Development of Rechargeable Li-air battery – overcoming the major obstacles

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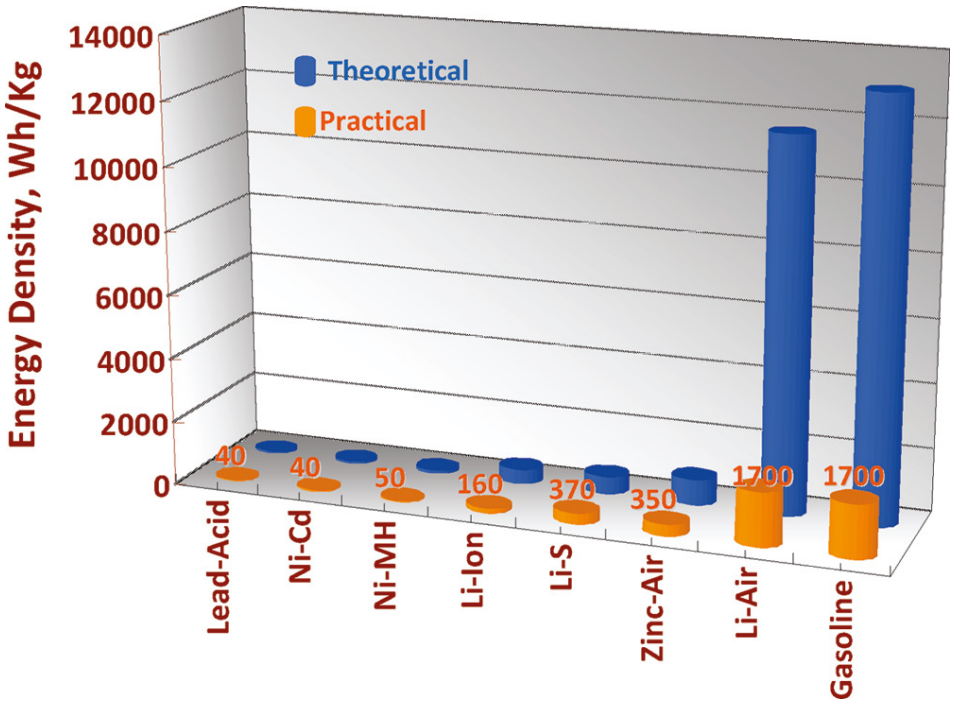
Dilemma of Li air cell



G. Girishkumar etc. J Phy. Chem. Lett. 2010, 1, 2193

System	Gravimetric Wh/kg	Volumetric Wh/liter
Li-Ion	450	1450
Li-Oxygen	> 1000	1250
LiC_6-Oxygen	900	1880

Weight/volume of carbon and electrocatalyst not included

M.S. Whittingham, The Holy Grail of Batteries – Lithium air: Reality vs Hype, 219 ECS, 2011 Montreal, Canada

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The obstacles need to be overcome

- **Rechargeable metallic Li anode**

- **Rechargeable Gas-Diffusion-Electrode**
  - Formation of superoxide ion during the reduction of oxygen – chemical reaction with electrolyte, e.g. PC
  - Oxygen solubility of diffusion rate – discharge rate.
  - Solid products from the reduction of Oxygen - Capacity.

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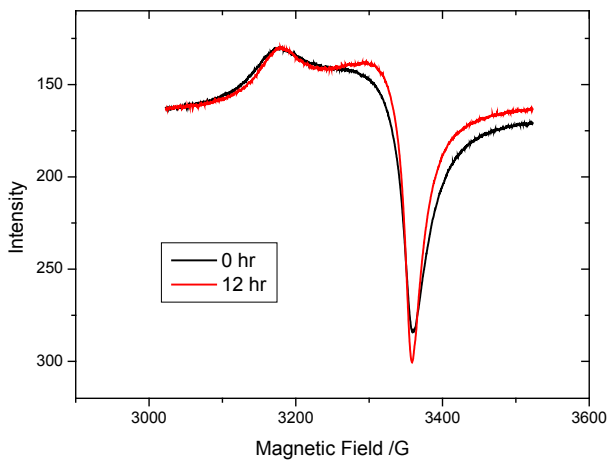
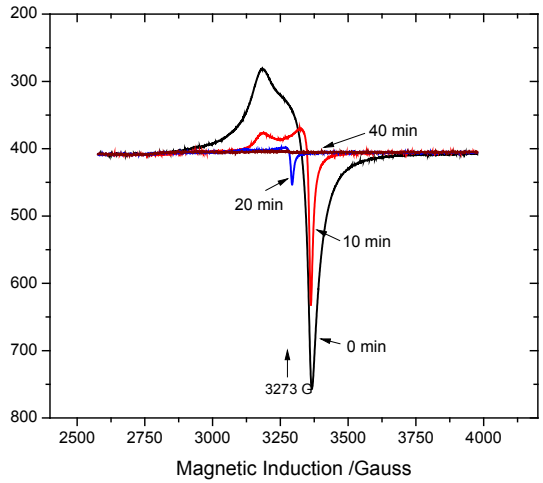
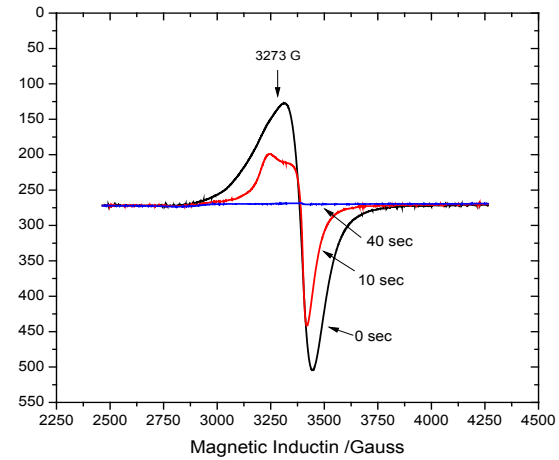
Catalytic Disproportionation of O_2^- is much faster then its reaction with PC



