高能量密度电池用多电子材料及锂空电池研究

Multi-electron Materials for High Energy Density Batteries and Researches on Li-air Batteries

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高容量电极材料设计的理论基础

Theory of Designing a High Capacity Electrode Material

The Faraday's Law ⇒ $$C = \frac{F \times n}{3.6 \times M}$$

C _ the theoretical capacity of the electrode material
F _ the Faraday constant
n _ the total electric charge passed through the electrode
M _ the molar mass of the electrode material

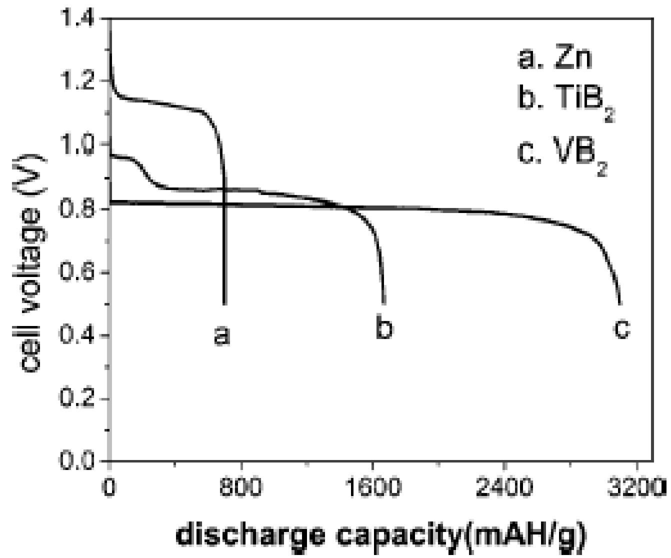
"……one mole of such borides can transfer more than one mole of electrons through specific electrochemical reactions, such that they can be regarded as **multi-electron materials** and thus have the potential to achieve extremely high-capacity……"

1摩尔这种硼化物在特定电化学反应中能够转移的电子数大于1摩尔，因而被视为多电子材料，并具有实现超高比容量的潜力。

C. Wu, et al. *Electrochem. Commun.* 11 (2009) 2173
Y. Bai, et al. *Electrochem. Commun.* 11 (2009) 145

典型的多电子金属硼化物实例：晶态VB_2和TiB_2

Typical Examples for Multi-electron Borides: Crystal VB_2 and TiB_2



A comparison of VB_2 and TiB_2 with Zn powder electrode.

VB_2和TiB_2与锌粉电极的比较。

$$VB_2 + 20\ OH^- \rightarrow VO_4^{3-} + 2\ BO_3^{3-} + 10H_2O + 11e^-$$

> 3100 mA h/g

$$TiB_2 + 12\ OH^- \rightarrow 2\ BO_3^{3-} + Ti(amorphous) + 6H_2O + 6e^-$$

>1600 mA h/g

Both the metal and the inert boron are activated with each.

金属以及惰性的硼发生了相互的活化。

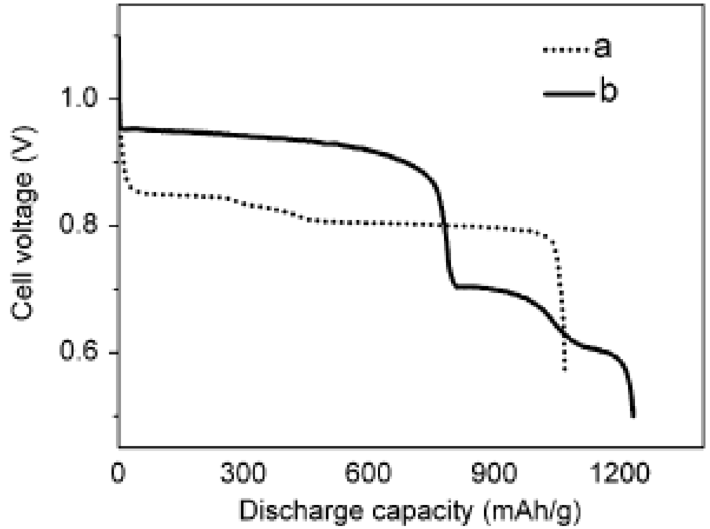
Serious alkaline corrosion, only for primary batteries。

严重的碱腐蚀，只适用于一次电池。

H. X. Yang, et al. *Electrochem & S. S. Lett.* 7 (2004) A212-A215

耐碱的金属硼化物：Co-B 与Fe-B

Alkaline-resistant Metal Borides: Co-B and Fe-B



(a) Co–B electrode
(b) Fe–B electrode

30% KOH solution

$$FeB_x + (6x+3)OH^- \rightarrow 0.5Fe_2O_3 + xBO_3^{3-} + (1.5+3x)H_2O \quad (1)$$

