: 1.6 kg

http://ww.byd.com.cn

BYD, 1 MW,

Single cell: $LiFePO_4/C$
Voltage: 3.25 V
Capacity: 200 Ah
Weight: 6.7 kg

Challenge issues of large-scale energy storage by electrochemical power sources

Characteristics in large scale storage:

Scalable (~MW → GW) ,

Long-life(> 300000 cycles),

Safe,

Low-cost,

Fast-response and environmental-friendly

Some challenge issues

- **It is not easy to scale up electrochemical power sources (for single cell, normally low voltage, < 5V single cell..), thus uniformity , assembling and management of battery system is more important supposing the system is defined**

- **For single cell, chemistry(or electrochemistry) should be considered carefully according to above-mentioned factors**

- **In a defined system, materials is one of determining factor for good performance.**

Systems and Materials Aspects: Problems

- Redox-flow cells: Stability of Electrode /current collector/membrane, high electrolyte concentration and stability…??,

- Na-S battery: Stability of current collector, sealing/safety, cost, …

- Li-ion battery: Long cycle life, safety, low-cost and large-scale….

The energy storage challenges for Chinese economic growth

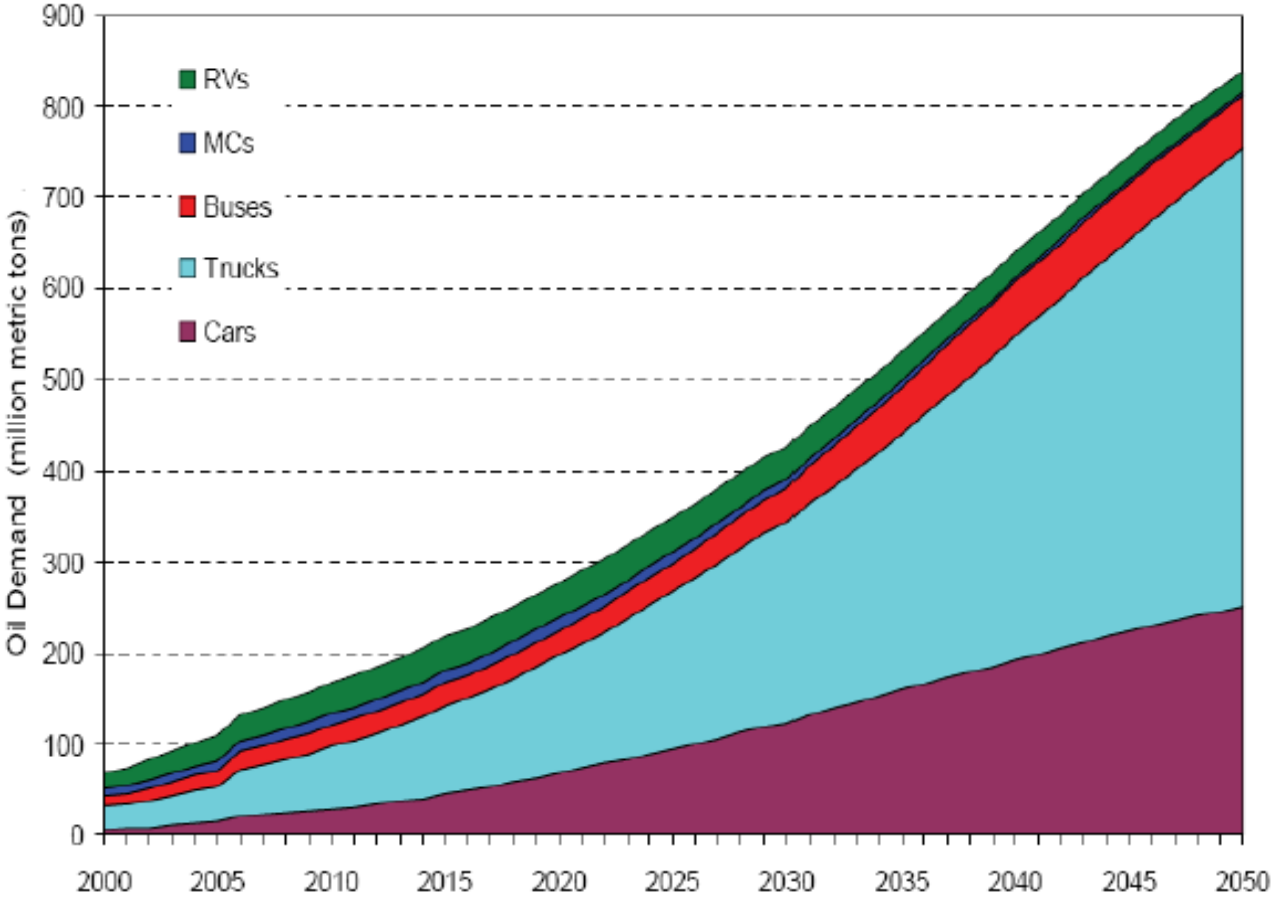
- China is becoming an important energy consumers in the last thirty years and will be an important player in the energy consumption in the next thirty years

- Renewable energy will be a fastest growing ratio in the energy consumption of China, thus electrochemical energy storage is important way to realize.

- China have setup several national programs to develop electrochemical energy storage for EV and smart grid, either in Li-ion battery or redox flow battery and Na-S battery

- For example, China plans to spend 500billion RMB to develop electric vehicles(PHEV or EV), and 1 billion RMB for battery R&D in High-tech program in the next five years…

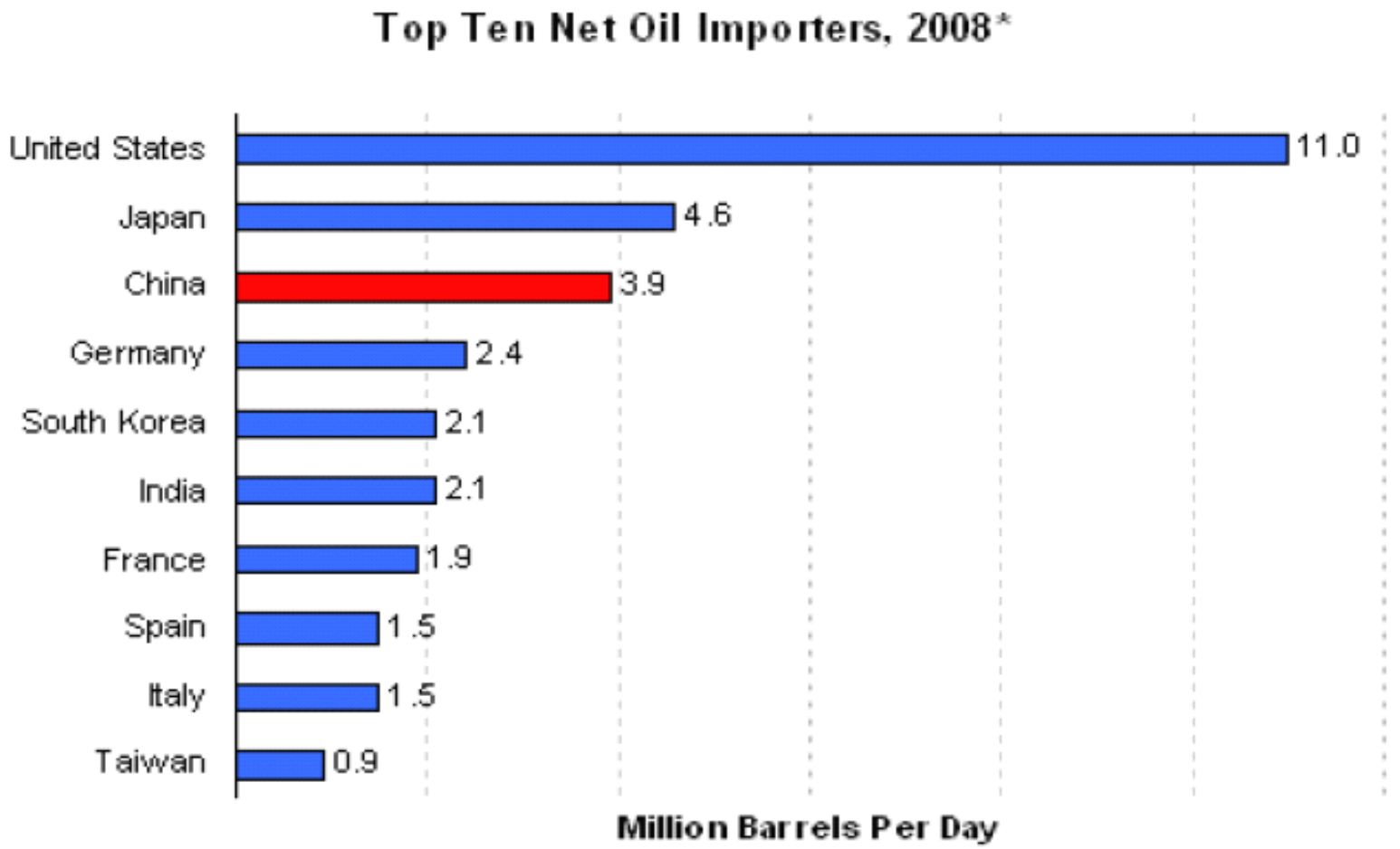
Chinese vehicle fleet projected to grow rapidly through 2050, with a corresponding growth in oil demand



Source: "Projection of Chinese Motor Vehicle Growth, Oil Demand, and CO2 Emissions through 2050", Argonne National Lab, 2006.

Newest News: China is becoming the No.1 car-maker country in the world in 2009, car-consumption in China also increase sharply in recent years.

China is the third largest oil importing country after US and Japan



Source: EIA Short-Term Energy Outlook (July 2009)

*estimate

- How about the system we studied…

- How choose the next energy-storage system beyond Li-ion battery,

Li-based battery ??