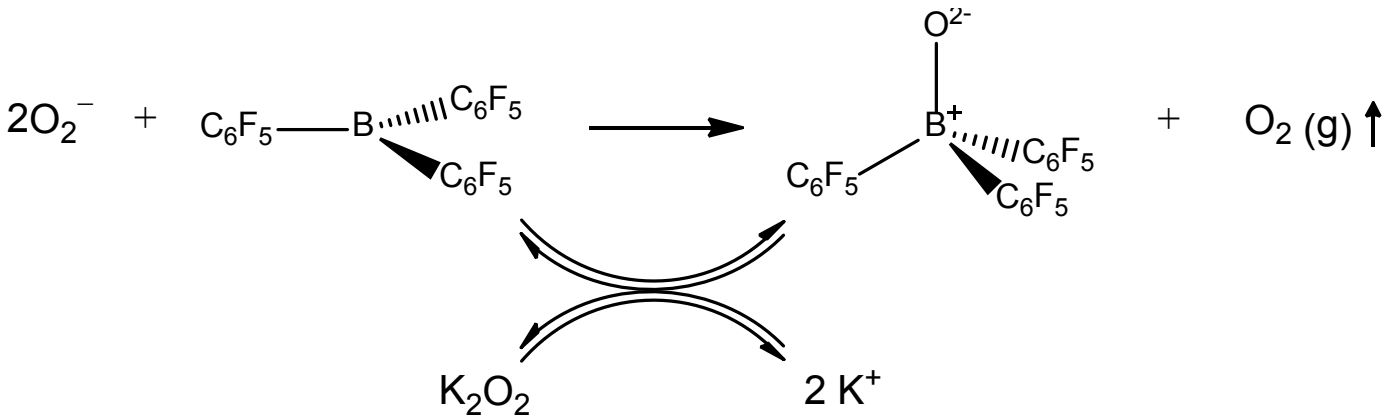
0.075 M KO_2 DMSO solution



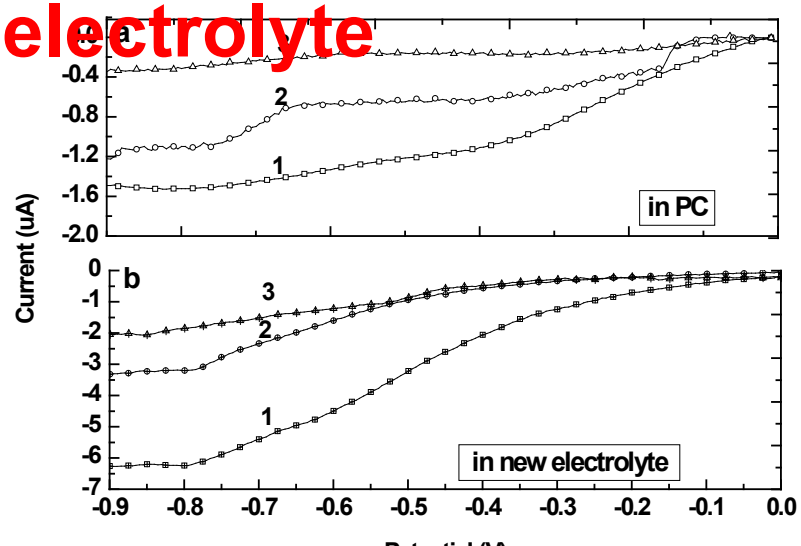
1:1 PC: KO_2

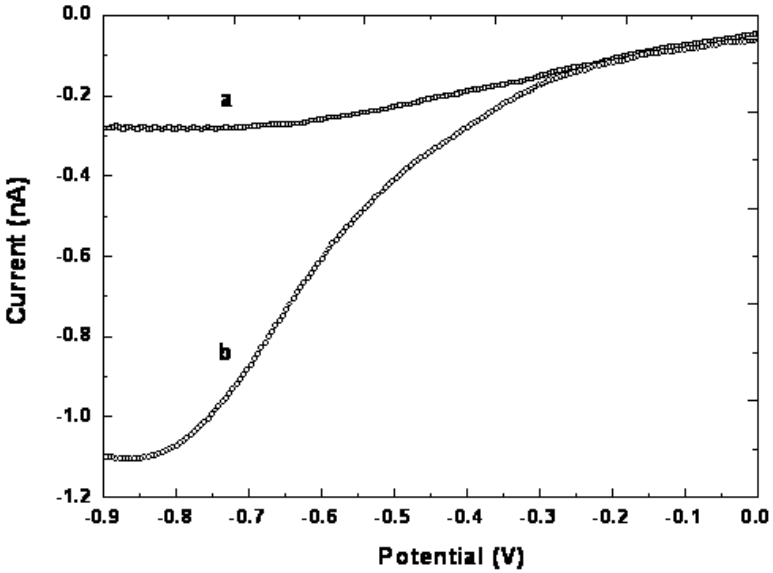


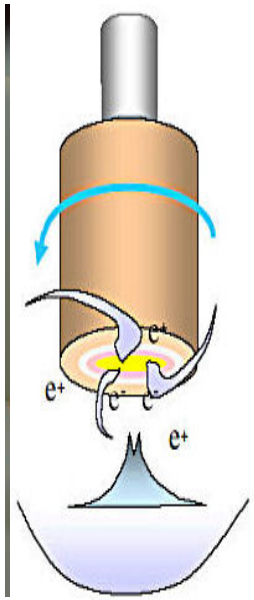
1:5 Catalyst: KO_2

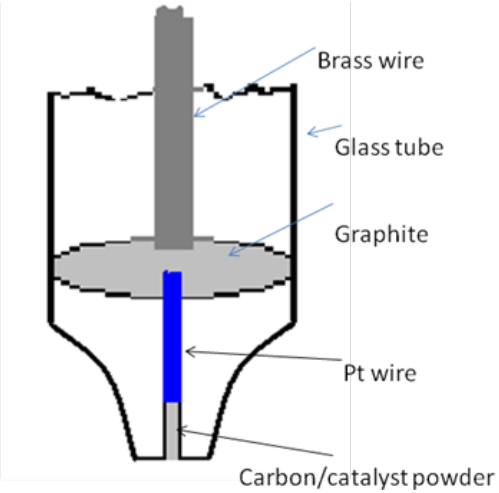


Oxygen solubility can be significantly increased by using proper additives electrolyte









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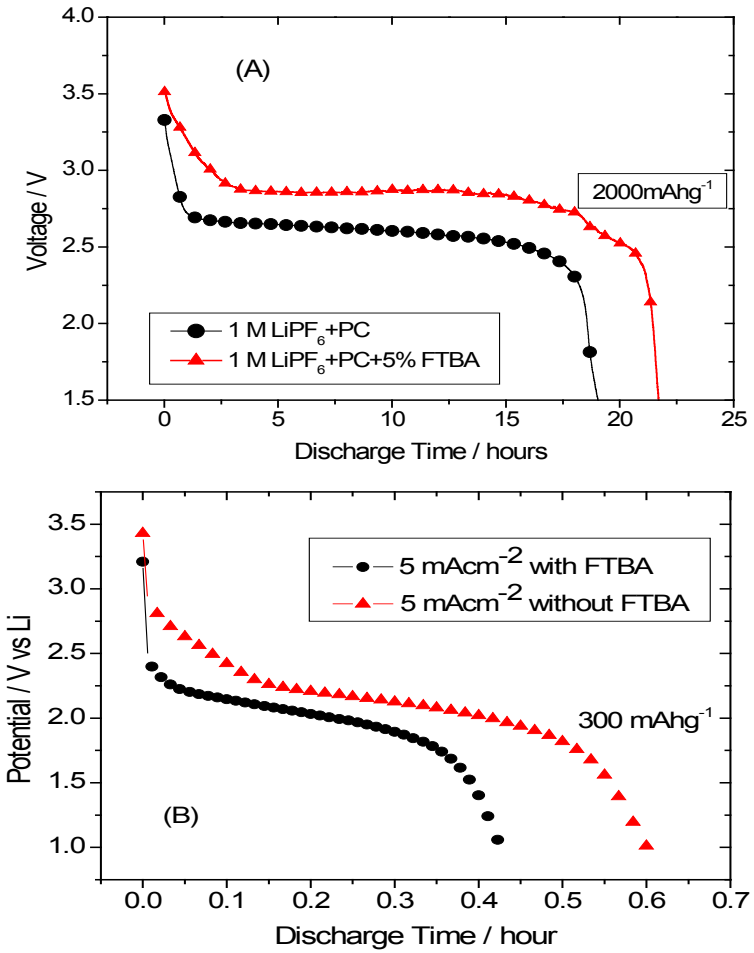
The performance of Li-air cell with new electrolyte is significant improved.