>1200 mA h/g

$$CoB_x + (6x+2)OH^- \rightarrow Co(OH)_2 + xBO_3^{3-} + 3xH_2O \quad (2)$$

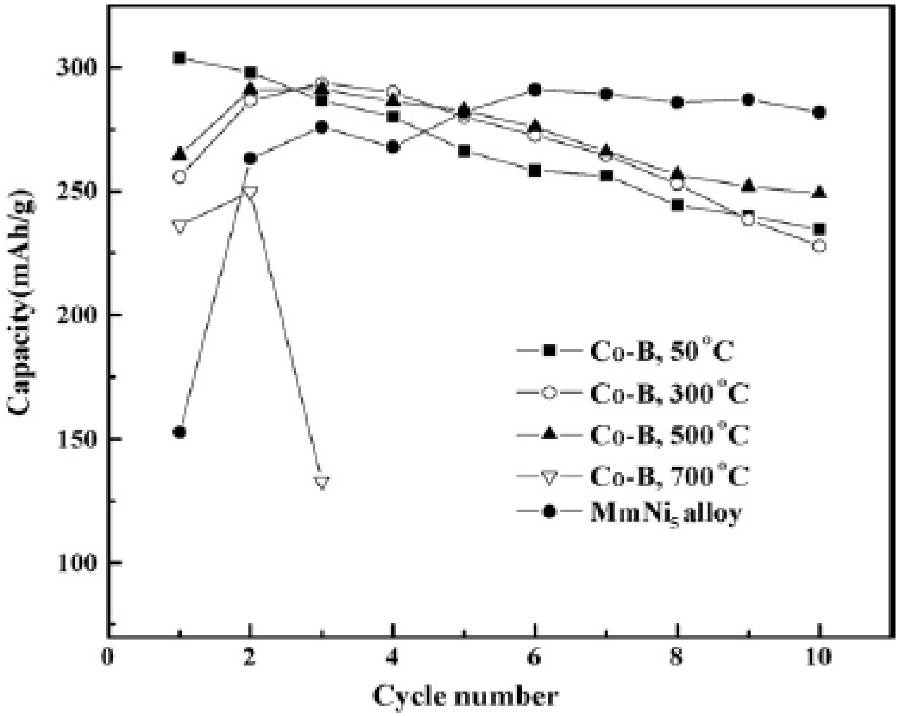
>1100 mA h/g

Primary batteries 一次电池

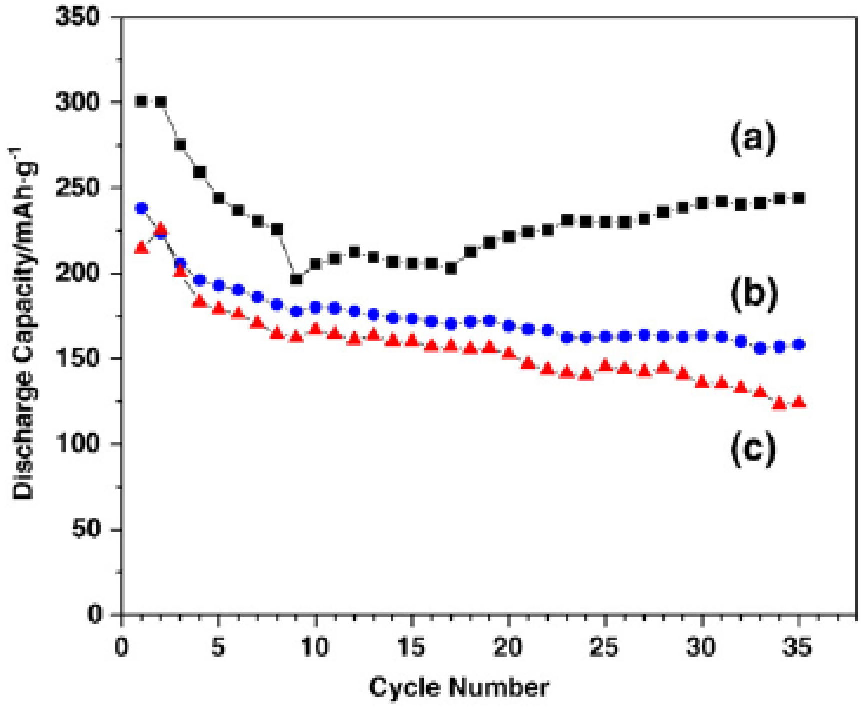
Y.D. Wang, et al. *Electrochem. Commun.* 6 (2004) 780

二次电池用金属硼化物： 非晶态Co-B

Metal Borides for secondary batteries: amorphous Co-B



Cycling performances of the batteries adopting Co–B alloys and $MmNi_5$ alloy as anode materials in alkaline secondary batteries discharged at a constant current of 60 mA/g.



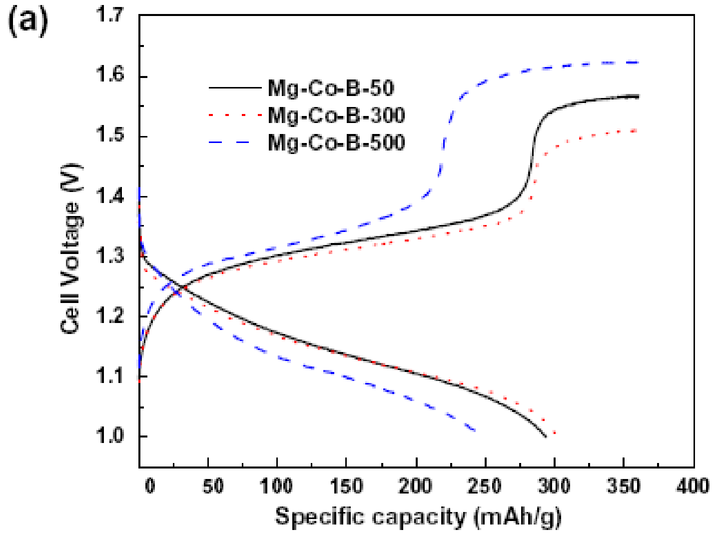
Cycling performances of the Co–B samples synthesized via different methods at a rate of l30 mA/g. (a) via chemical reduction method, (b) via ball milling method, (c) via electric arc method

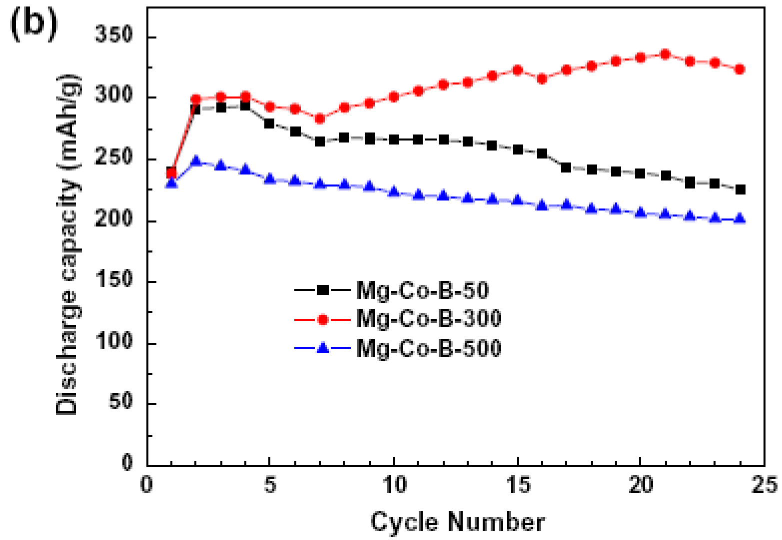
C. Wu, et al. ***Electrochimica Acta*** **53 (2008) 4715**