Li-air battery: a possible to way to get high energy density

- High voltage: ~ 2.8V (non-aqueous system)

- High capacity of both cathode (O_2, > 1000mAh/g) and anode materials (Li, > 4000mAh/g)

- Easy to get reactant such as O_2 from air directly, may combine with advantage of fuel cells and batteries…

Questions and Problems:

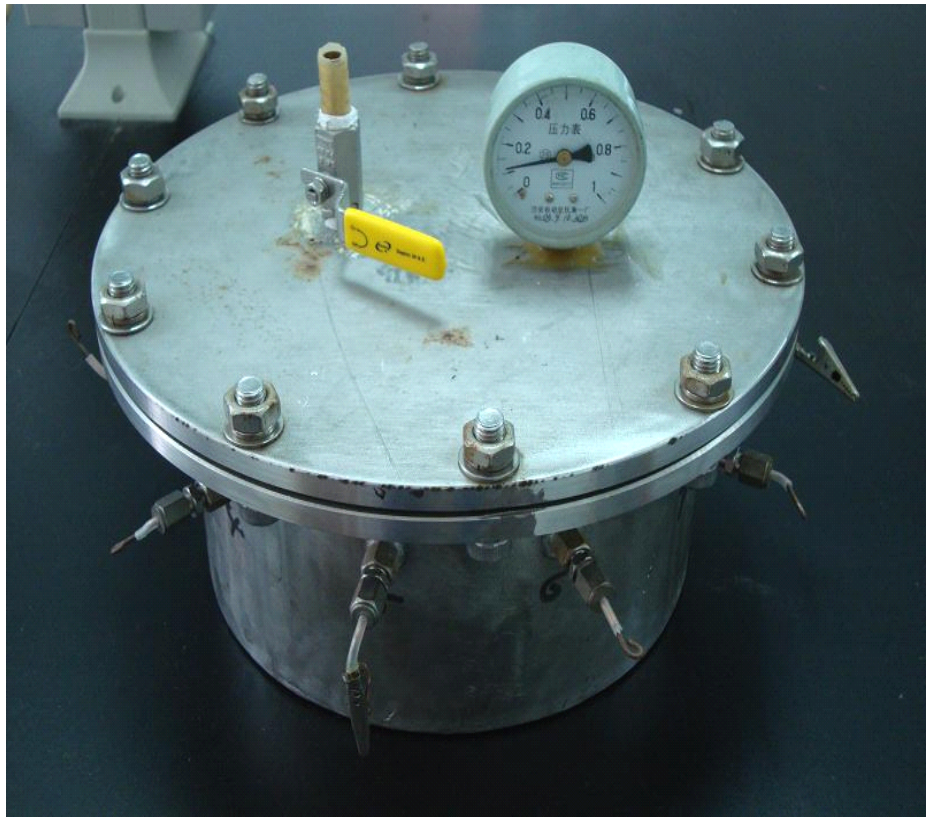
High performance of oxygen electrode performance (rate performance, reversibility of the reaction, and reaction mechanism is not very clear) .

Rechargeability of Li anode, and SEI …

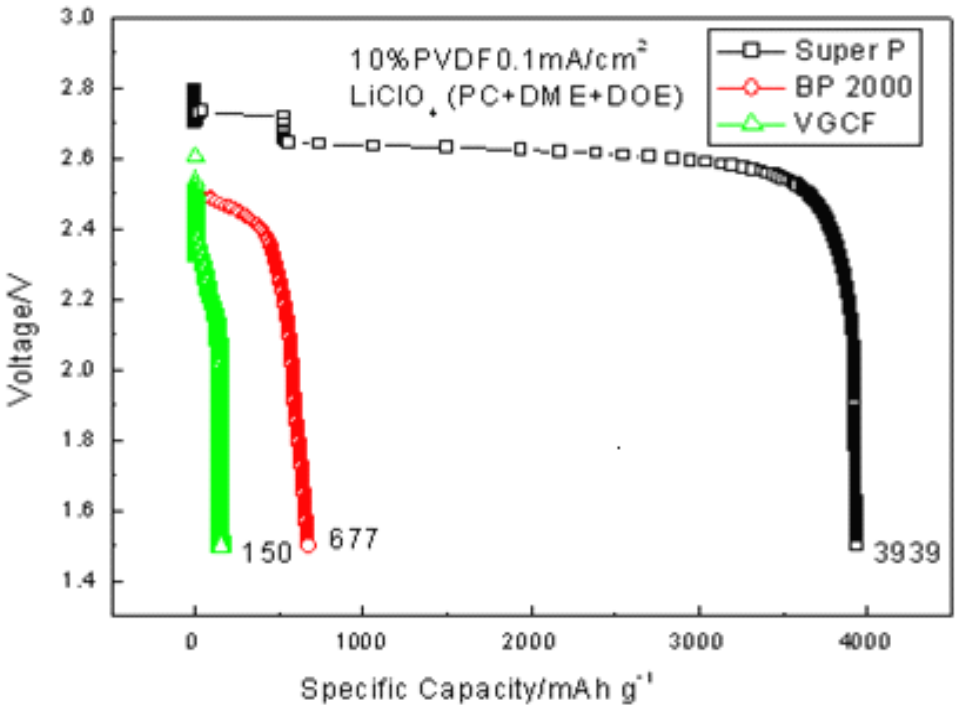
Electrochemical study of oxygen reduction in non-aqueous solution

Cathode: carbon + binders; Anode: Li, Reference Ag/AgCl

Electrolytes: Different salts system as indicated

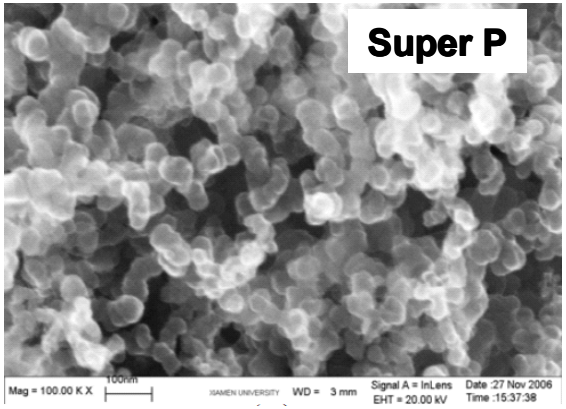


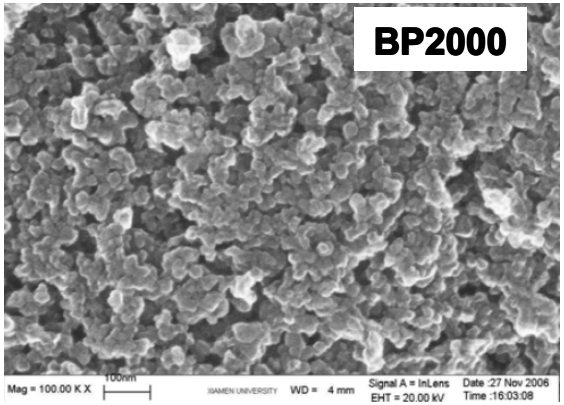
The effects of types of carbon on the oxygen electrode performance