D.Y. Qu, X.Q. Yang, etc., *Energy Environ. Sci.,* DOI:10.1039/C1EE01556G

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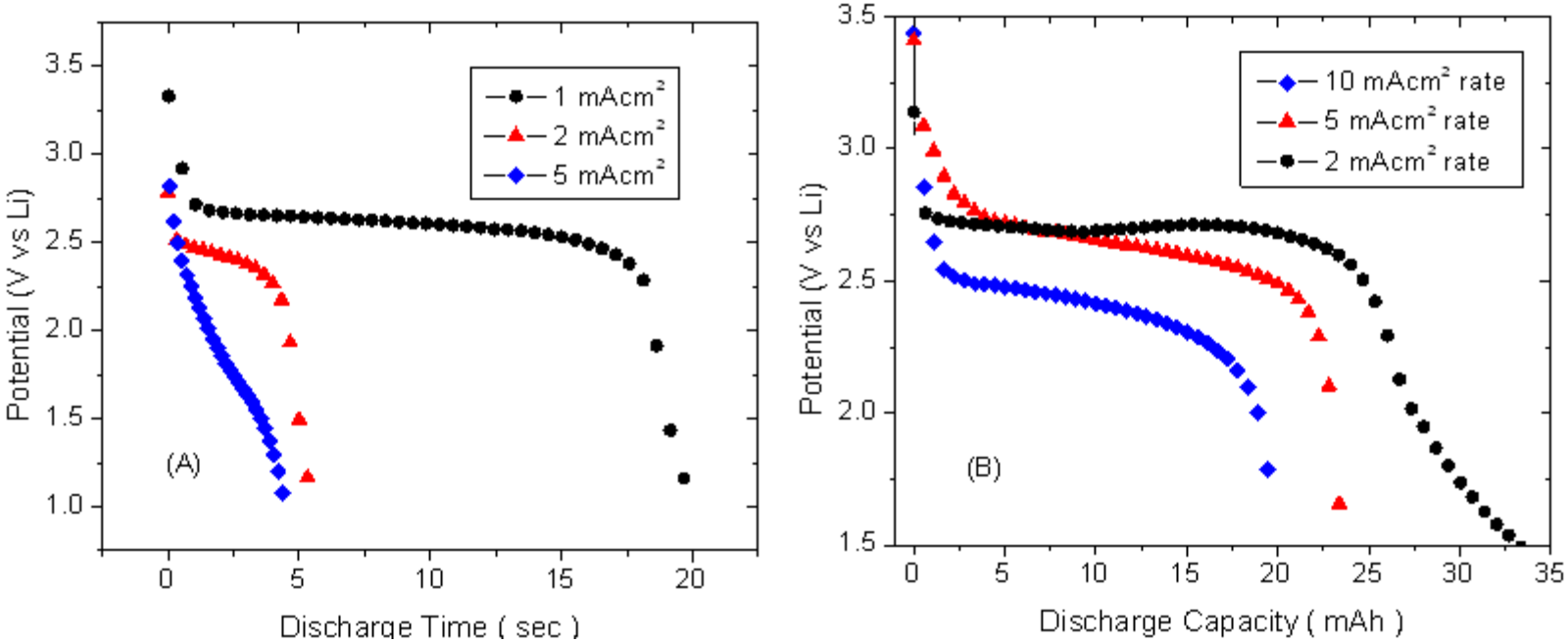
The performance of Li-air cell with electrolyte containing ACN is significant improved.



D.Y. Qu, X.Q. Yang, etc., *Chem. ASIAN J. 6(2011)3306-3311.*

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The difference between the GDE in aqueous and non-aqueous electrolytes?

Zn air cell:

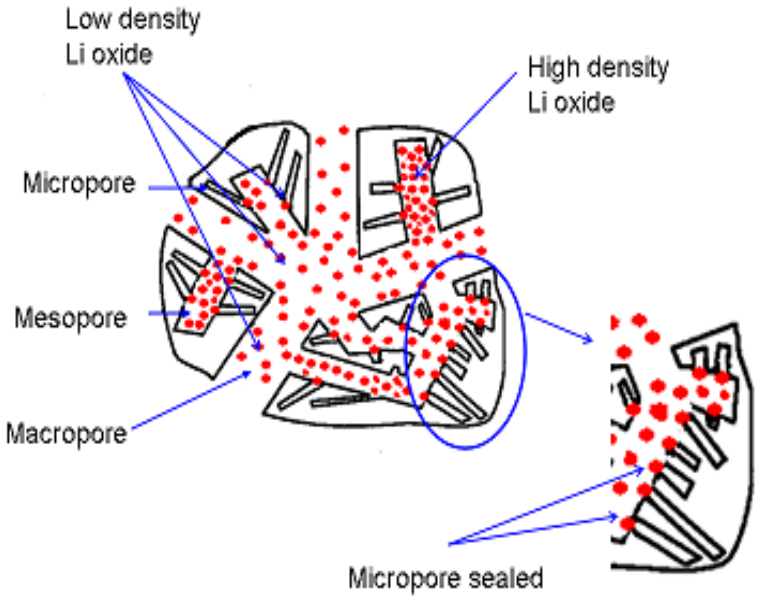
$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$

Fuel cell (PEM):

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Li-air:

$2O_2 + 4Li^+ + 4e^- \rightarrow 2Li_2O_2$



- Solid Li oxides precipitate on the surface of carbon inside the pores.
- Small pores are immediately sealed.
- Most of solid reaction products locates in the meso- and macro-pores.
- The passivation of GDE results from the formation of dense oxide layer on the carbon surface.

To solve the problem:

- Prevent the formation dense solid layer, instead forming porous precipitate.
- Remove the solid from the cell - flow cell design.

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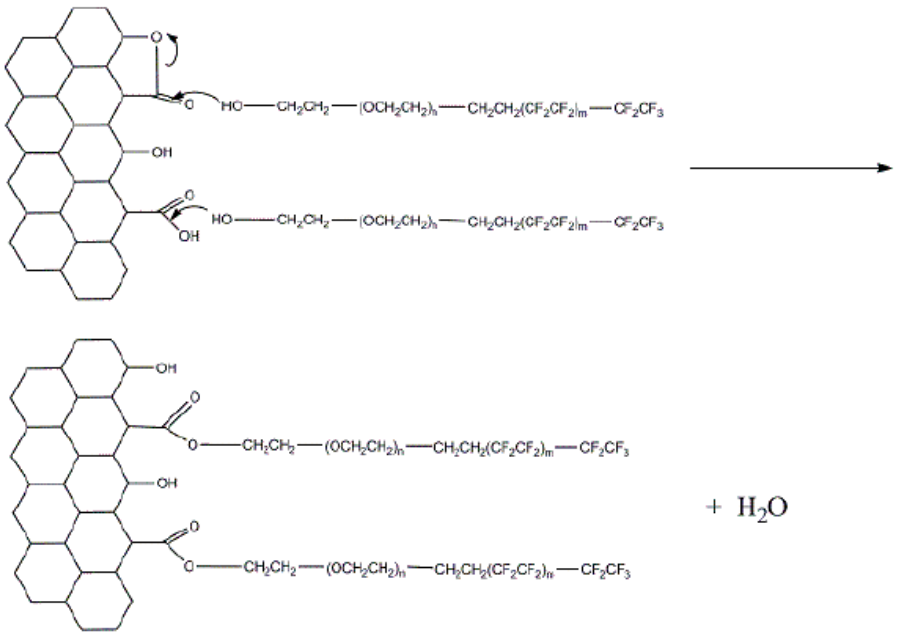
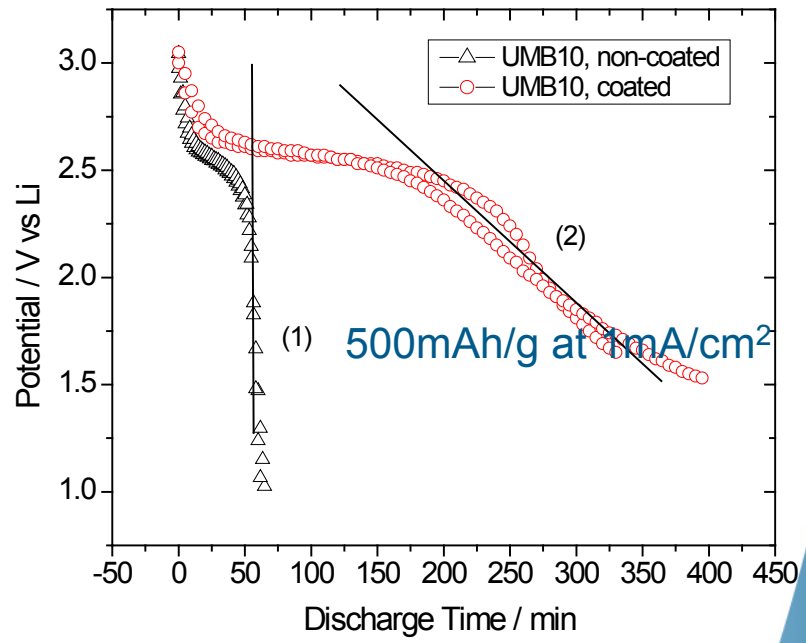
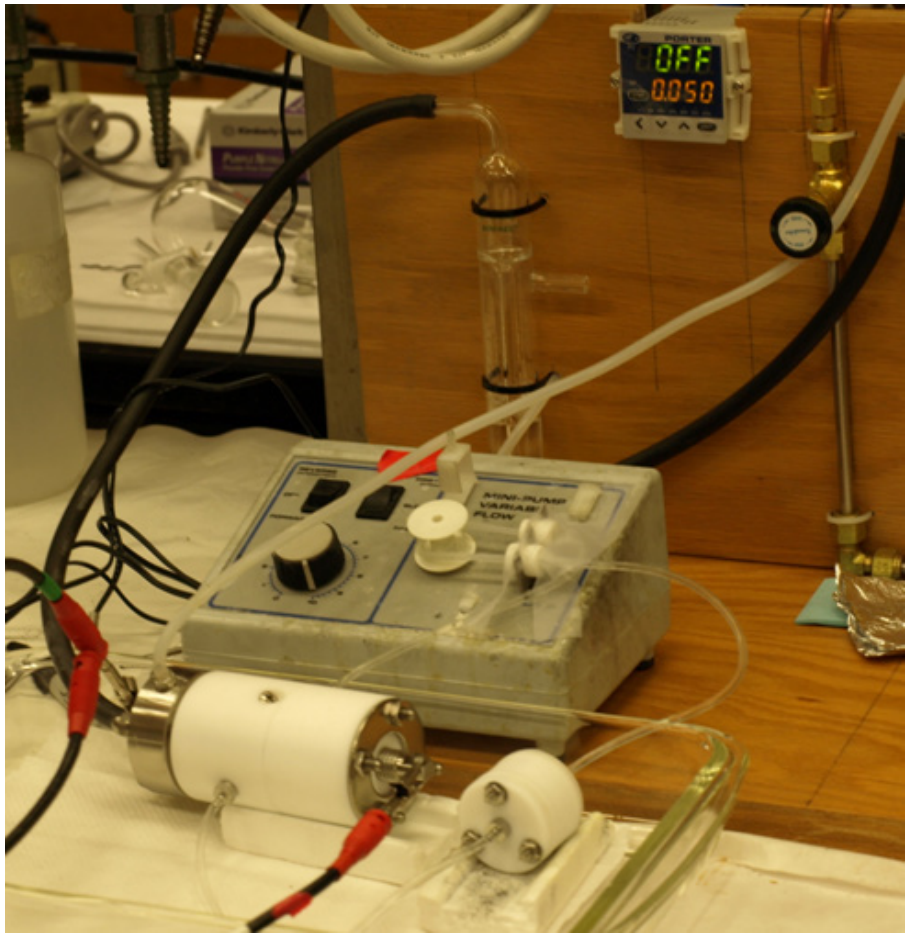
Formation of the Compact and dense surface Li oxides passivation film can be delayed by modifying the carbon surface with long chain functional groups