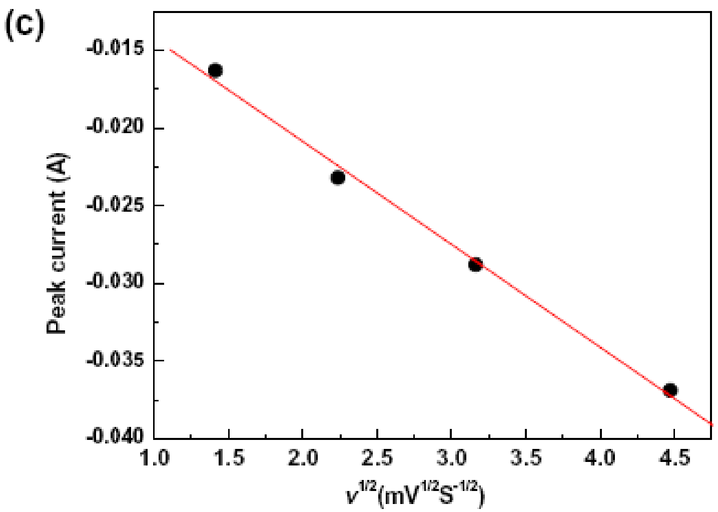
C. Wu, et al. ***Solid State Ionics*** **179 (2008) 924**

二次电池用金属硼化物：非晶态Mg-Co-B

Metal Borides for secondary batteries: amorphous Mg-Co-B







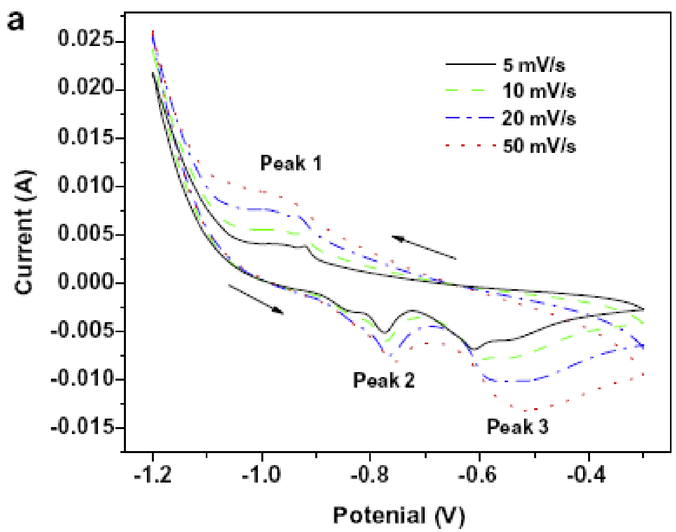
A stable Mg-based electrode in 6mol/l KOH + 1mol/l LiOH alkaline solution.

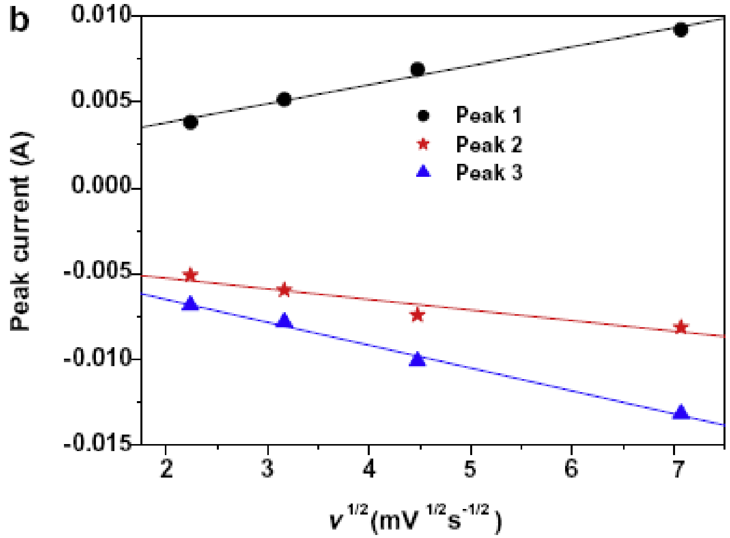
在6mol/L KOH + 1mol/L碱性电解液中稳定的镁基电极。

C. Wu, et al. *Electrochem. Commun.* (2009) 2173-2176

二次电池用金属硼化物： 晶态Fe-B

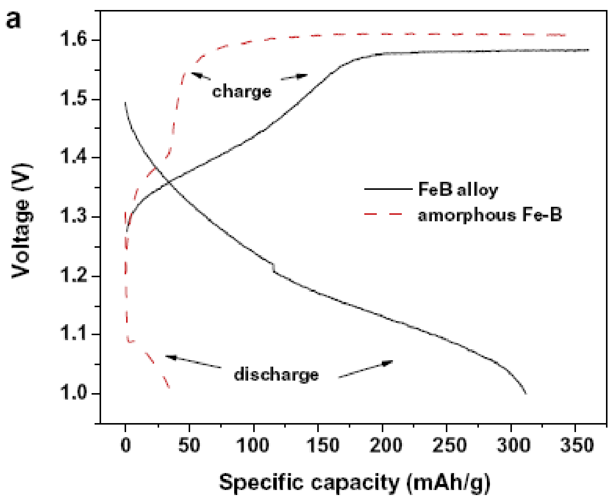
Metal Borides for secondary batteries: Crystal FeB





The multi-electron reactions of FeB are in two or more steps.

