Aqueous Rechargeable Lithium Batteries (ARLBs) of High Energy Density

Prof. Dr. Yuping Wu

New Energy and Materials Laboratory (NEML),
Department of Chemistry,
Fudan University, Shanghai 200433

Tel/Fax: +86-21-5566 4223
Email: wuyp@fudan.edu.cn

@ 6th US-China Electric Vehicles and Battery Technology Workshop, Boston
23-24 August, 2012

Motto of NEML

4E + E

Electrochemical technologies

Solve

Reduce

Energy problem

Environmental pollution

Enjoy life

To cultivate **E**lites for the society.

1. Chemical Power Sources

- Supercapacitors
- Polysulfide bromide battery (PSB)
- Zn/Br battery
- Vanadium redox couples (VRC)
- Sodium sulfur battery (Na/S)
- Lead acid battery
- **Metal-air battery**
- Ni-MH
- **Lithium ion battery**
- **Aqueous rechargeable lithium battery (ARLB)**
- ……

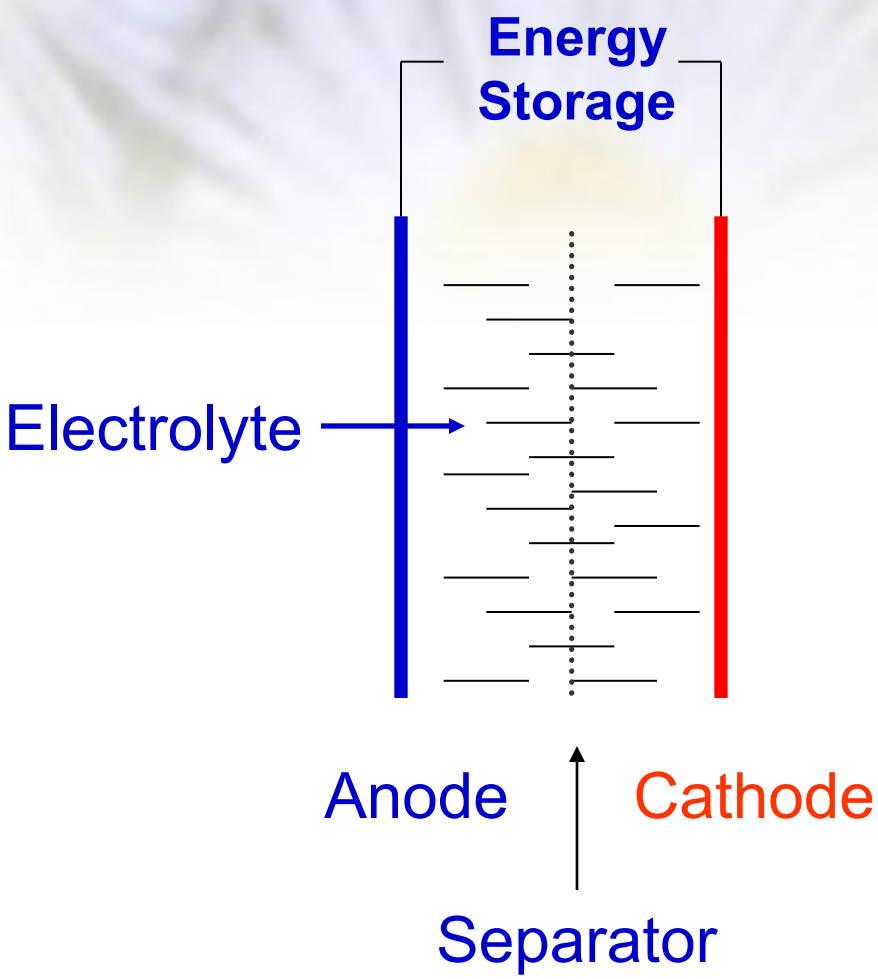
- Safety
- Rate capability
- Energy density
- Energy efficiency
- Cycling life
- Maintenance
- Capital cost for kWh
- Per-cycle cost

Lithium Ion Batteries

Characteristics of lithium ion batteries:

- High output voltage (average 3.6V) and power
- High energy density (UR18650: >500 Wh/dm^3, >200Wh/kg)
- Low self discharge (<10%/month)
- No memory effect
- Long cycle life (>1000 times)
- High rate capability (1C)
- High coulomb efficiency (near 100% except in the 1st cycle)
- Easy to measure the residual capacity
- Maintenance free
- No environmental pollution (**green** battery)
- Wide work temperature (-25 - +45°C, extended to –40 – 70°C)

Main Materials for Lithium Ion Batteries



Inner safety

- Anode material
- Cathode material
- **Electrolyte**
- Separator

Safety during Abuse

Field Failure

– Manufacturing defects

• Loose connection, separator damage, foreign debris

• Can develop into an internal short circuit

• Can lead to overheating and thermal runaway

Abuse Failure

– Mechanical

• crush, nail penetration

– Electrical

• short circuit, overcharge

– Thermal

• thermal ramp, simulated fire

A123: PHEV (Jun. 2008)

(April. 2011)

A flammable, solvent-based electrolyte is used.

One conclusion @5th China-U.S. Electric Vehicle and Battery Technology Workshop

- **Safety & reliability for lithium ion batteries is the challenging problems for electric vehicles.**

- **Gel lithium ion batteries (GLIBs) is surely the true choice as power source for EVs.**

GMs: Self-distinguishing

Safety time: **Another importance**

Full charge and then put on **electric oven**: at least 1 min and 10 seconds (even for C//$LiCoO_2$) to escape when EVs are on fire.