D.Y. Qu, X.Q. Yang etc., Carbon *Carbon*, 49(2011)1266-1271

Rechargeable Li-Air Flow Cell



- 1cm^2 interface; 0.2 mm thick(0.008 inch); 10 mg carbon (90% carbon+10% Teflon).
- discharge and recharge
- The forming gas and electrolyte composition can be monitored real-time by GC-MS and HPLC-MS, respectively.

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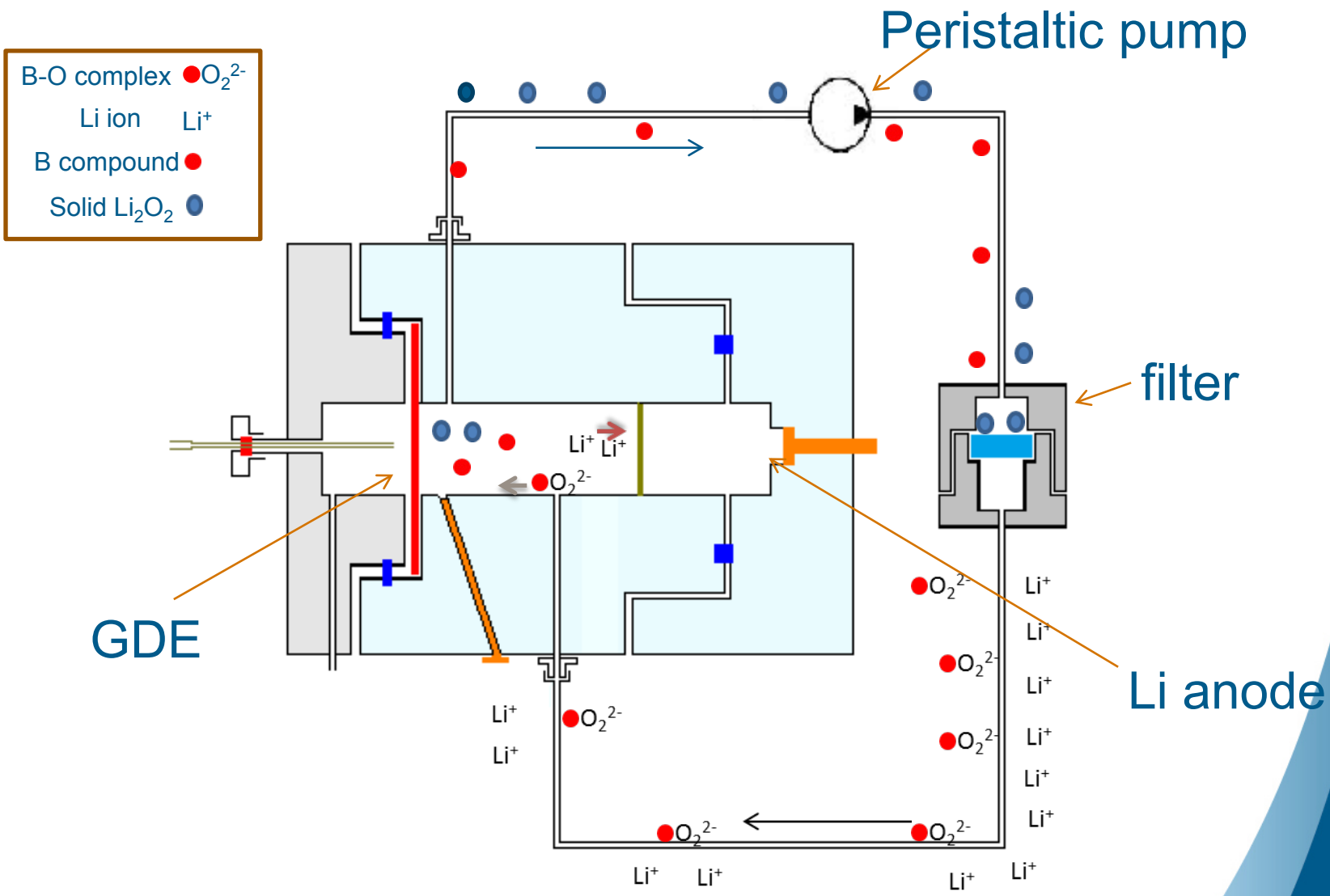
Rechargeable Li-Air Flow Cell



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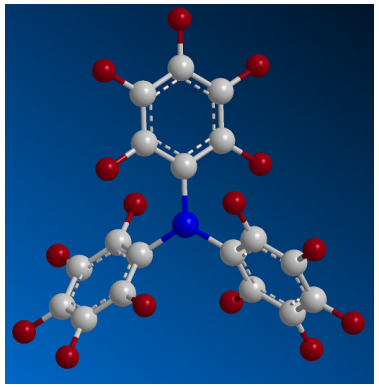
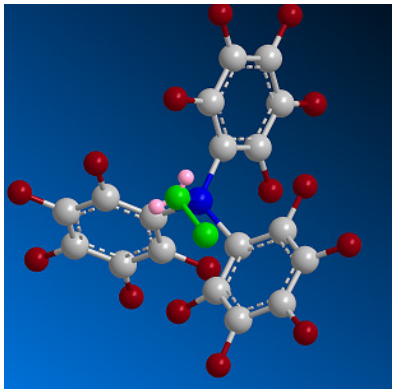
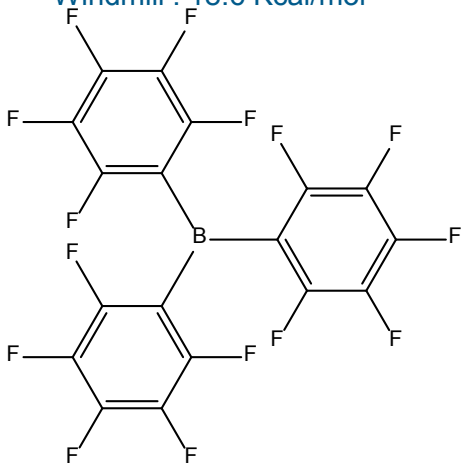
Tris(pentafluorophenyl)borane (TPFPB) – strong Lewis acid