FeB的多电子反应分多步完成。

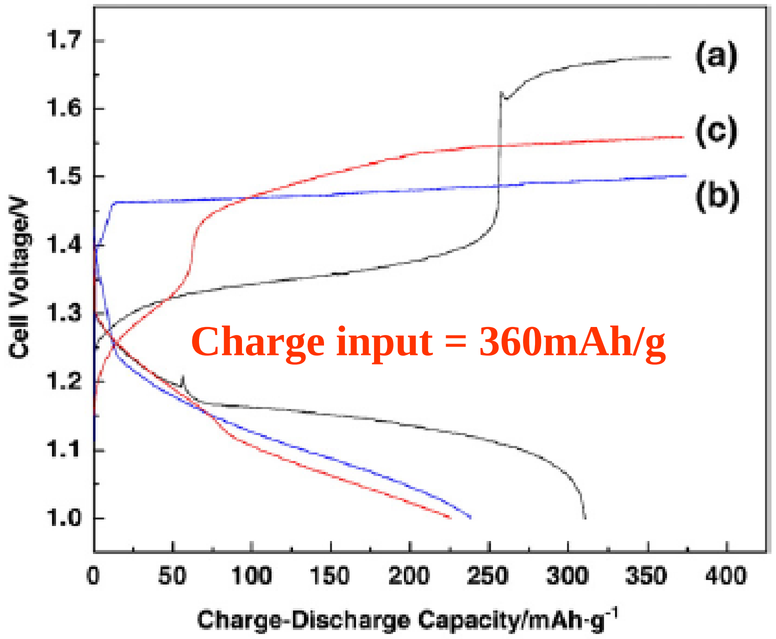


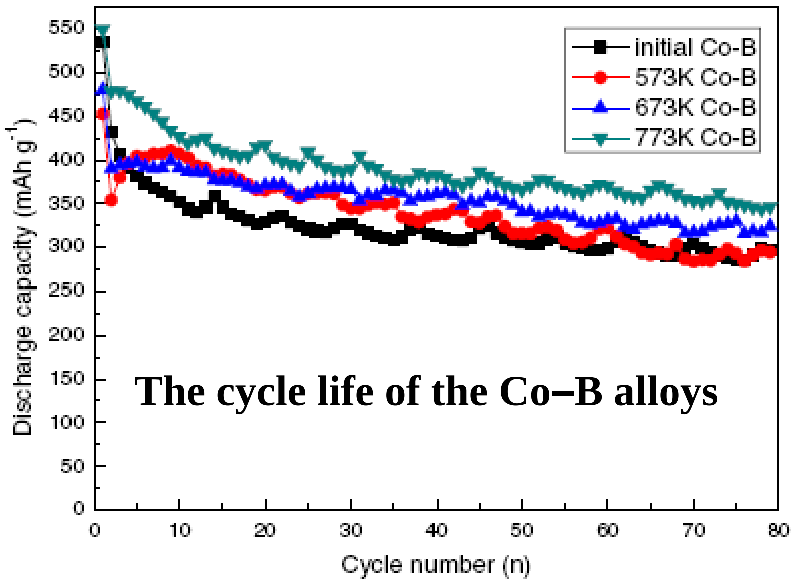
The multi-electron reactions of FeB are diffusion-controlled reactions.

FeB的多电子反应为扩散控制反应。

Y. Bai, et al. *Electrochem. Commun.* 11 (2009) 145–148

Effect of Charge Input





Typical charge–discharge curves of the Co–B alloys synthesized via different methods at a constant current of 30 mA/g. (a) via chemical reduction method, (b) via ball milling method, (c) via electric arc method.

200mA/g for 3hrs

Charge input = 600 mAh/g

C. Wu, et al. *Solid State Ionics* 179 (2008) 924

D. W. Song, et al. *Electrochem. Commun.* 10 (2008) 1486

电化学转化反应：金属氟化物正极材料

Electrochemical Conversion Reactions: Metal Fluoride Cathode Materials

The strong electronegativity of F^- results in high conversion reaction potentials for metal fluorides, which are regarded as potential cathode materials and paid more and more attentions.

金属氟化物由于F^-较强的电负性，具有比较高的转换反应电动势，是近年来备受关注的具有较大应用前景的锂二次电池新型正极材料。

$$MF_n + nLi^+ + ne^- \longleftrightarrow M + nLiF$$

MF_n	$\triangle_r G_m^0$ [kJ mol^{-1}]	E^0 [V]	C_0 [mAh g^{-1}]	MF_n	$\triangle_r G_m^0$ [kJ mol^{-1}]	E^0 [V]	C_0 [mAh g^{-1}]
CoF_3	-1047	3.617	694	CuF_2	-686	3.553	528
FeF_3	-794	2.742	712	NiF_2	-572	2.964	554
MnF_3	-766	2.647	719	CoF_2	-551	2.854	553
CrF_3	-660	2.280	738	FeF_2	-514	2.664	571
VF_3	-539	1.863	745	AgF	-401	4.156	211
TiF_3	-404	1.396	767				

Typical fluoride: FeF_3（典型氟化物：FeF_3）

$$FeF_3 + 3Li^+ + 3e^- \longleftrightarrow 3LiF + Fe$$

Abundance of iron, low cost, environmental friendly

资源丰富、价格低廉、环境友好

High capacity, high potential, 3e⁻ reversible conversion

高容量、高电压、3电子可逆转化

C_0 = 712 mAh g^{-1}；E^0 = 2.74V

Poor kinetics 动力学性能较差

Poor conductivity 导电性极差

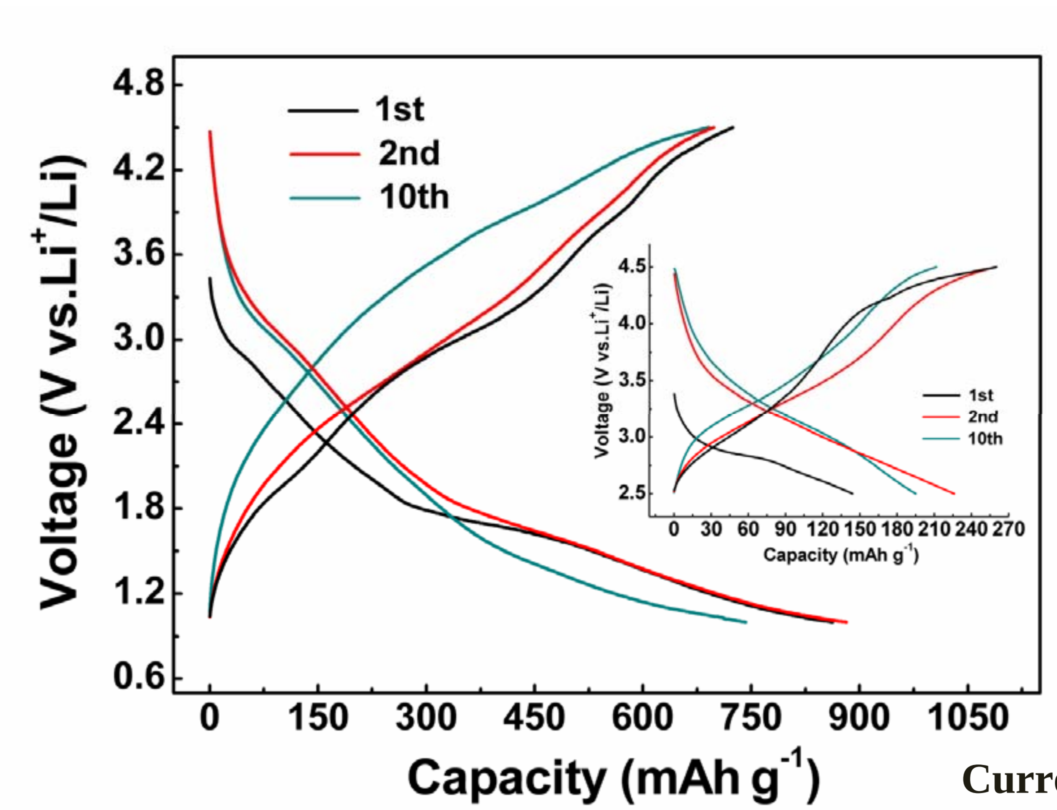
Very sensitive to temperature and current density.
对充放电的温度和电流密度极为敏感。