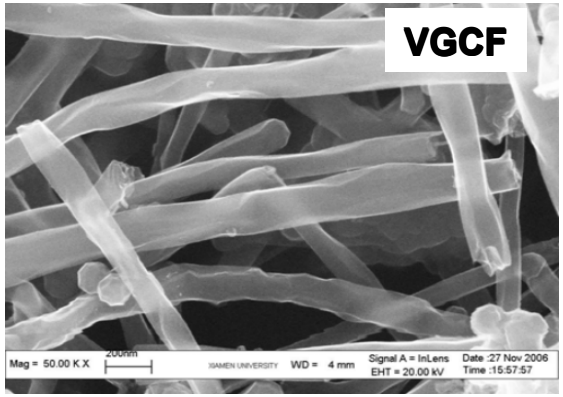


Discharge curves of the oxygen electrode with various carbon material

Carbon	Super P	BP2000	VGCF
Specific Surface Aera (m^2g^{-1})	59.6	1282.6	11.1







The effects of the binder on the oxygen electrode performance

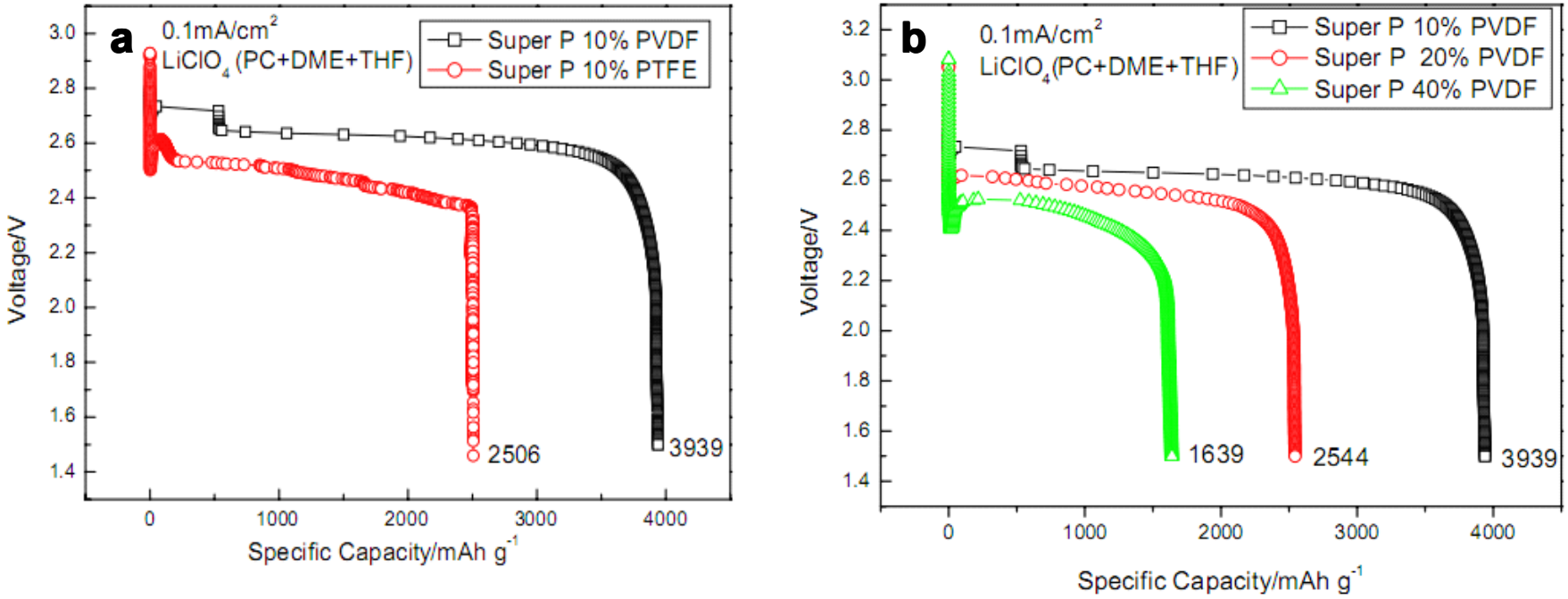
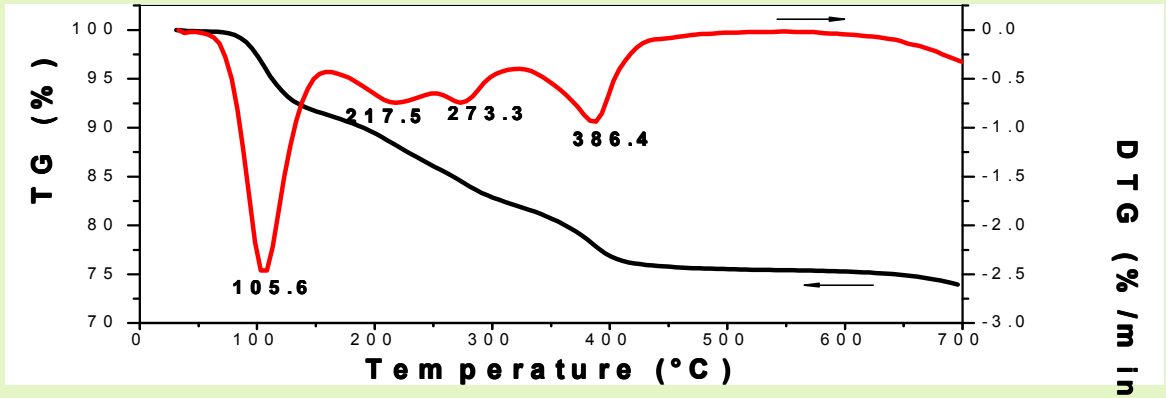
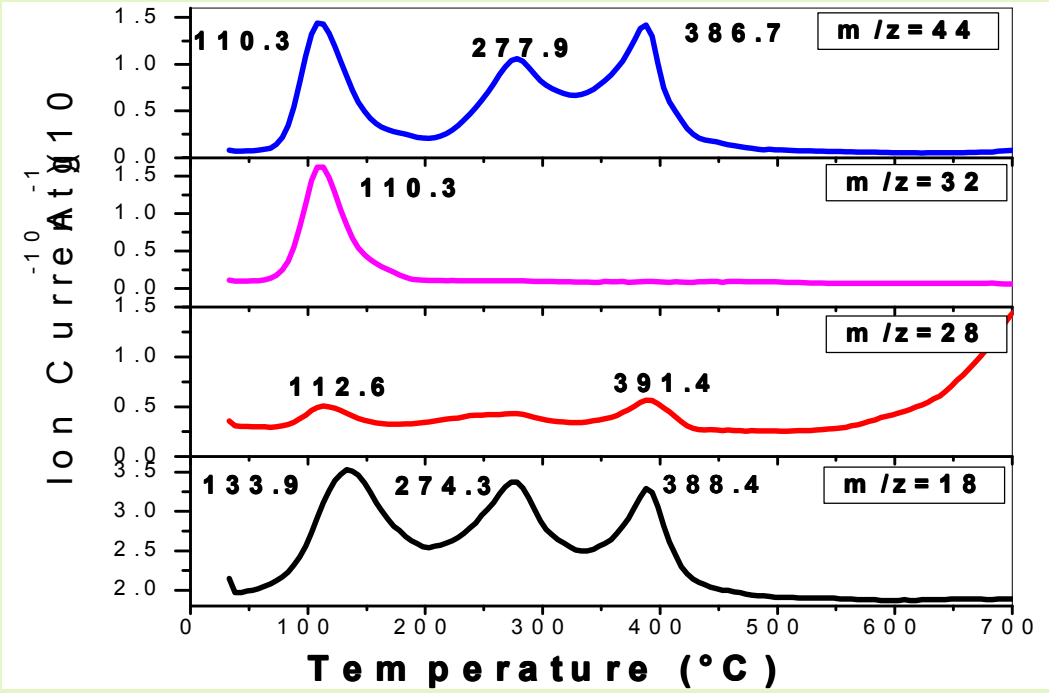


Figure Discharge curves of the oxygen electrode with: a) different kinds of binders; b) different content of PVDF.

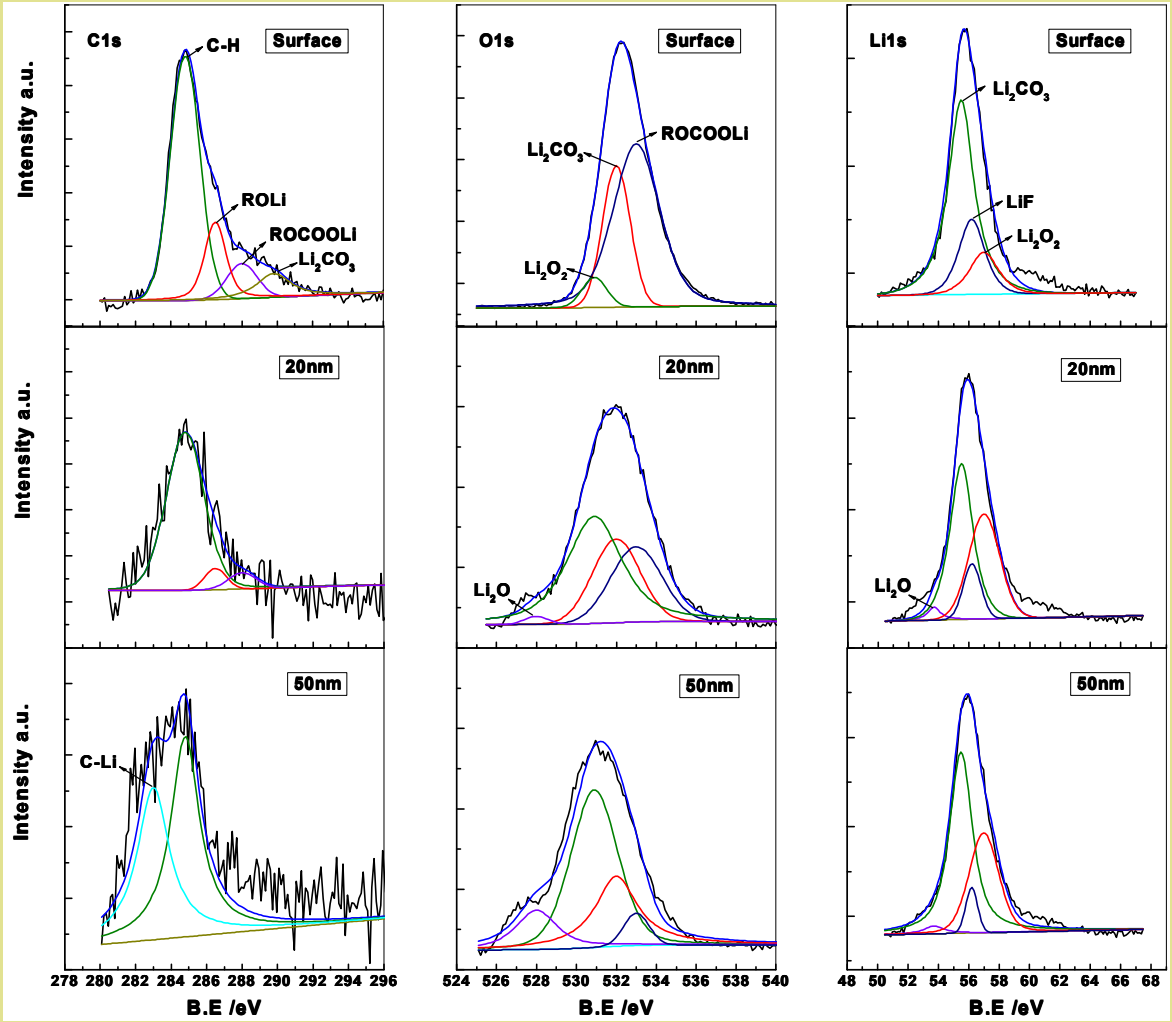
TG-MS experiments of the cathode after discharging





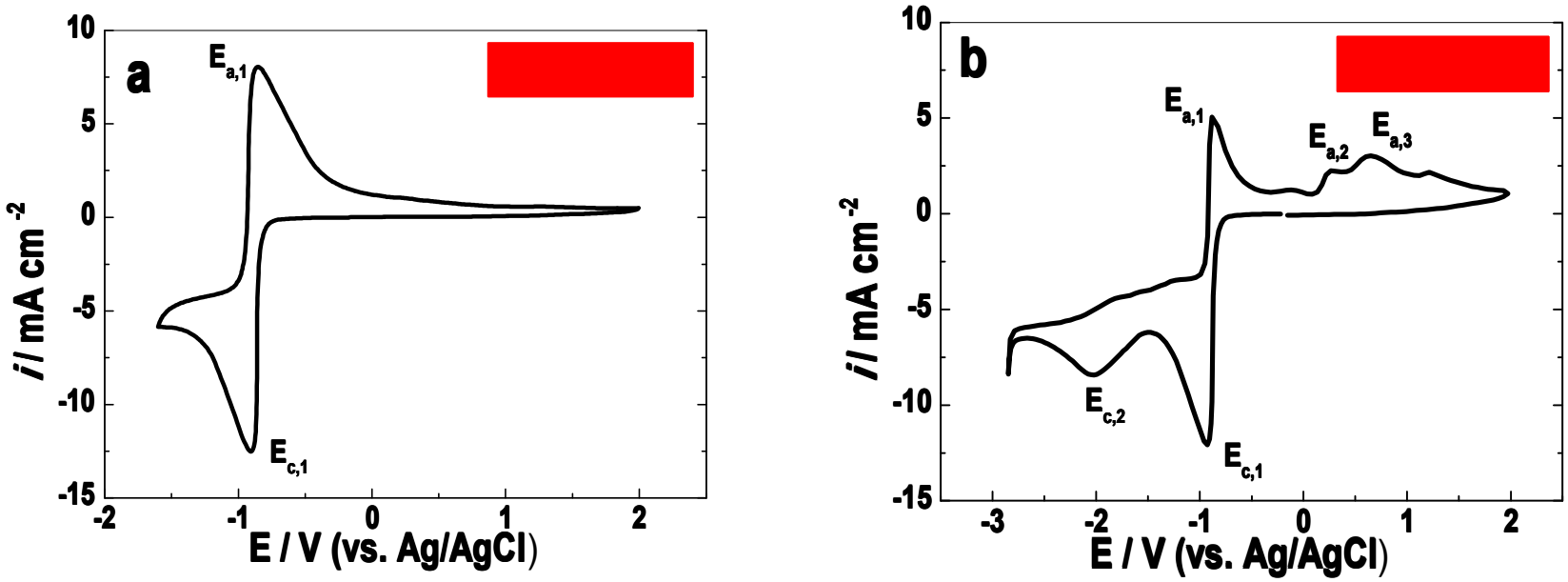
The weight loss between 50℃ and 150℃ is attributed to the decomposition of LiO2 and ROCOOLi, and the loss between 330℃ and 450℃ is due to the produced gas of H_2O ,CO and CO2 coming from the reaction of Li_2O_2 and PVDF.