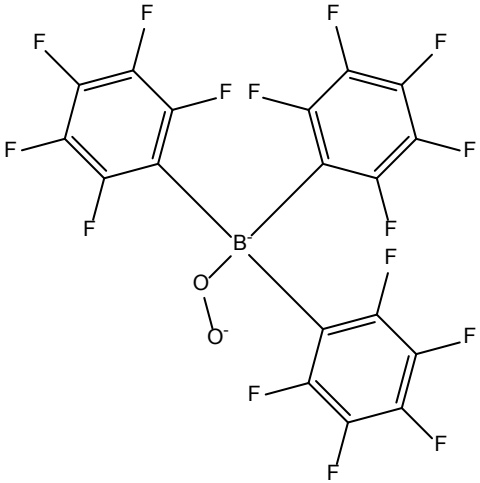


Planar : 228 KCal/mol
Windmill : 18.6 Kcal/mol

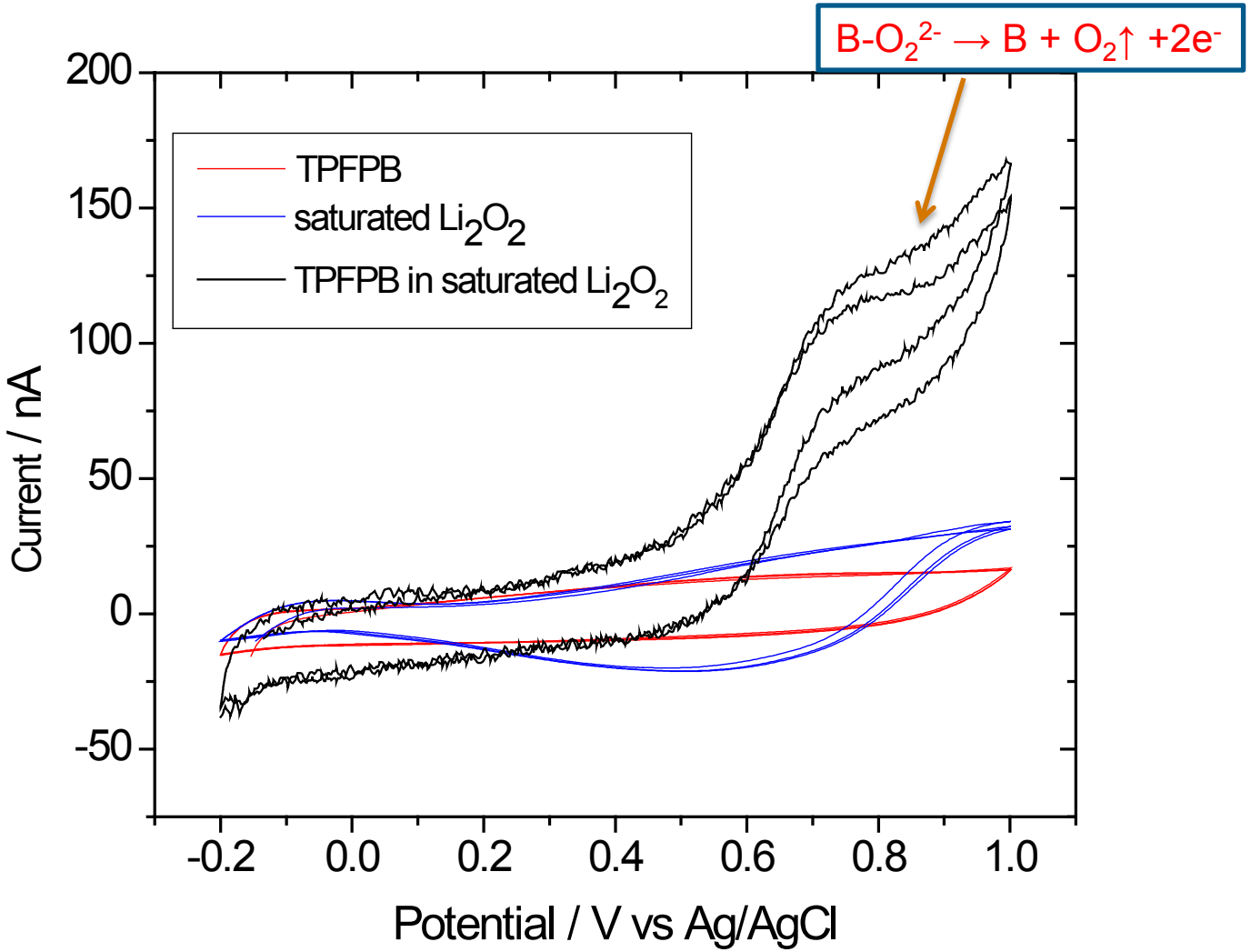
Total energy : -25.27 Kcal/mol



$$+ Li_2O_2 \rightarrow 2Li^+ +$$



Peroxide complex can be reoxided



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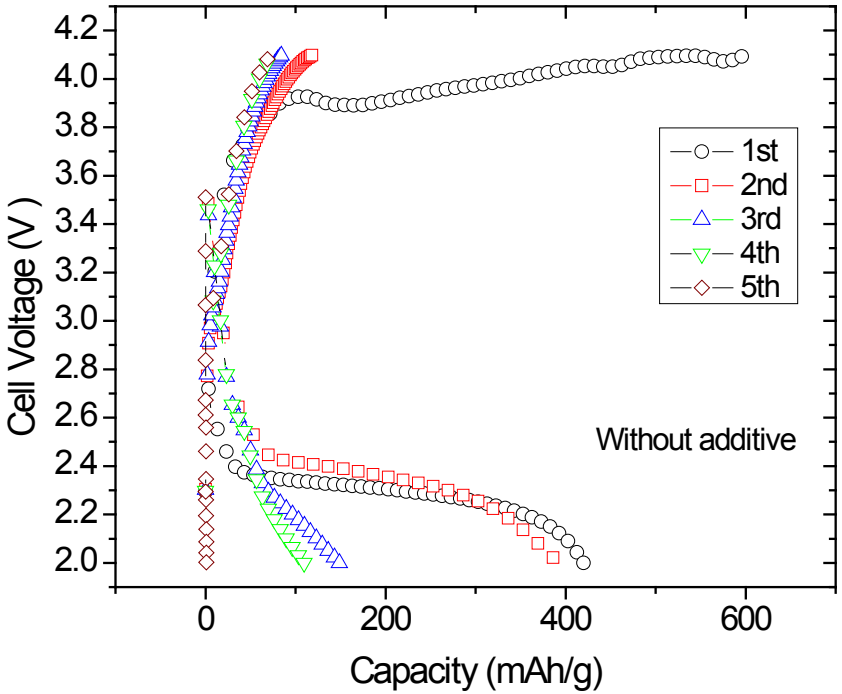
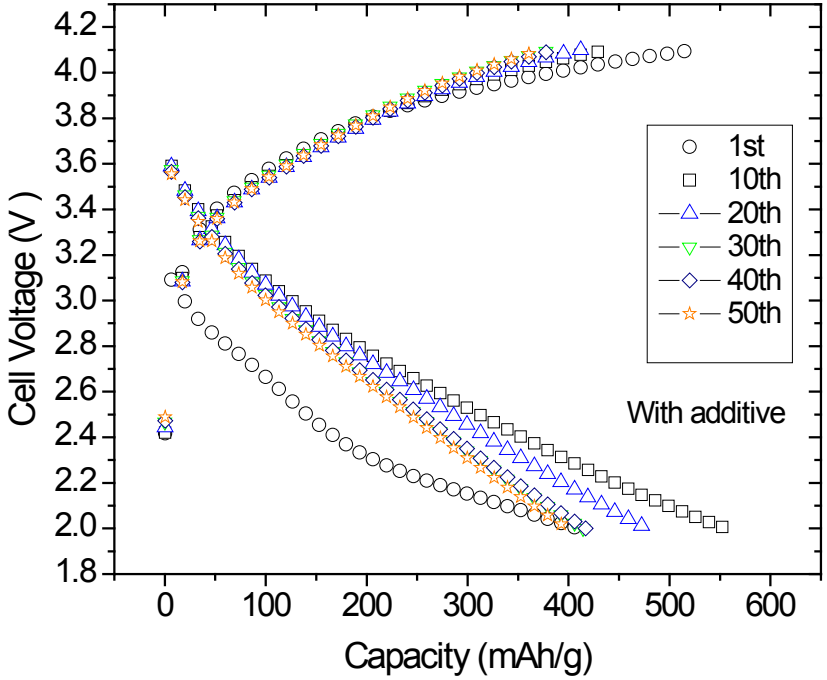
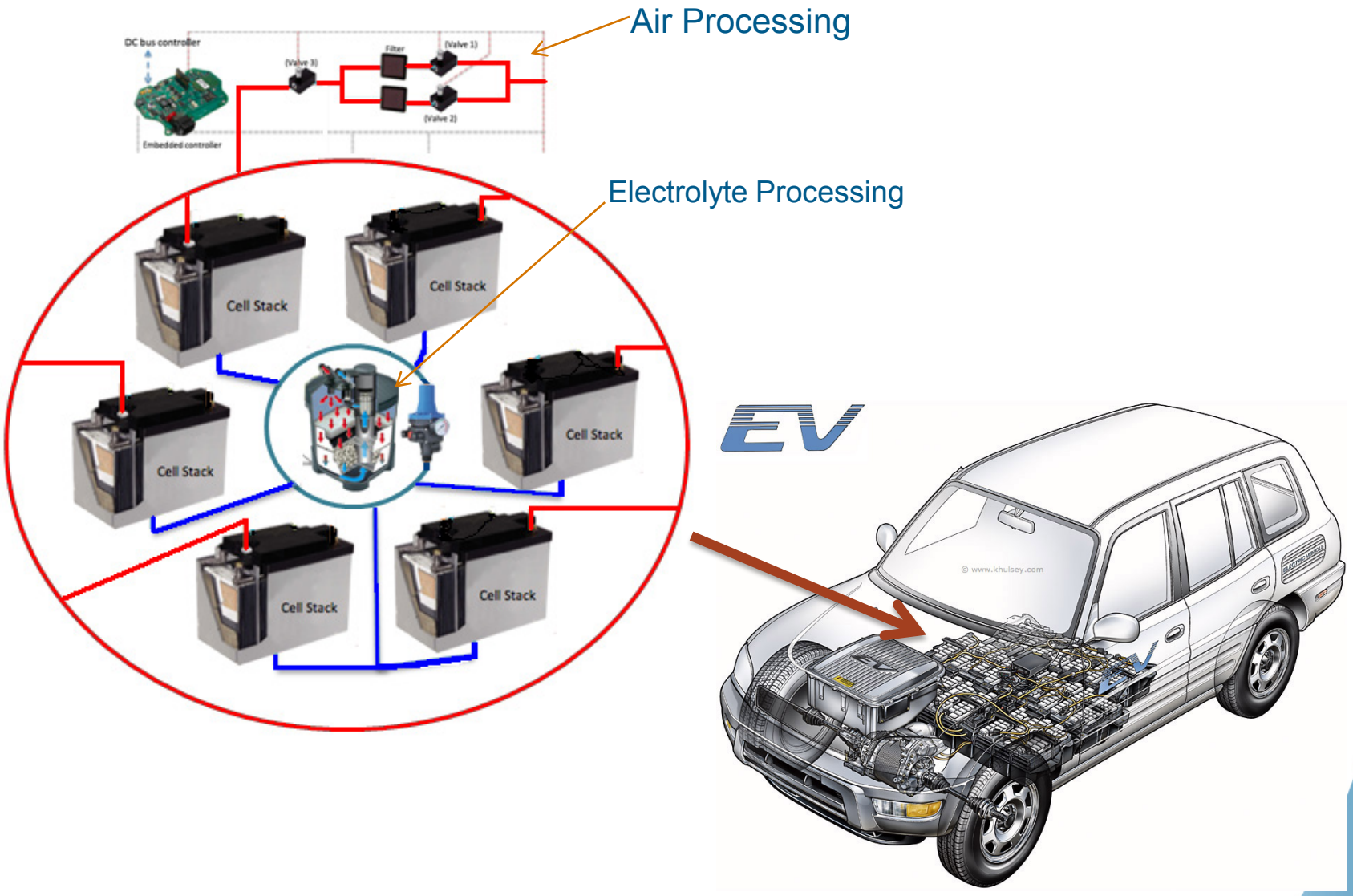
Rechargeable Li-air Flow cell





To Power a EV


Air Processing
DC bus controller
Embedded controller
(Valve 3)
Filter
(Valve 1)
(Valve 2)
Electrolyte Processing
Cell Stack
Cell Stack
Cell Stack
Cell Stack
Cell Stack
Cell Stack
EV