The efficient approach to improve the kinetics: Nanostructures

优化动力学性能的有效途径：纳米化

FeF_3纳米晶的电化学性能

Electrochemical Performance of FeF_3 nano crystal



$Fe^{+3} \xleftrightarrow{3e^-} Fe^0$

$E^0 = 2.74V \quad C_0 = 712 \text{ mAh g}^{-1}$

20℃， 100 mA g^{-1}

2.5~4.5 V， ~200 mAh g^{-1}

1.0~4.5 V， >700mAh g^{-1}

Current density 电流密度: 100 mA g-1;
Cut-off voltages 电压区间: 1.0-4.5V，2.5-4.5V

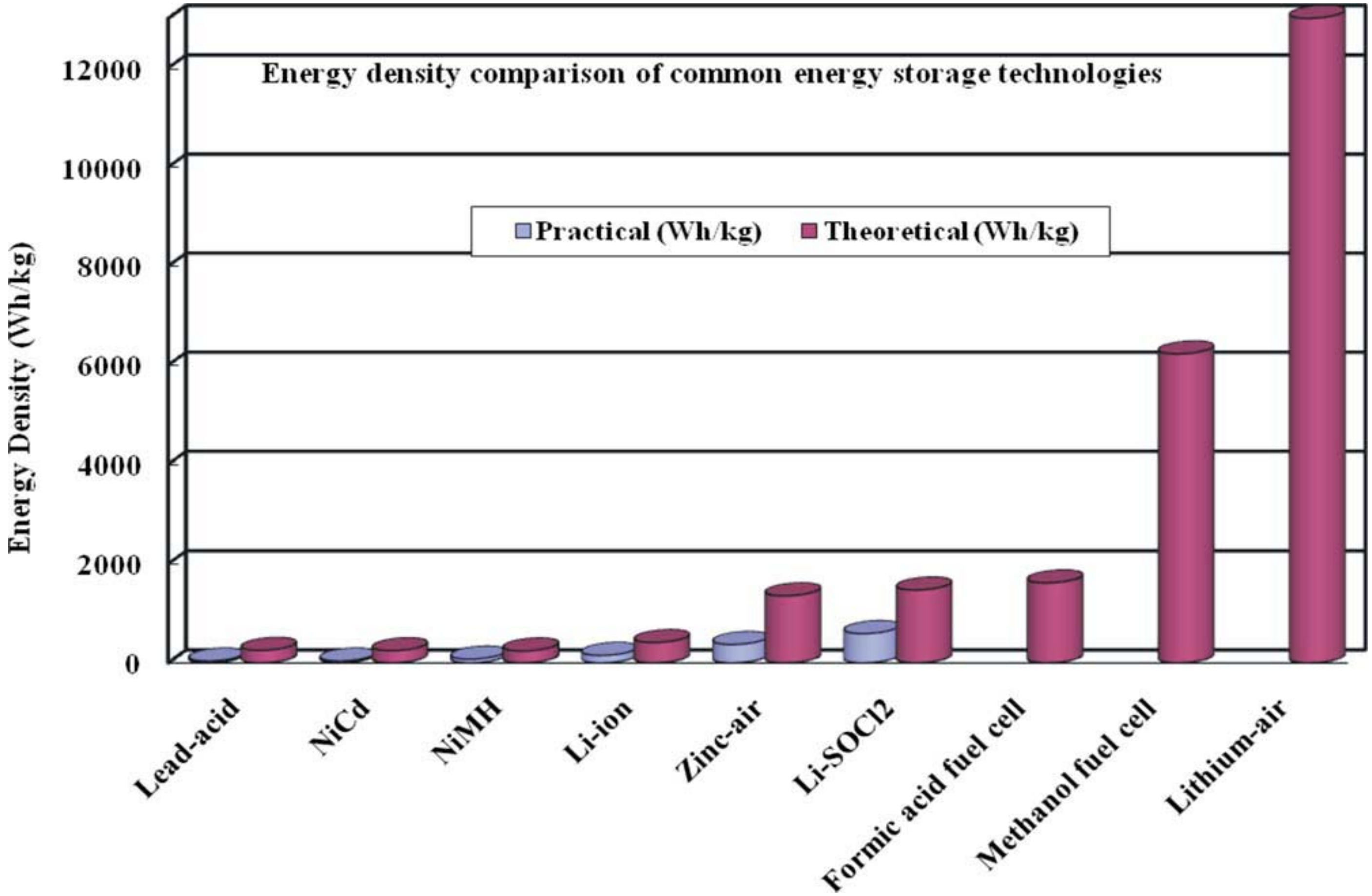
The reversible capacity and the plateaus are in consistent with theoretical 3e$^-$ conversion.

电极的可逆容量和电压平台与FeF_3发生3e$^-$转换的理论容量和电动势基本吻合。

T. Li,, *J. Phys. Chem. C*, 114 (2010) 3190

锂空电池研究

Researches on Li-air Batteries



Lithium air battery possessing one of the largest theoretical specific energy of 11140 Wh kg^{-1} excluding O_2 in present energy storage systems.

Research progress on non-aqueous lithium air battery

❖ K. M. Abraham first report a novel non-aqueous electrolyte lithium air battery in 1996.

❖ J. Read further studied the effect of electrolyte composition, cathode formulation and discharge mechanism on the electrochemical properties of Li/O_2 cells.

❖ P. G. Bruce demonstrated the electrochemical reaction of $2Li + O_2 = Li_2O_2$ is reversible, proper oxygen catalyst could facilitate the process and as a result, Li/O_2 battery could have adequate cycling life.

❖ P. G. Bruce elucidated a variety of reactions among dicharge process with alkyl carbonate electrolytes. Due to electrolytes decomposition, $C_3H_6(OCO_2Li)_2$, Li_2CO_3, HCO_2Li, CH_3CO_2Li, CO_2, and H_2O could be formed.

❖ Yang Shao-Horn employed platinum-gold nanoparticles as bifunctional electrocatalyst for Li/O_2 batteries, which rendered a considerable round-trip efficiency of 77%

.