XPS analysis of surface species on the cathode materials



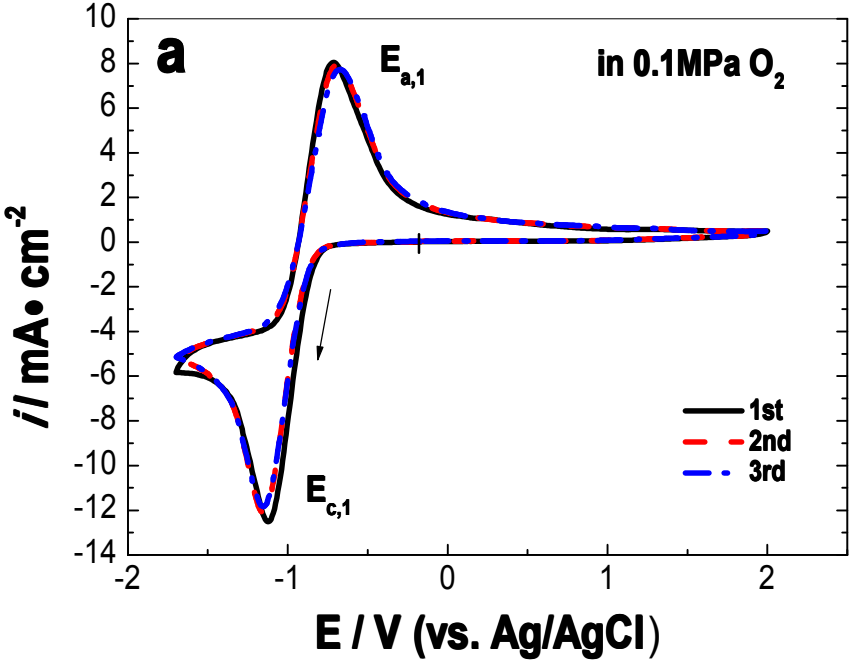
The results indicate that the main discharge product is Li2O2, though there are some ROCOOLi and Li2CO3 due to the reaction between the oxygen radical and the solvent during the discharge process.

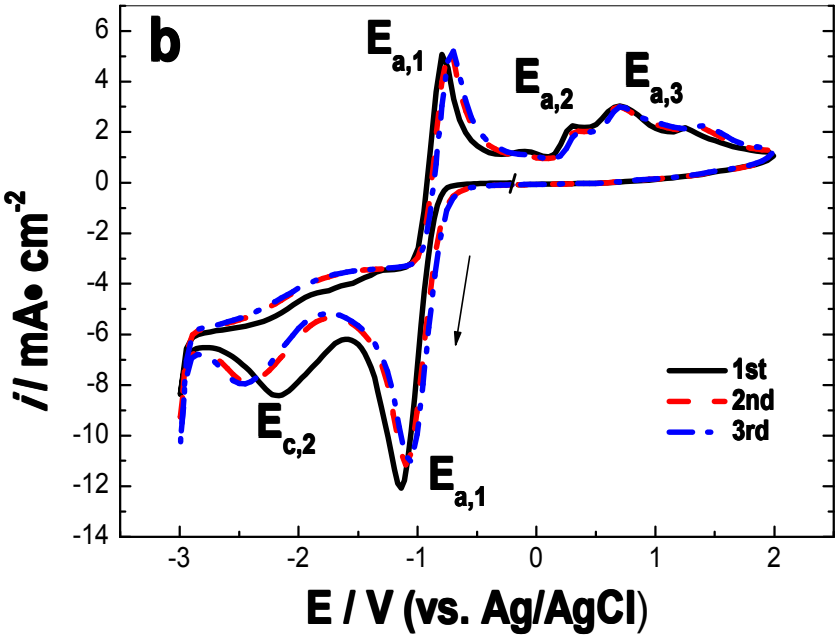
Reversible Single electron reduction of oxygen: $TBAPF_6$ / MeCN



CV for ORR at a GC electrode in 0.1M $TBAPF_6$/MeCN electrolyte (iR corrected), scan rate: 100 mV/s

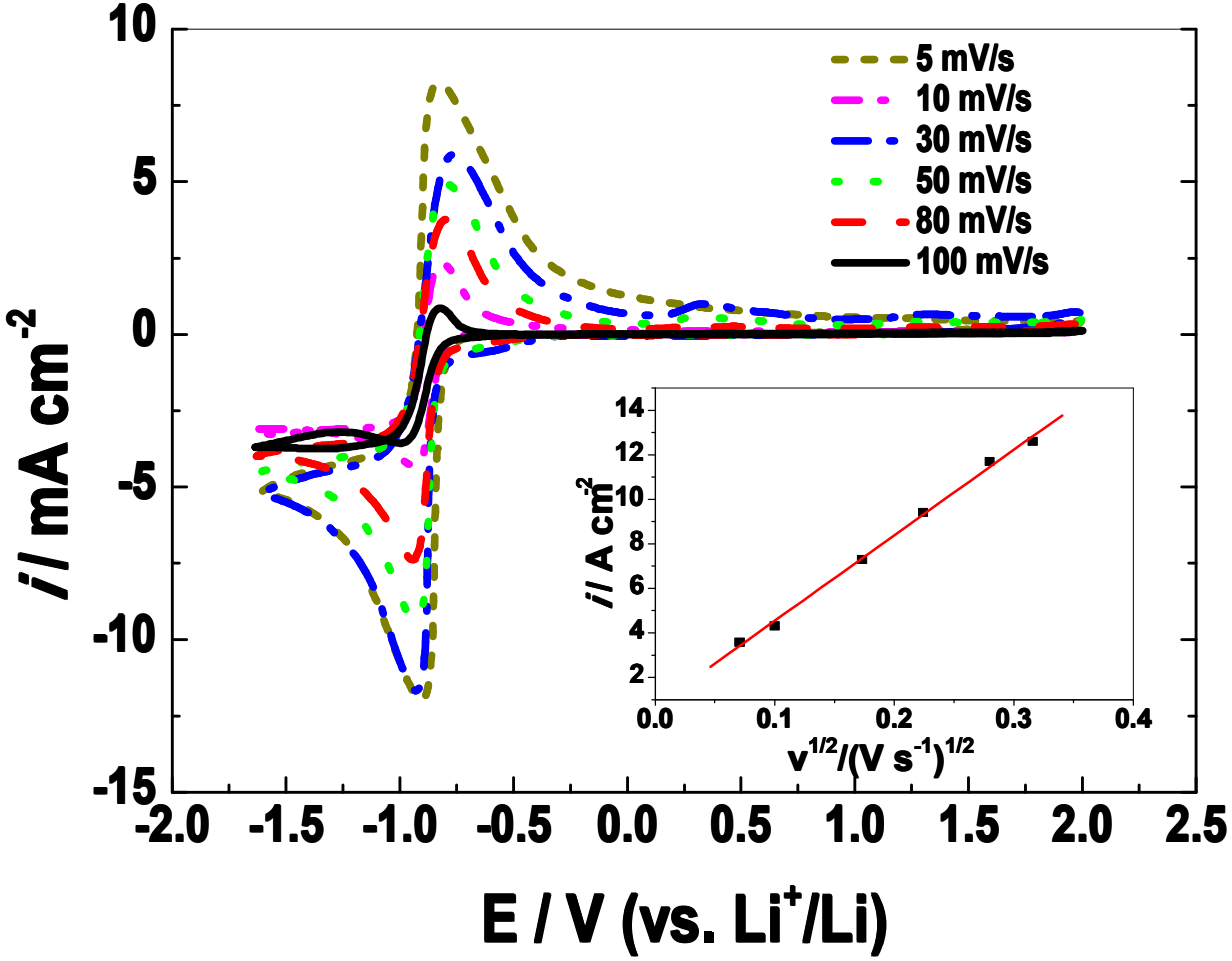
Good cyclic stability of oxygen reduction in $TBAPF_6$ / MeCN





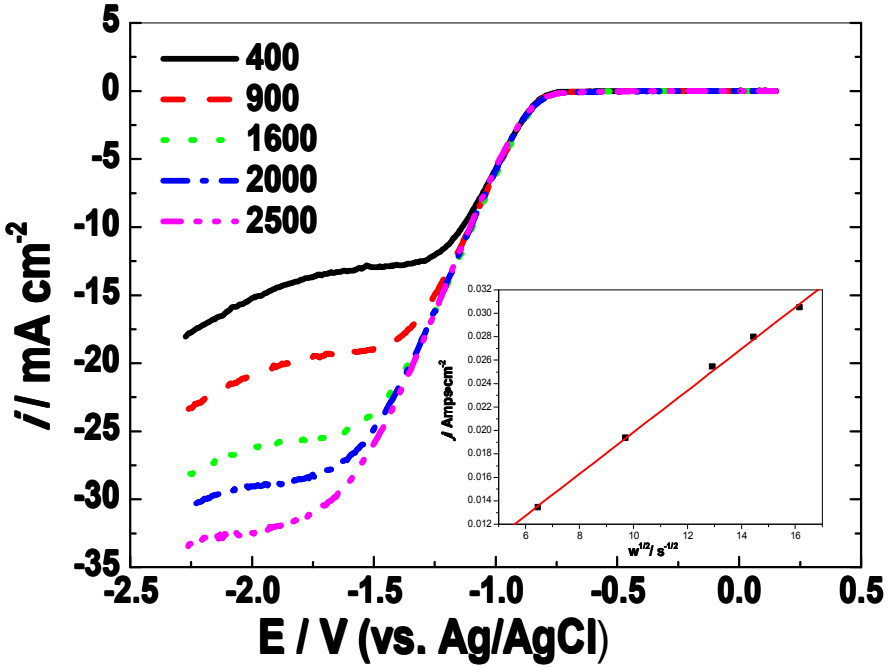
CV curves for ORR at a GC electrode in 0.1M $TBAPF_6$/MeCN electrolyte (iR uncorrected), scan rate: 100 mV/s

Diffusion-controlled reaction of oxygen reaction



CV curves of oxygen reduction at GC electrodes at different scan rates in 0.1M $TBAPF_6$/MeCN; the inset shows the relation of peak currents and square roots of the scan rates.