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Conclusion

- The solid reaction products have to be removed from the cell and form a porous solid.
- Electrolyte and additives have to be found to increase the solubility and diffusion rate of oxygen/.
- A good catalyst is needed to induce superoxide disproportionation.

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Acknowledgment

Deyang Qu and Xiao-Qing Yang are grateful for the financial support from the Department of Energy, EERE, OVT.

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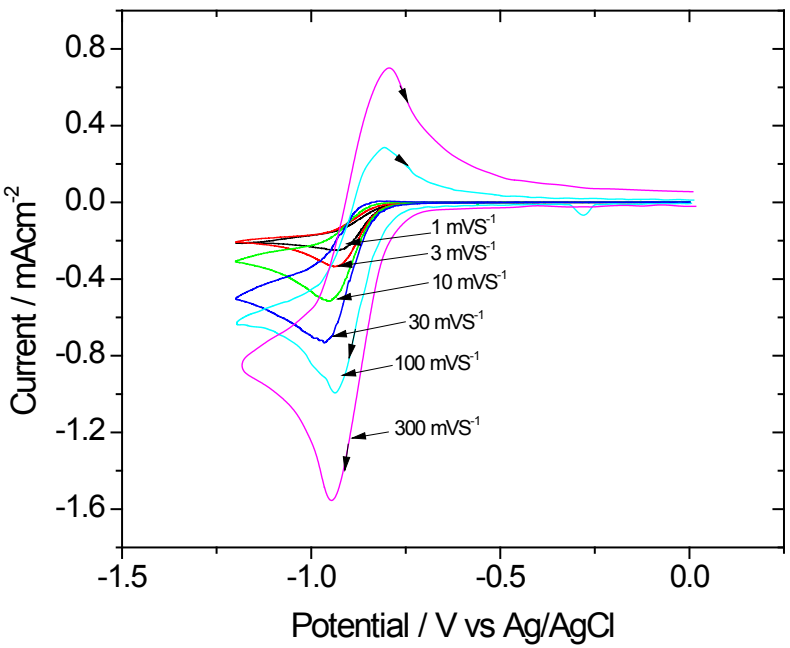
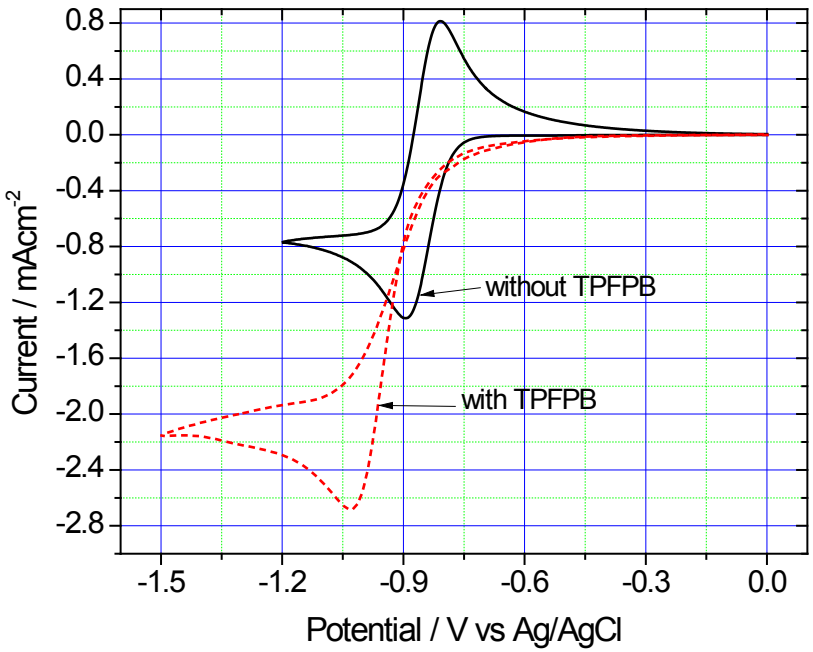
1 M $TEABF_4$ PC, Glassy Carbon