❖ Tatsumi Ishihara introduced the mix use of Pd and mesoporous α -MnO_2 . showing high activity to oxidation and reduction of Li to from Li_2O_2 or Li_2O_2. Enengy efficiency for charge and dischange can be achieved to be 82%.

❖ Others:

Argonne National Laboratory

University of Mass.

Northwest pacific national Laboratory

TOYOTA CHUO KENKYUSHO KK;

EXCELLATRON SOLID STATE LLC

Yardney Technical Products, Inc.

Toshiba Corporation;

Tekion, Inc.

☺ Benefits

- ❖ High energy density

  11140 Wh kg^{-1} excluding O_2 ; an order of magnitude larger than achievable using conventional batteries.
- ❖ Technology amenable to a low cost
- ❖ Excellent carbon footprint

☹ Challenges

- ❖ Electrolyte (open battery system)

  e.g. conventional organic electrolyte: hydrophilic and volatility
- ❖ Cycle life
- ❖ Oxygen selecting membrane
- ❖ Lithium corrosion

Facing the Challenges

Investigate electrode formulation, seek efficiency and selectivity of catalysts for oxygen reduction and search proper electrolyte for lithium air cells:

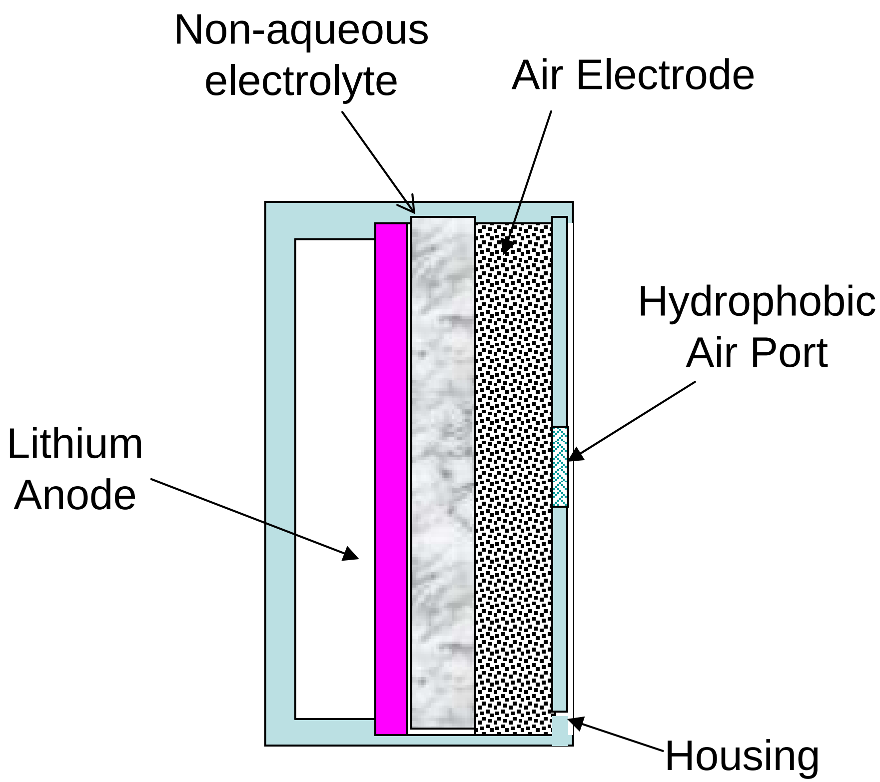
1) Nano-structured MnO_x catalyst;

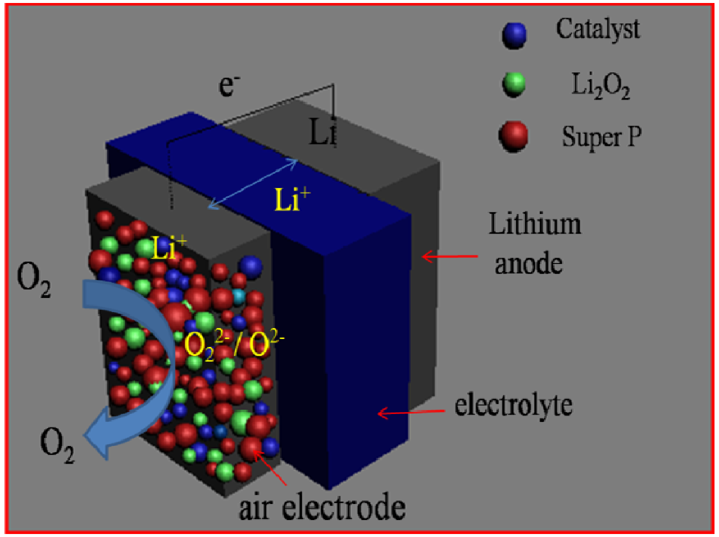
2) Nano-sized $La_{0.8}S_{r0.2}MnO_3$ catalyst;