RRDE experiments of oxygen reduction process



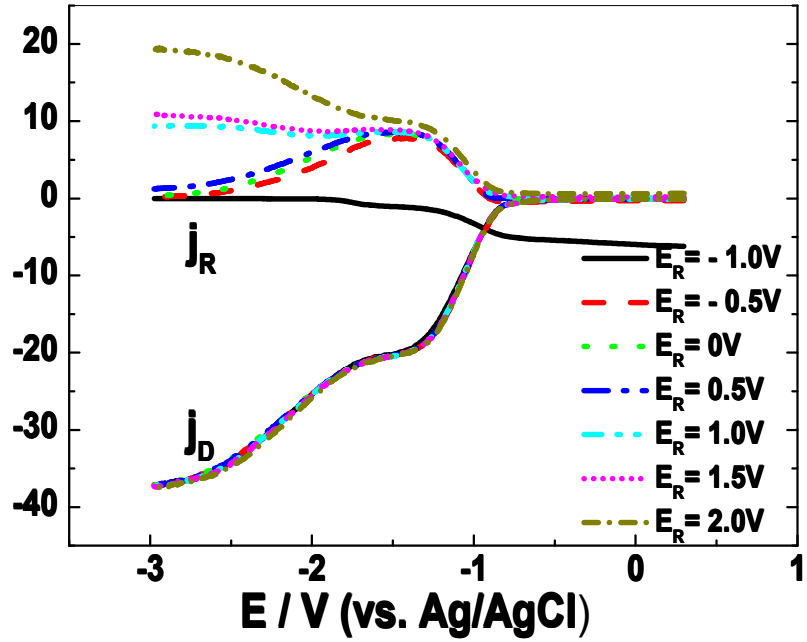
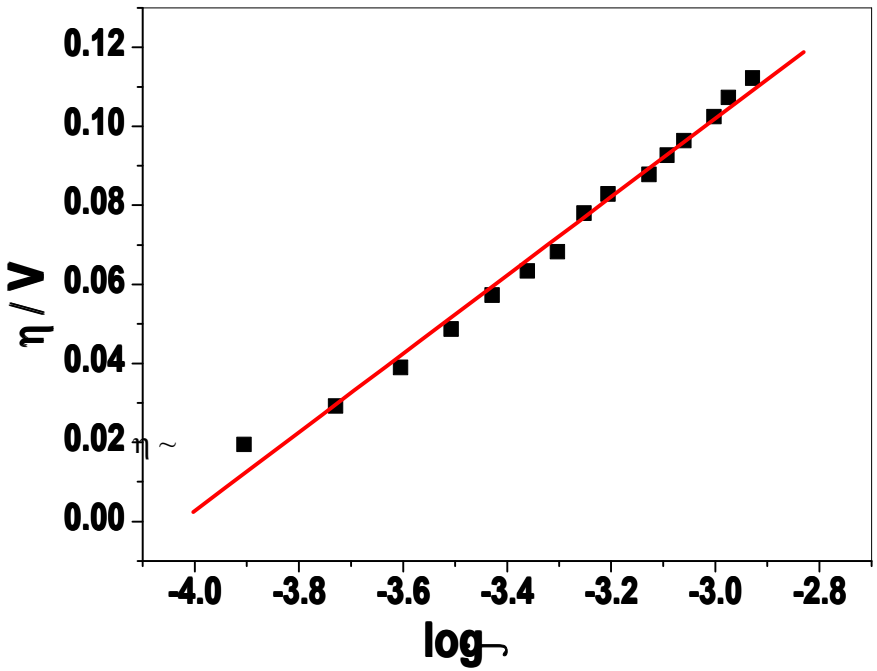


Fig. a) RDE of GC rotating disc electrode at various rotation speeds; b) RRDE plots for the electrochemical process of oxygen at the rotating rate of 900 rpm in 0.1 M $TBAPF_6$/MeCN, sweep rate: 100 mV/s.

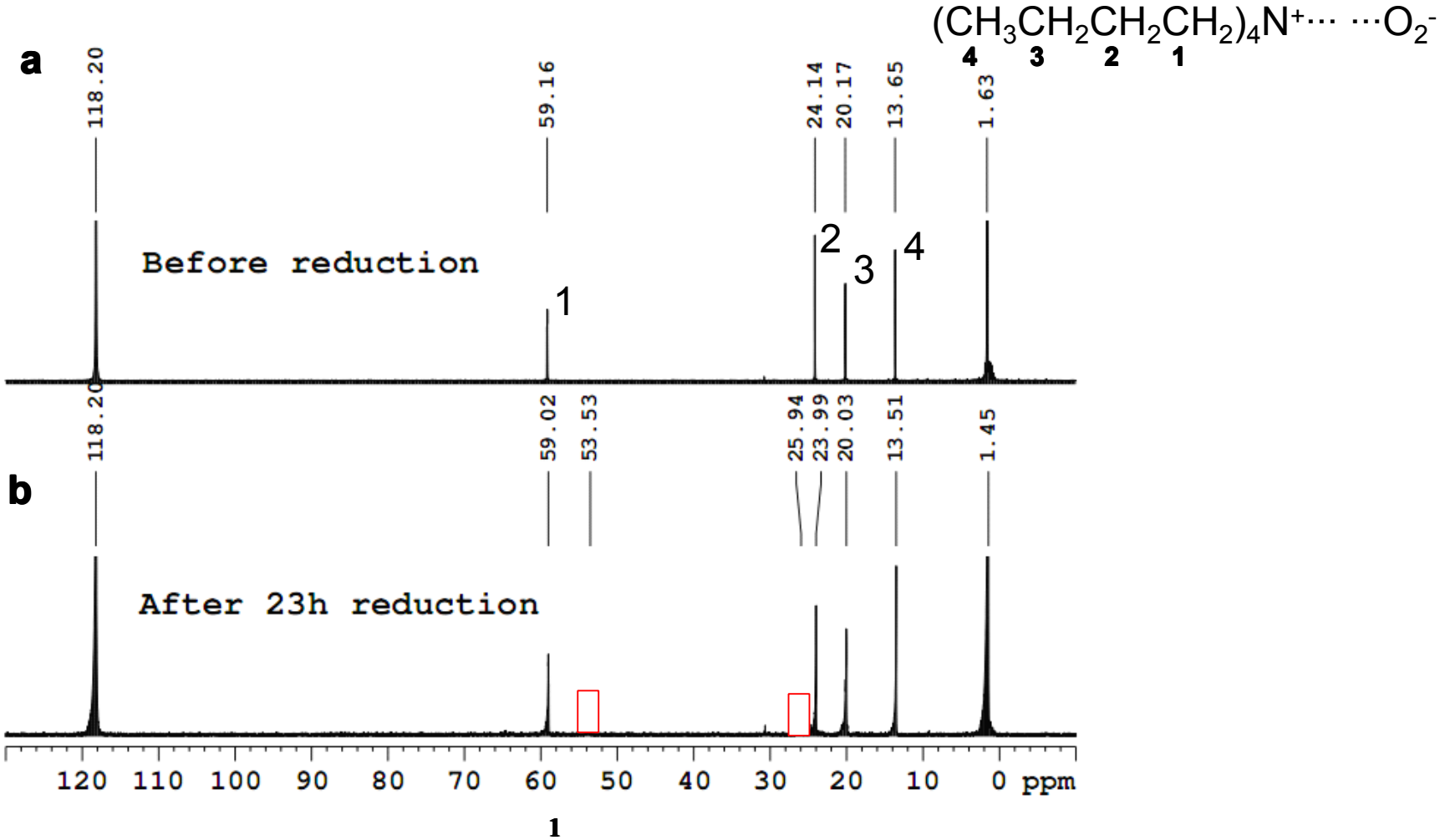
$$j_{lim} = 0.62\, nFD^{2/3}\omega^{1/2}\upsilon^{-1/6}C \Longrightarrow \mathbf{n = 0.87}$$

Tafel-Plot of oxygen reduction in 0.1M $TBAPF_6$ / MeCN



Tafel-plot for the electrochemical process of oxygen in 0.1 M TBAPF6/MeCN

NMR detection of reactive intermediates



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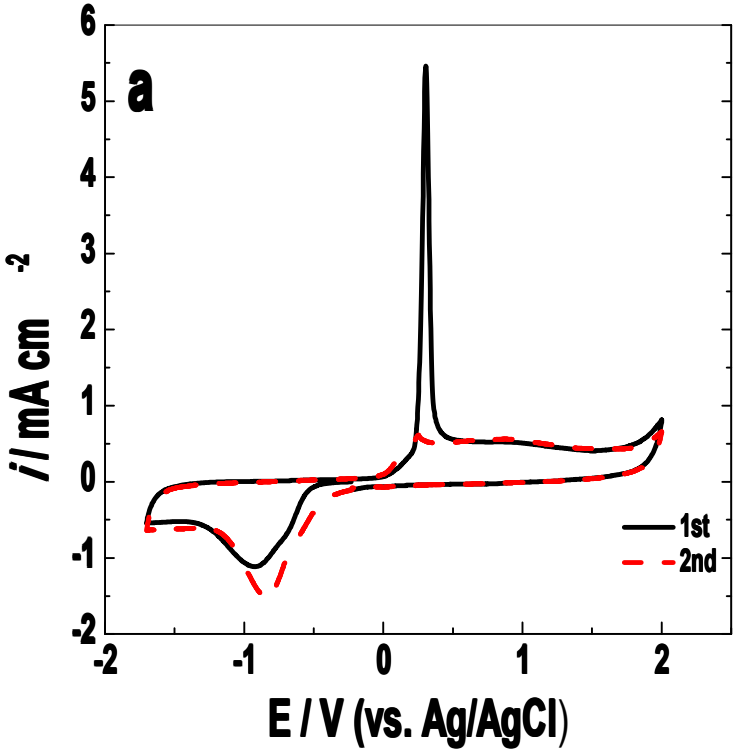
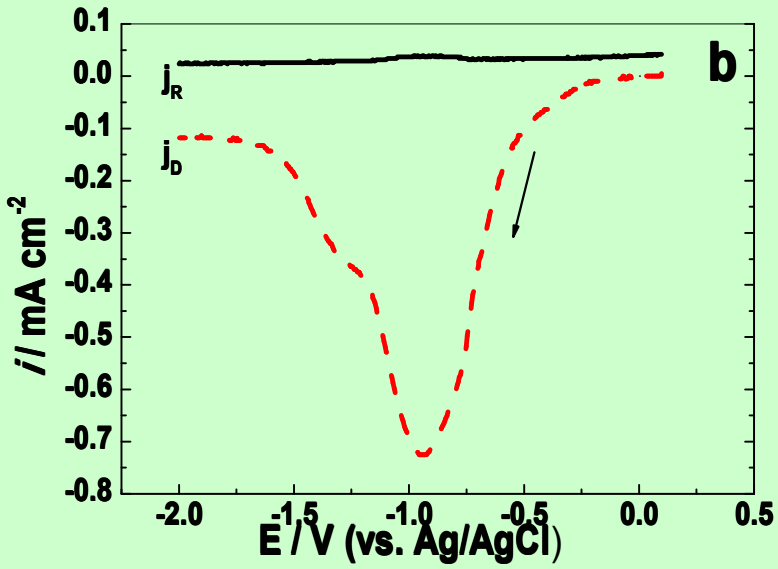
13C NMR spectra of electrolytes of 0.1M $TBAPF_6$/MeCN: (a) before reduction of oxygen; (b) after 23 h electrolytic reduction of oxygen at -2.5V