1 M $TEABF_4$ acetonitrile, Glassy Carbon



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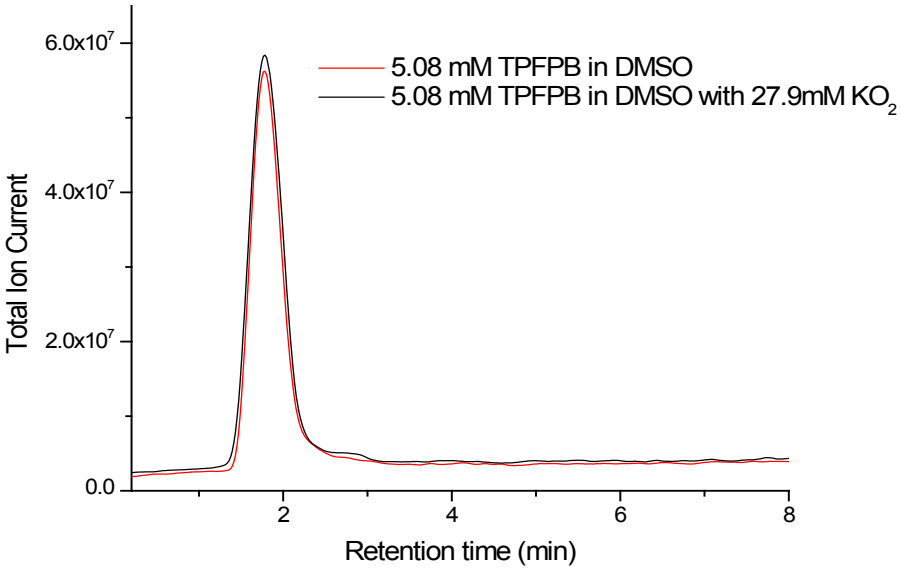
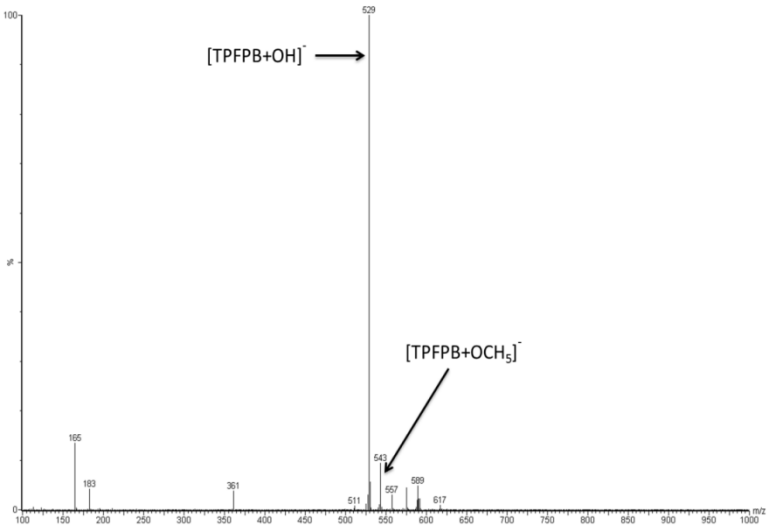
TPFPB is a catalyst, not a reactant





Mobile phase: Methanol with 0.01% (v/v) ammonium hydroxide

Figure 1, The chromatogram of TPFPB in DMSO with and without KO_2 obtained by HPLC ESI/MS

Figure 2, Mass spectrum of TPFPB in ESI(negative)/MS

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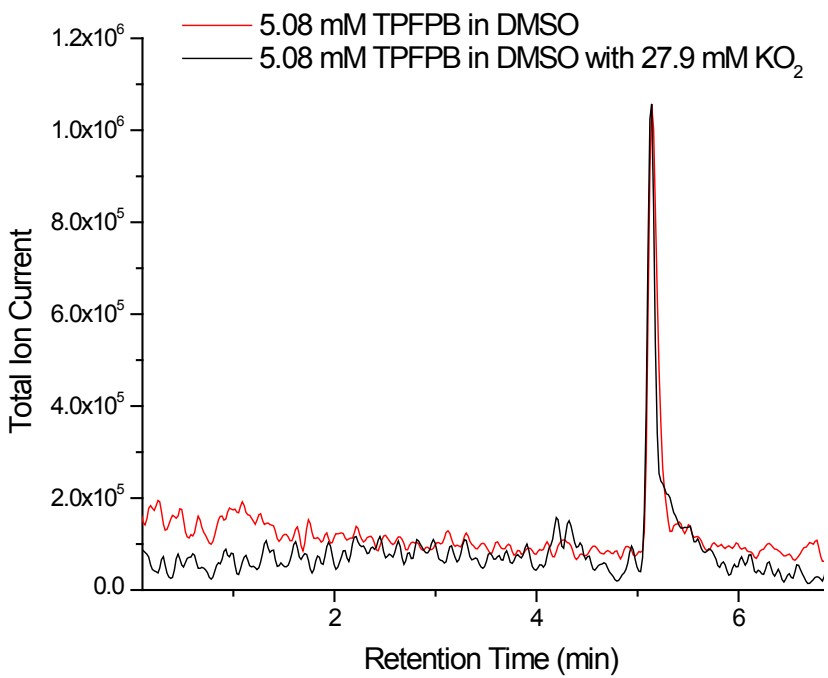

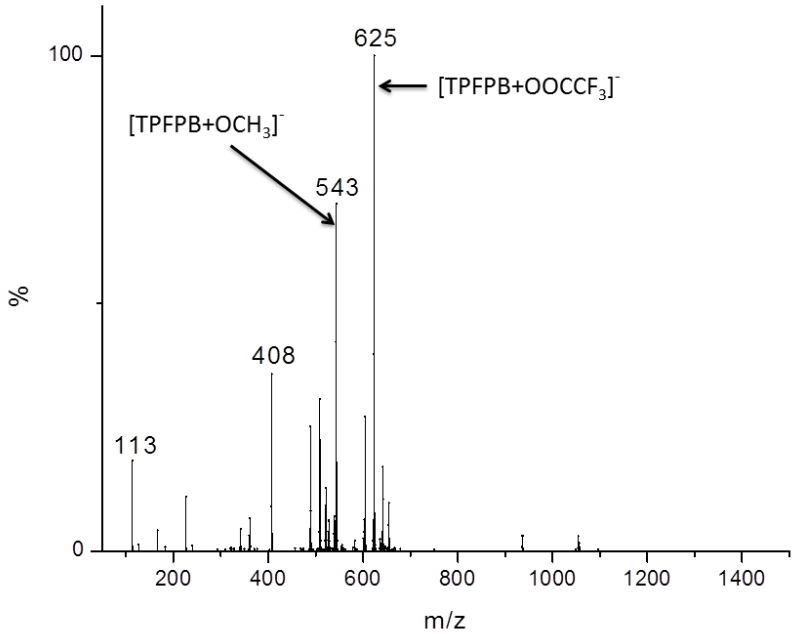

Phase A is water, phase B is methanol both with 0.01% (v/v) trifluoroacetic acid

Mass spectrum of TPFPB in APCI(negative)/MS

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Possible parallel reactions for Superoxide