3) Ionic liquid electrolyte

团队的研究进展

Approaches in Progress in Our Team



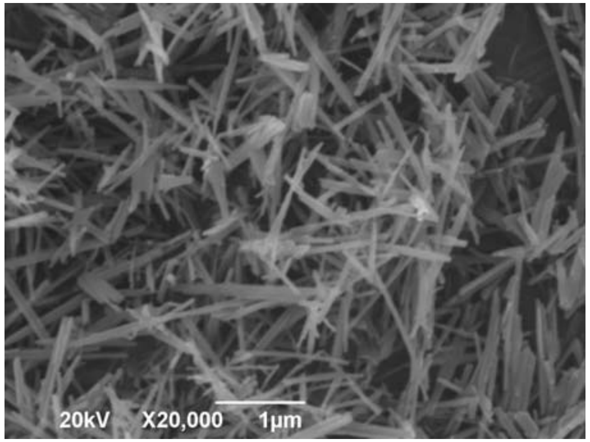


The Lithium air battery prototype

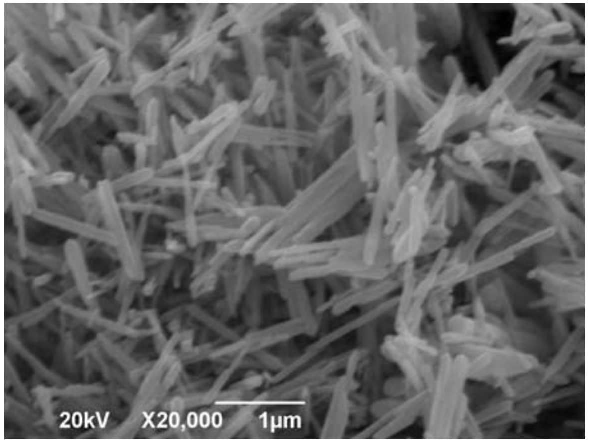
锂空电池的样机

采用纳米 MnOx作为催化剂的锂空电池

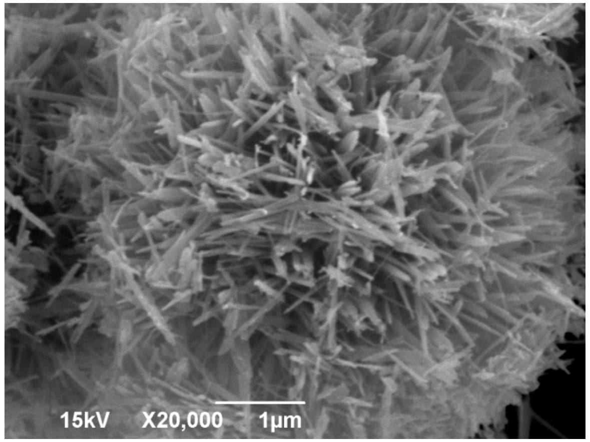
Nano-structured MnOx catalyzed rechargeable lithium air cells



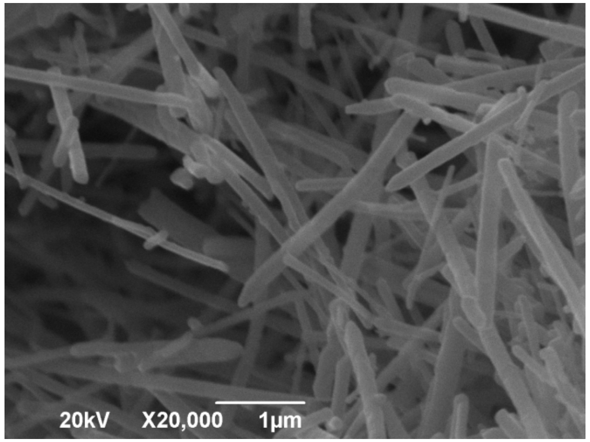
α -MnO_2



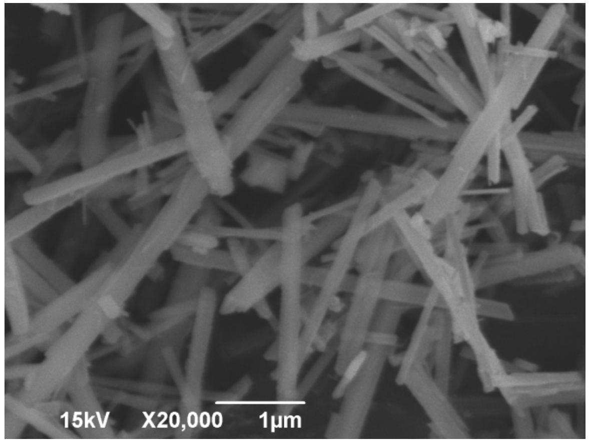
β -MnO_2



γ -MnO_2



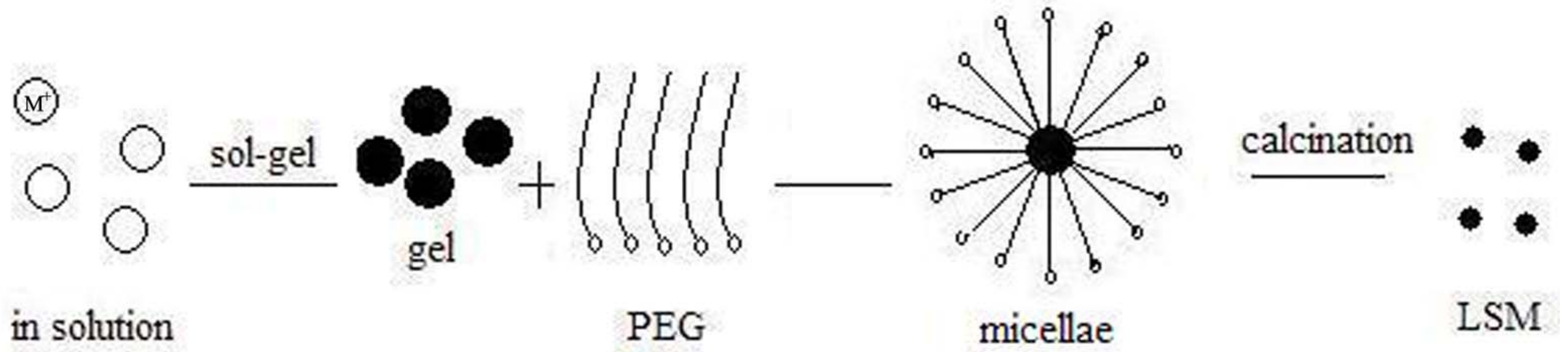
Mn_2O_3



γ -MnOOH

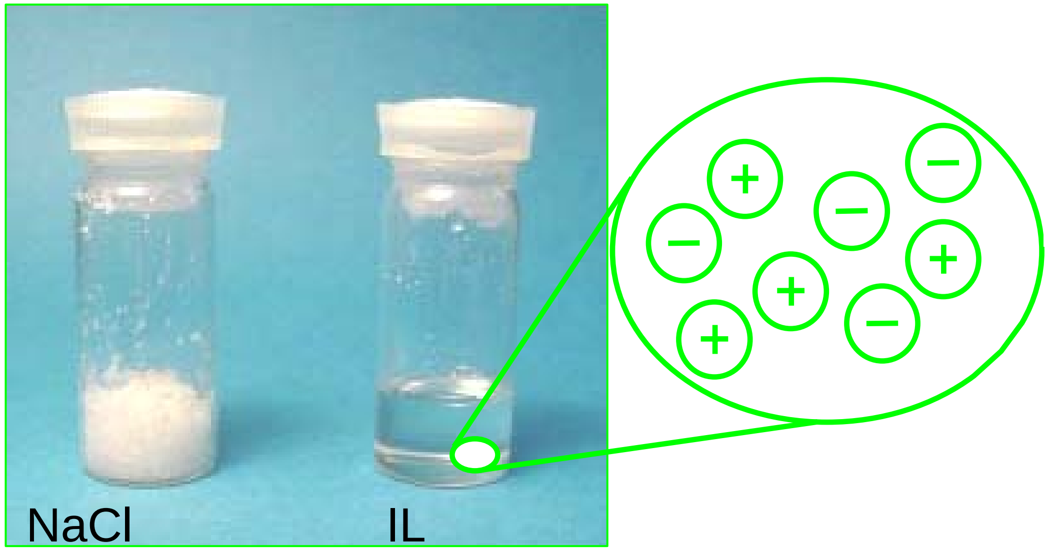
纳米$La_{0.8}Sr_{0.2}MnO_3$作为非水Li/O_2电池的氧还原催化剂
Nano-sized $La_{0.8}Sr_{0.2}MnO_3$ as oxygen reduction catalyst in non-aqueous Li/O_2 batteries