Cation effects on the oxygen reduction:0.1M$LiPF_6$ / MeCN

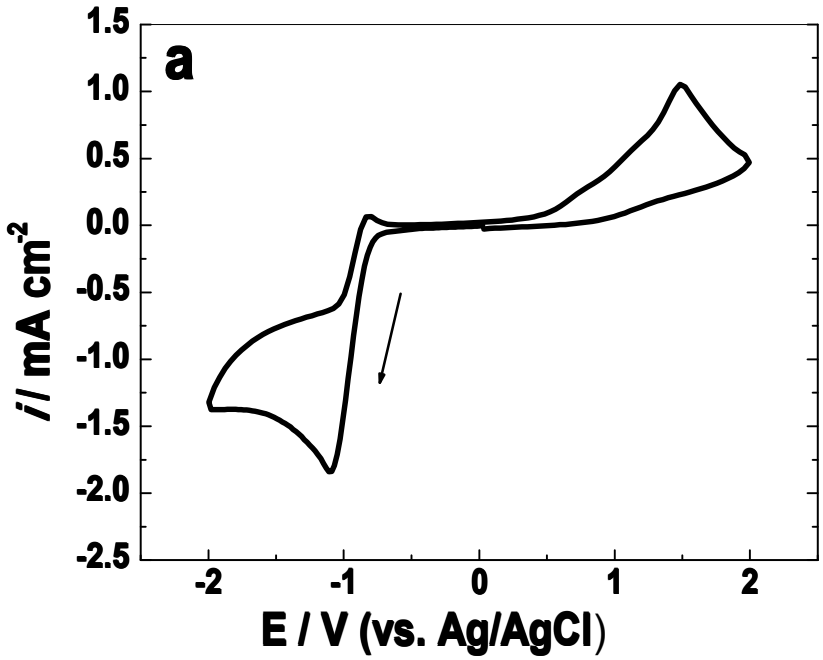




Irreversible formation of un-dissolvable species such as LiO2…

Fig. a) CVs for the reduction of oxygen at a GC electrode, b) RRDE curves at the rotating rate of 900 rpm in 0.1M $LiPF_6$/MeCN. Scan rate: 100 mV/s.

The effects of solvents: carbonate solvents -- PC



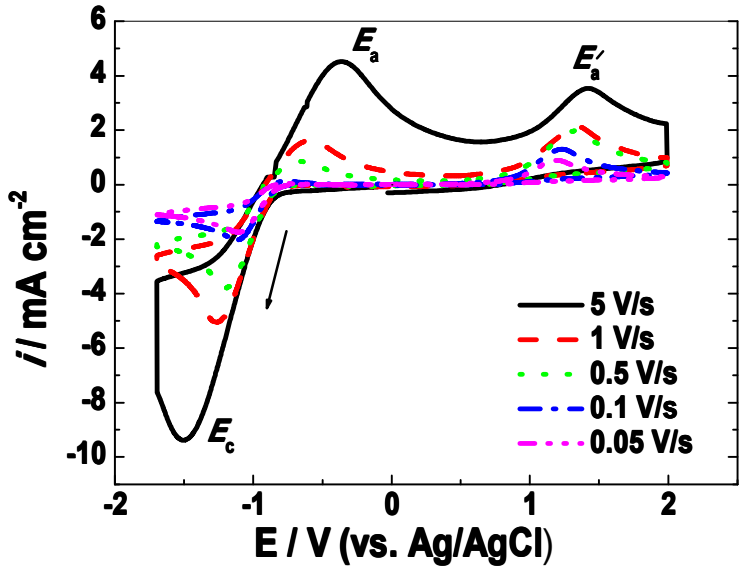
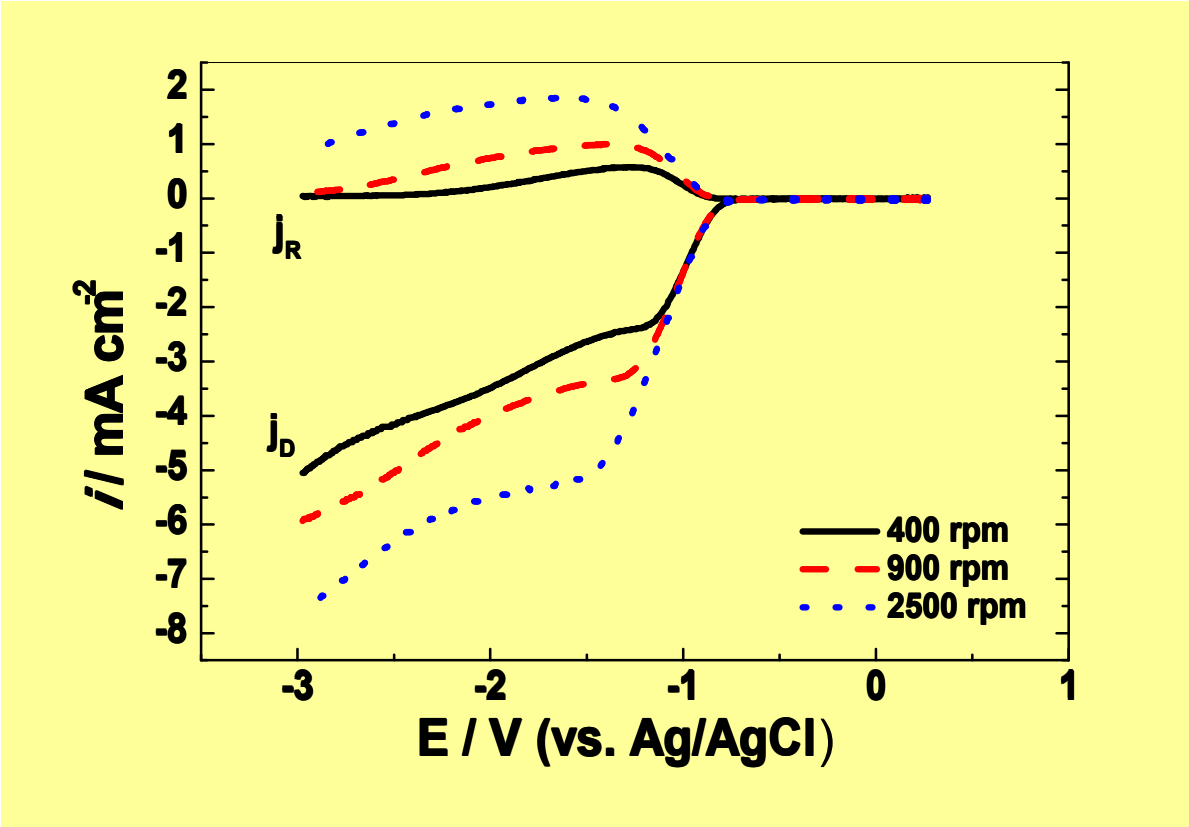


Fig. a) Cyclic voltammograms for the reduction of oxygen at a GC electrode in 0.1M $TBAPF_6$/PC electrolyte, scan rate: 100 mV/s.; right: CV curves at different scanning rates