Reduction of Oxygen
$O_2 + e \longrightarrow O_2^-$
(superoxide ion)

Reaction with PC forming Li_2CO_3 (hard to be recharged, consumption of electrolyte

Disproportionation
$2O_2^- \longrightarrow O_2 + O_2^{2-}$

Further reduction of O_2^-
$O_2^- + e \longrightarrow O_2^{2-}$ (-2.05 V vs SCE)

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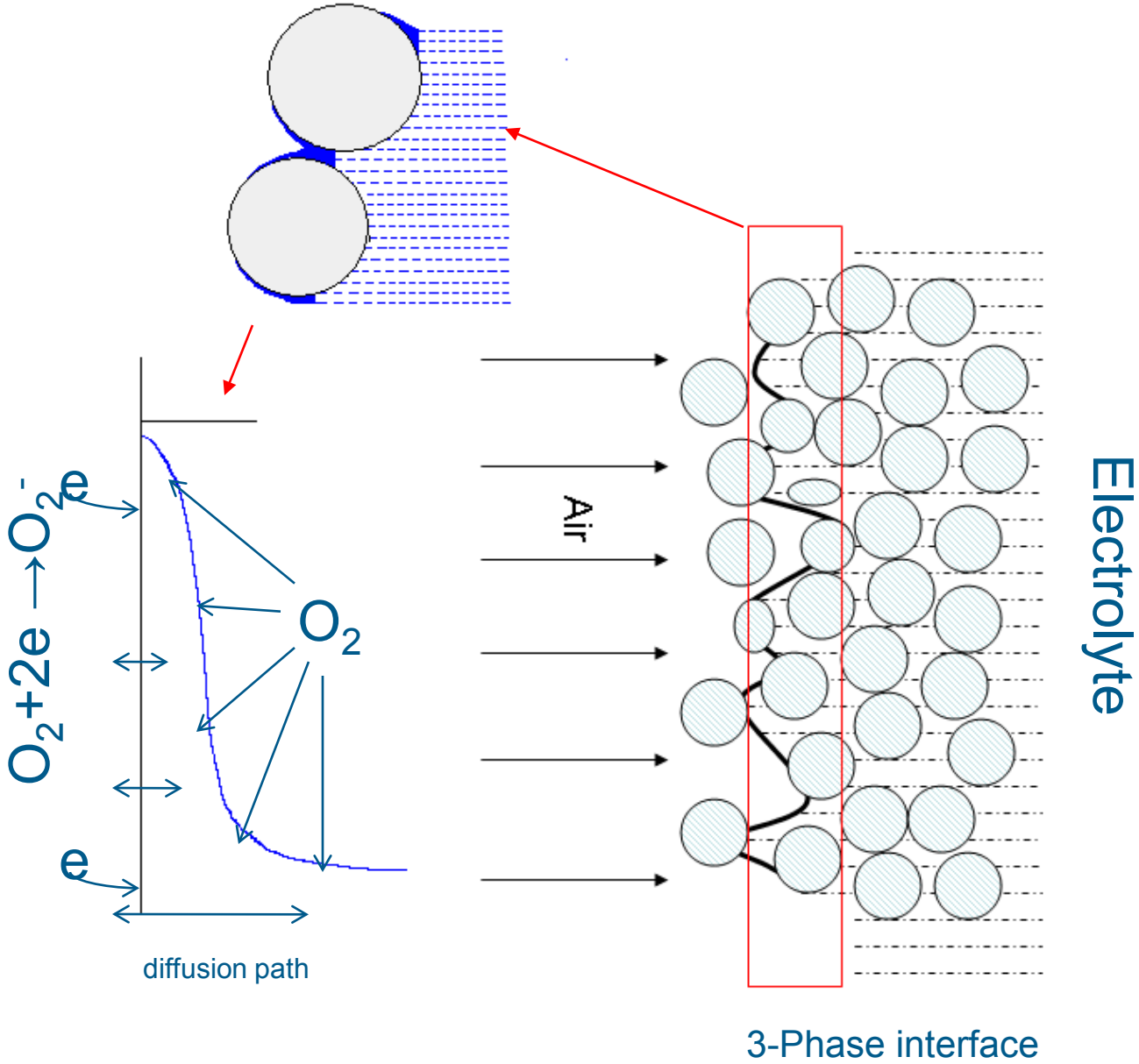
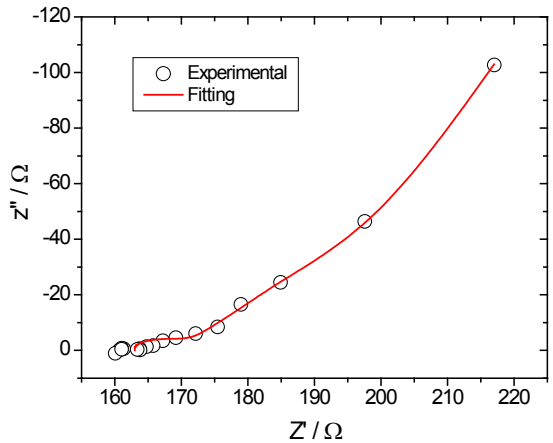
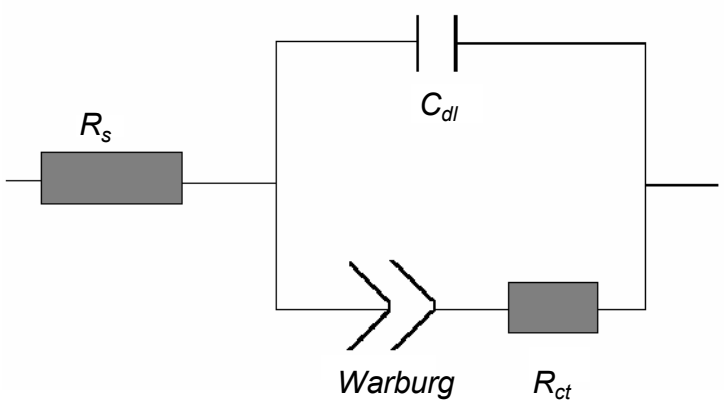
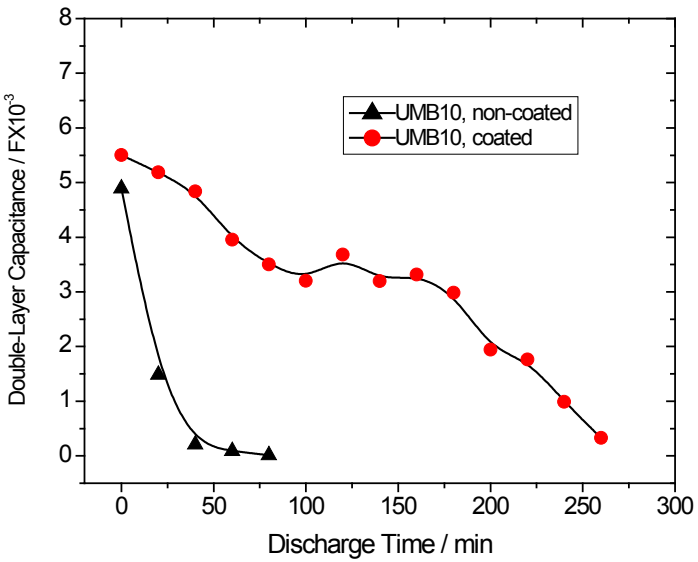
Developing effective Gas-Diffusion-Electrode



Active carbon surface is preserved by surface modification







D.Y. Qu, X.Q. Yang etc., Carbon *Carbon*, 49(2011)1266-1271

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