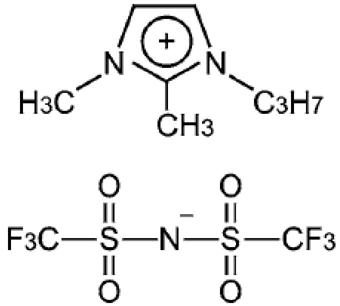
Formation Mechanism of g- $La_{0.8}Sr_{0.2}MnO_3$ (LSMO) Particles by Sol-gel Method

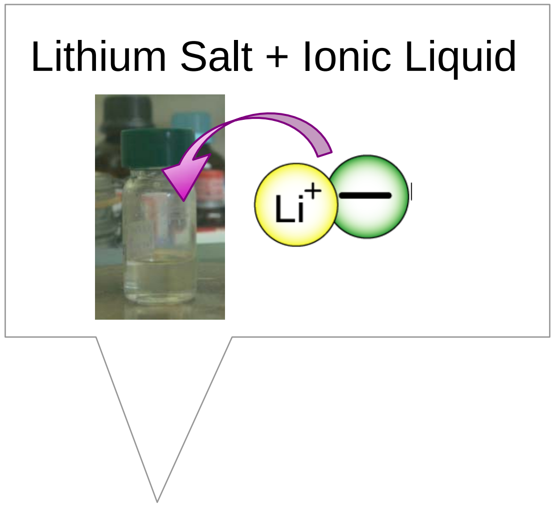


室温锂空电池用离子液体

Ionic liquids for ambient lithium air cells



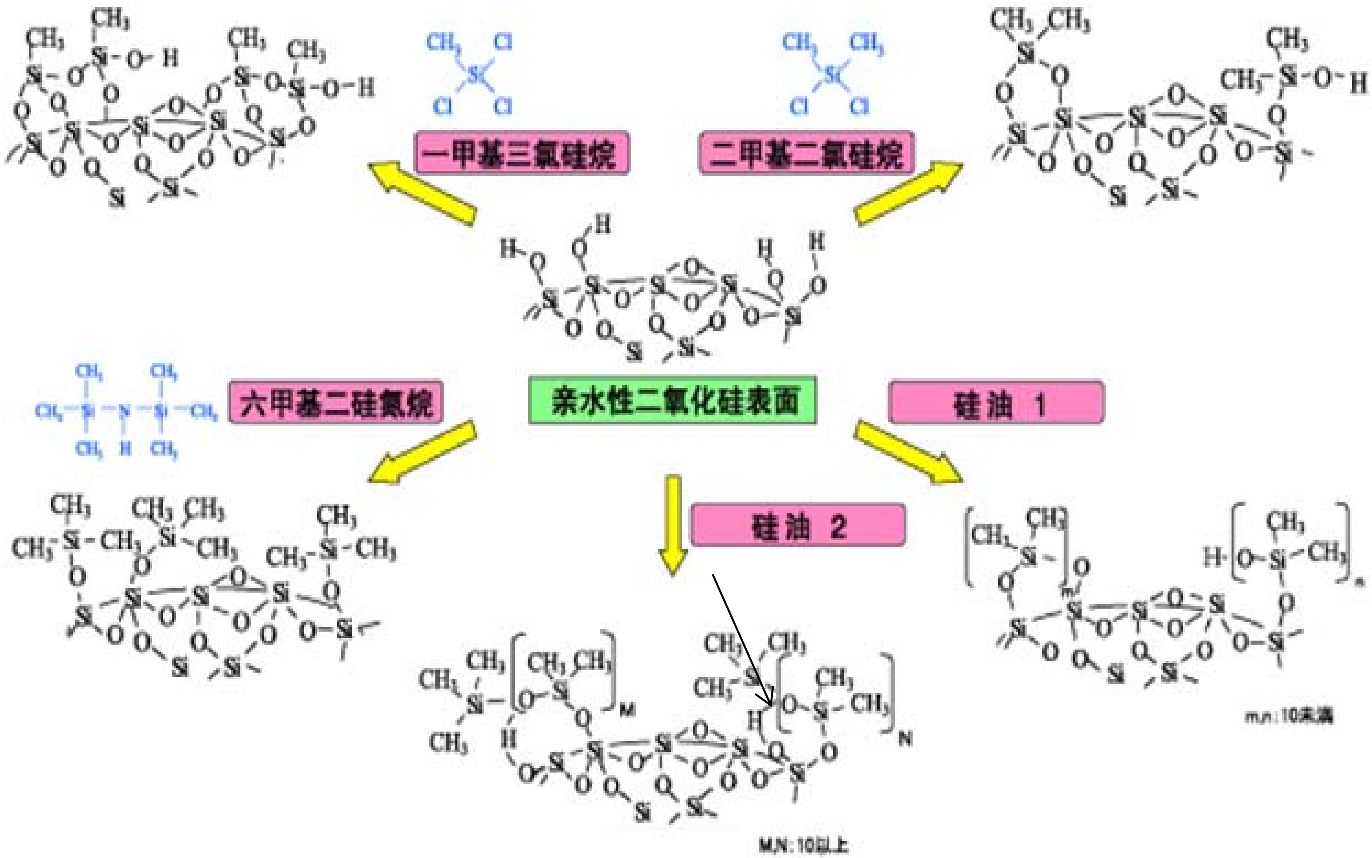




Ionic liquids melts at much lower temp (Cool solution).

1M LiTFSI-PMMITFSI

阻水的离子液体基复合聚合物电解质隔膜
Hydrophobic ionic liquid-silica composite polymer electrolyte membrane



Hydrophobic ionic liquid + hydrophobic silica + PVdF-HFP

Thank you for your attention !