RRDE experiments in 0.1M $TBAPF_6$ / PC

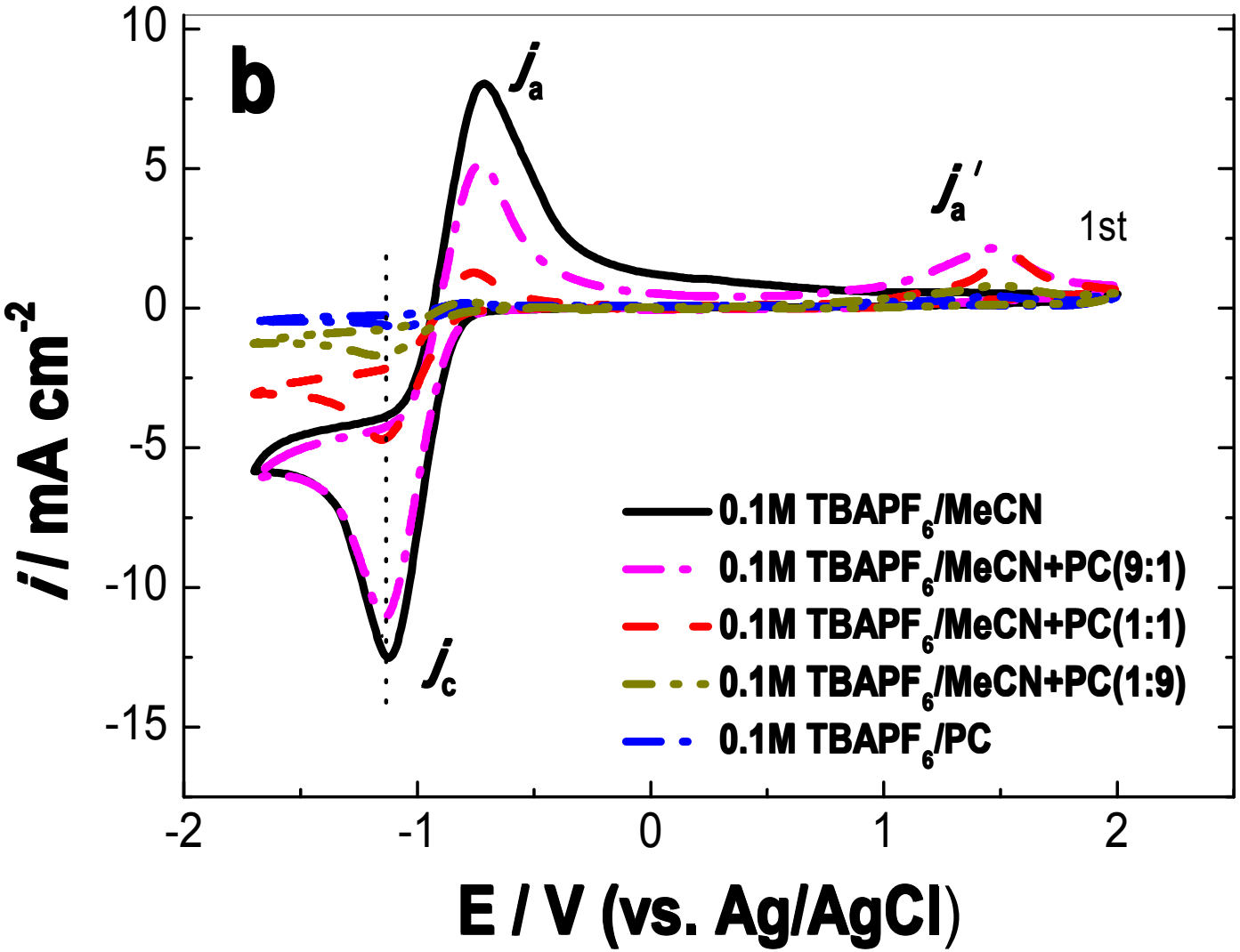


Rotation rate 400，900，2500

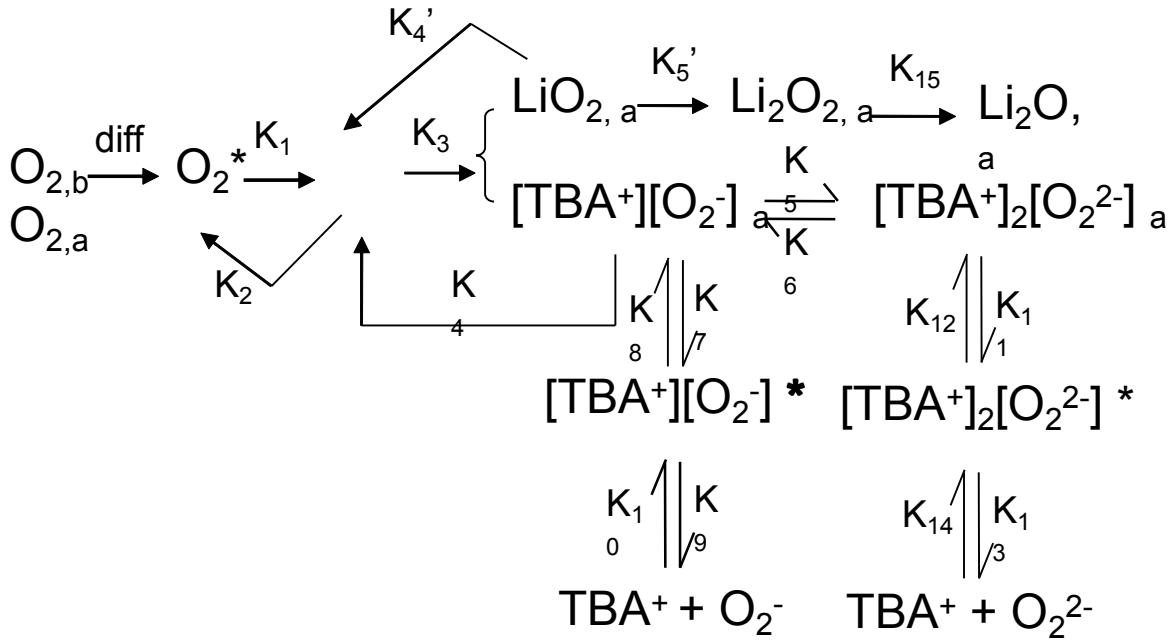
Collection efficient 23%, 29%, 35%

Reactive intermediates react with PC solvents and results in low collection efficiency

The CV curves in the mixed solvents



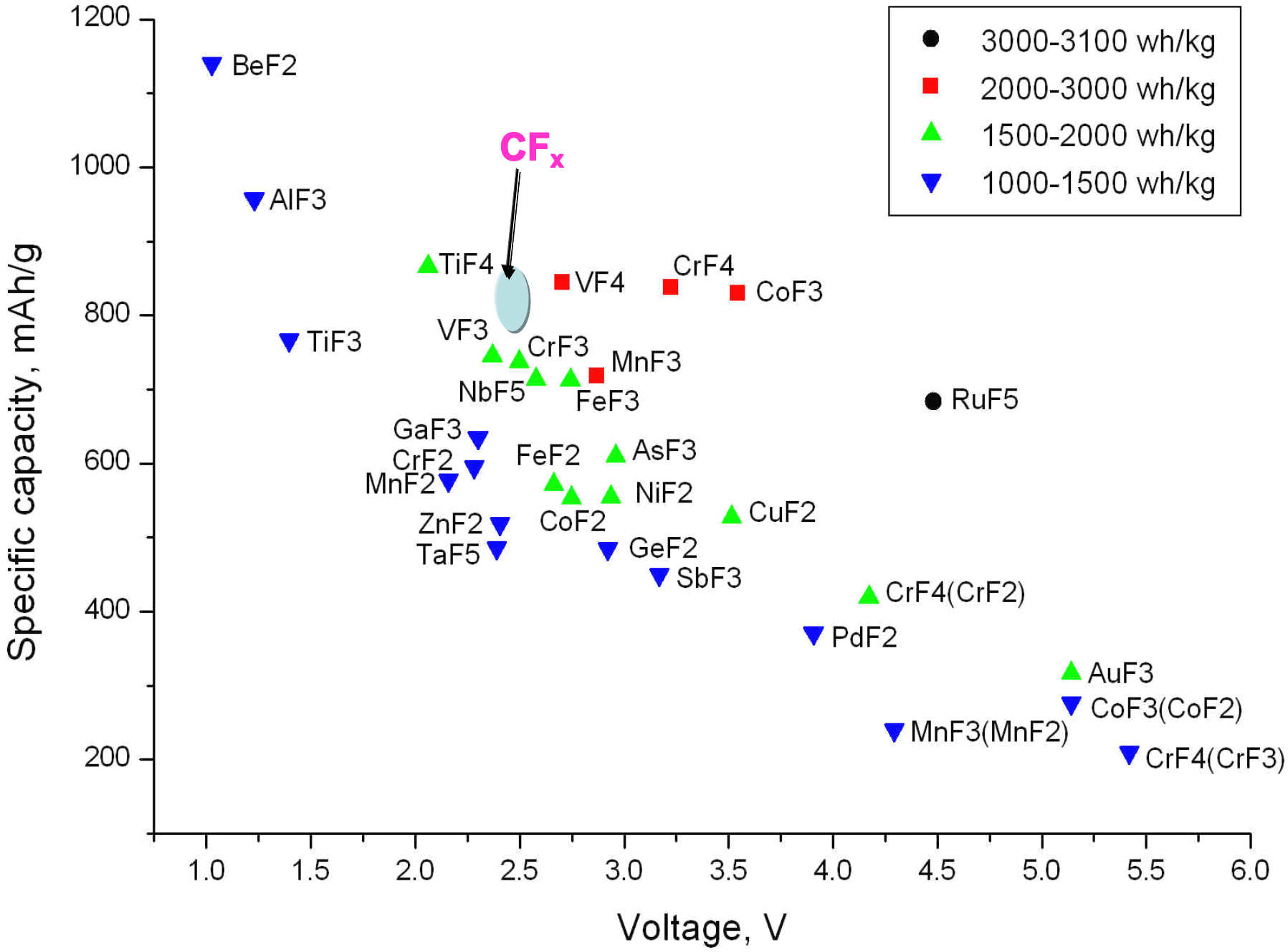
Reaction mechanism of oxygen reduction in TBA+-based electrolytes



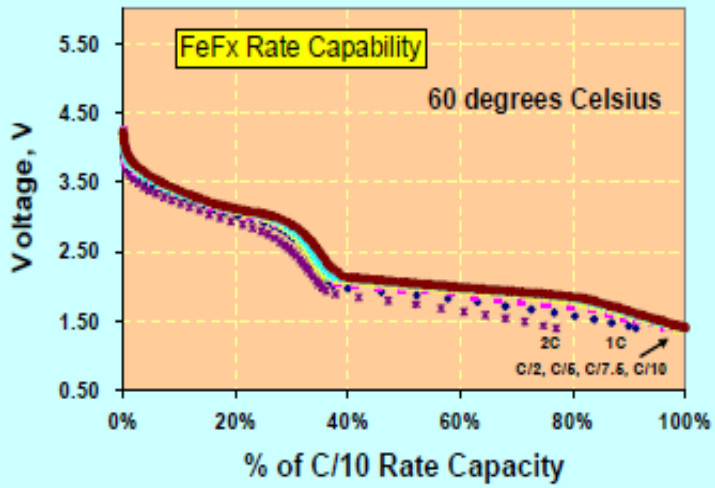
- In Li^+-based organic, the reduction of oxygen is not reversible and complex

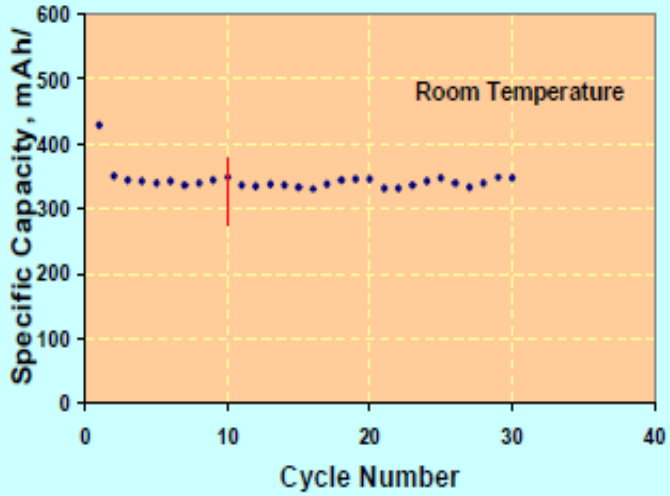
Some other battery systems with high energy density

- Li – F_2 battery ~ 6V , 5000Wh/kg
- Li – MF_x battery
- Li – CF_x battery


3000-3100 wh/kg
2000-3000 wh/kg
1500-2000 wh/kg
1000-1500 wh/kg
CFx
BeF2
AlF3
TiF4
TiF3
VF4
CrF4
CoF3
VF3
CrF3
MnF3
NbF5
FeF3
RuF5
GaF3
CrF2
MnF2
FeF2
AsF3
NiF2
CuF2
ZnF2
CoF2
TaF5
GeF2
SbF3
CrF4(CrF2)
PdF2
AuF3
CoF3(CoF2)
MnF3(MnF2)
CrF4(CrF3)
Specific capacity, mAh/g
Voltage, V
1200
1000
800
600
400
200
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0

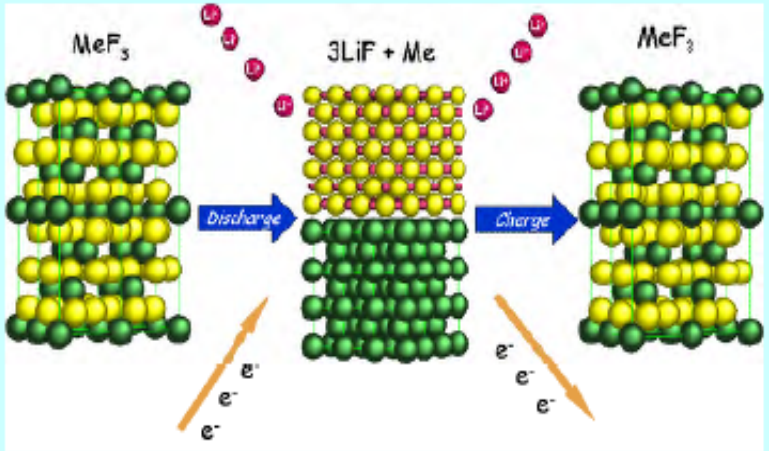
Multi-electron Displacement Reactions





$$FeF_3 + 3\,Li = Fe + 3LiF$$

Carbon/FeF_3 nanocomposite



Charge/discharge process of FeF_x (G.G. Amatucci, and N. Pereira,

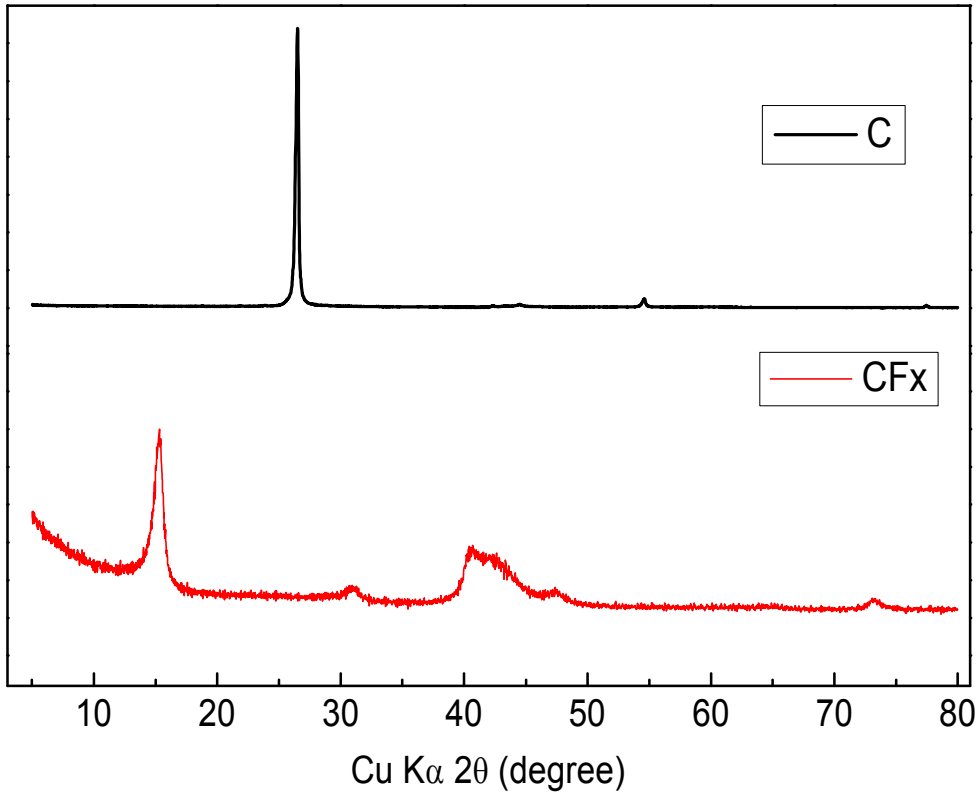
- Lithium anode cyclability and safety are serious issues to overcome

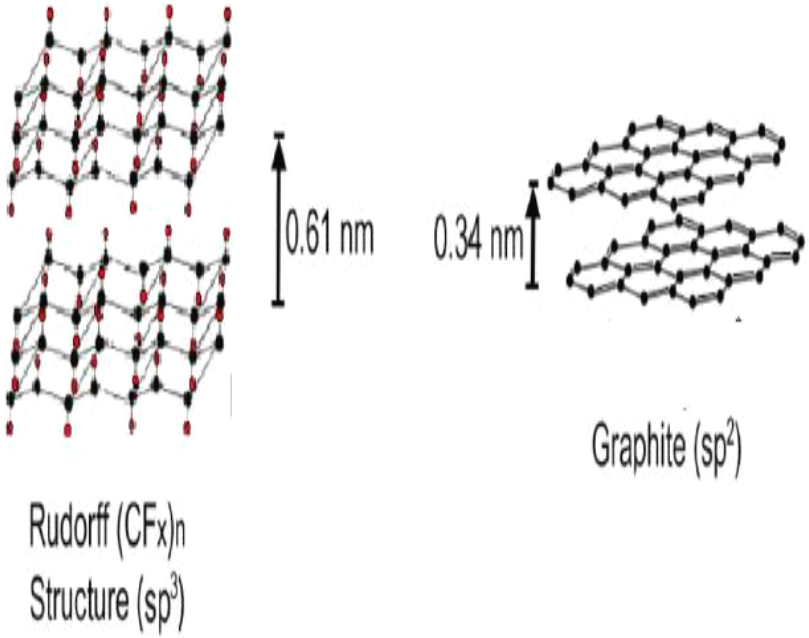
Fluoride electrode materials

- We have built up a quite convenient synthetic system for synthesis of fluoriated compounds, thus it make us to make different MFx, CF_x and so on. And it can be scalable up ….

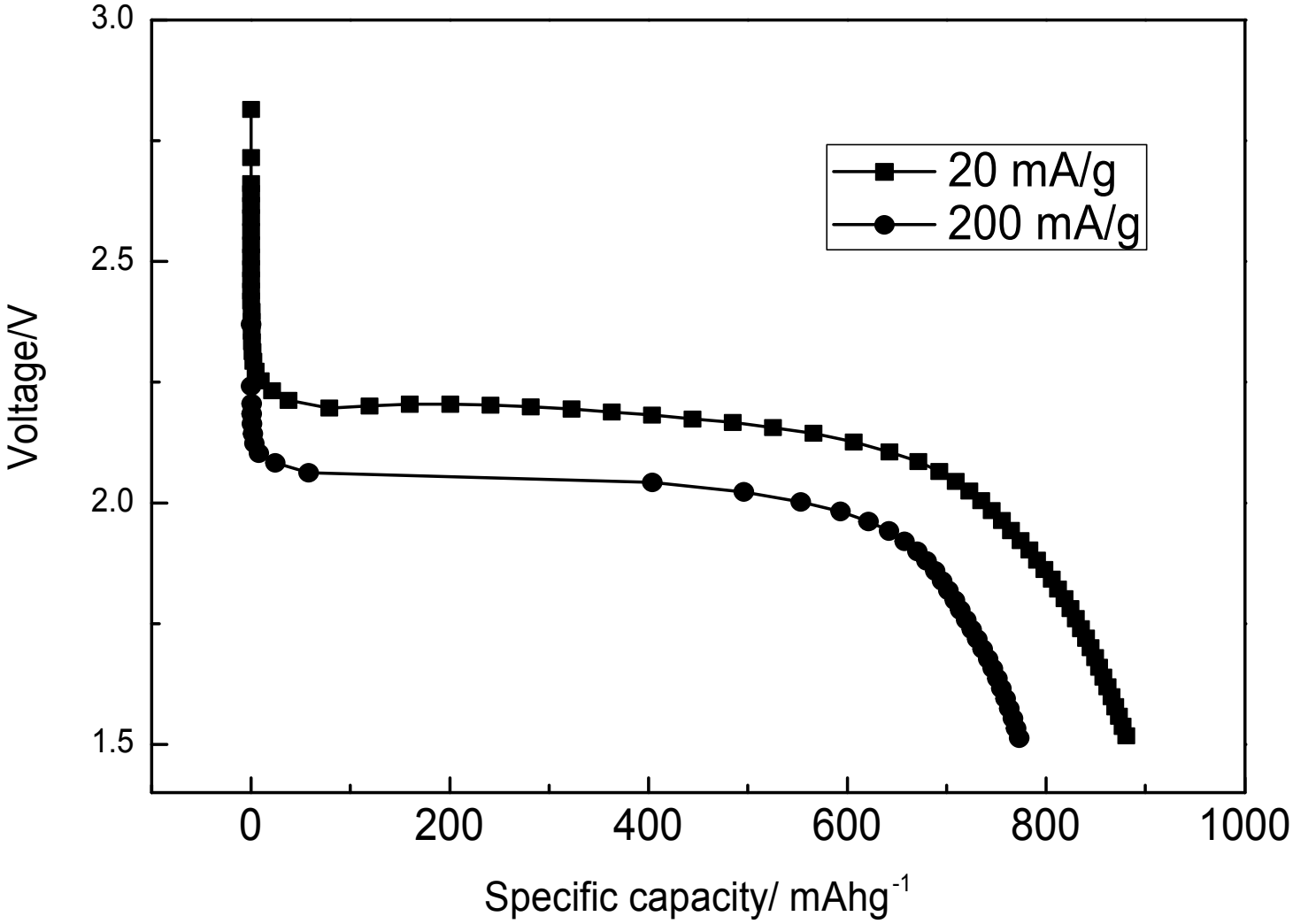
- Some results about CF_x

XRD patterns of graphite before and after fluoriation





Charge-discharge curves of graphite fluoride



Conclusions

- In the non-aqueous electrolyte solution, either solvents or electrolytes has big effects on the reduction of oxygen reduction. If we want use these electrolytes in the future Li-air battery, we must consider their side effects and choose/design good electrolyte system.

- Fluoride systems have very high energy density, some fluoride systems should be investigated as potential reversible system, e.g. carbon fluorides.

Thank you!