Li//Air

Challenging problems

- Conductors of low ionic conductivity
- Low stability: reaction with Li_2O_2
- Low O_2 solubility
- Low Li_2O_2 solubility
- Narrow temperature
- High overpotentials
- Low energy efficiency
- Low practical energy density
- Sensitive to the environment
- … …

Prof. Deyang Qu @5th China-U.S. Electric Vehicle and Battery Technology Workshop, 17-18 April, 2012

Li//S

- Li ???

Nobody should forget the story of MoLi Company (Li//MoS_2).

Some facts:

- MoS_2 is more reliable than S.
- Lithium dendrite is the main safety issue instead of S.
- Low volumetric energy density.

There is still quite some distance to go.

New Power sources

Cheap: Lead acid has the largest market

Green: The ultimate goal of electrochemists

Power density: Very high

Neutral aqueous solutions.

What is ARLB ?

Definition:

- Lithium intercalation compound(s) as one or both electrodes
- Redox reactions instead of absorption/ desorption
- Aqueous lithium-containing solution as electrolyte

Why not called as aqueous lithium ion batteries:

◆Misunderstanding: Aqueous to replace organic ???

◆Scope: Very narrow

2. Aqueous rechargeable lithium battery (ARLB)

Rechargeable Lithium Batteries with Aqueous Electrolytes

Wu Li, J. R. Dahn,* D. S. Wainwright

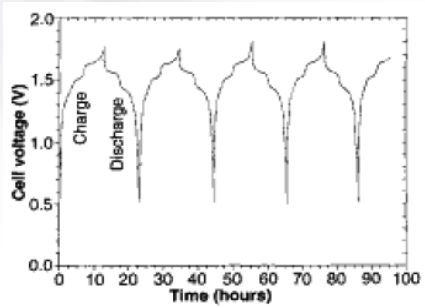
Rechargeable lithium-ion batteries that use an aqueous electrolyte have been developed. Cells with $LiMn_2O_4$ and VO_2(B) as electrodes and 5 M $LiNO_3$ in water as the electrolyte provide a fundamentally safe and cost-effective technology that can compete with nickel-cadmium and lead-acid batteries on the basis of stored energy per unit of weight.

During the 1970s and 1980s, rechargeable lithium batteries were touted by some researchers as providing a possible long-term solution to the electric vehicle (EV) battery problem. The cells had about twice the energy density (measured by watt-hours stored per kilogram of battery) of the best competing ambient temperature batteries. Many companies moved to commercialize the technology, beginning with small cells for consumer applications, in view of the large markets anticipated. These cells used lithium metal as the negative electrode, a transition metal oxide [such as MnO_2 (1)] or chalcogenide [such as $NbSe_3$ (2)] as the positive electrode, and a nonaqueous electrolyte containing dissolved Li ions.

The operation of such cells is based on the ability of the positive electrode material to reversibly "intercalate" Li. Intercalation is the insertion of a guest atom (Li, for instance) into a host solid (such as MnO_2), accompanied by only slight, reversible structural changes in the host. Hosts for intercalation are commonly layered compounds such as graphite (3) or tunnel compounds such as MnO_2 or $LiMn_2O_4$ (4), in which the intercalated Li can reside between the layers or in the tunnels. Intercalation of Li occurs because the chemical potential of Li can be lowered when the Li atom is inserted into the host, thus forming chemical bonds.

The binding energy of Li when intercalated into a variety of hosts has been measured with respect to the binding energy of Li metal (Fig. 1). In each of the hosts listed,

W. Li and J. R. Dahn, Department of Physics, Simon Fraser University, Burnaby, British Columbia, Canada V5A 1S6.
D. S. Wainwright, Moli Energy (1990) Limited, 20000 Stewart Crescent, Maple Ridge, British Columbia, Canada V2X 9E7.
*To whom correspondence should be addressed.



We calculated the energy density of the cell using the weight of the electrodes, the cell voltage, and the cell capacity (we did not include the electrolyte or cell-case weight). This cell's energy density is 75 watt·hours/kg. Typically, the active electrode weights are about 50% of the total weight of practical cells, if the Sony Li-ion product is used as an example. Thus, practical energy densities near 40 watt·hours/kg can be expected for this chemistry when used in larger cells. Furthermore, the theoretical energy density for this cell is 112 watt·hours/kg, assuming 0.5 Li per transition metal can be cycled in each electrode and that the average cell voltage is 1.5 V. These assumptions would give about 55 watt·hours/kg in a practical cell, which is competitive with both Pb-acid (about 30 watt·hours/kg) and Ni-Cd (about 50 watt·hours/kg) technologies.

$LiMn_2O_4$//VO_2(B)

Possibility and availability.

Poor cycling.

W. Li, J. R. Dahn, D. Wainwright, Science, 264, 1115 (1994).

Comments

TECHNOLOGY

Lithium Battery Takes to Water—And Maybe the Road

Playwright Arthur Miller had his own formula for the death of a salesman, but here's one that might work just as well: a showroom full of $60,000 electric cars whose top speed is 50 miles per hour when the air conditioner is on and whose batteries are prone to smoke or catch fire if ruptured. Some transportation researchers say that sale-killers like those are one possible outcome of the very work that aims to improve performance of electric vehicles (EVs): the development of advanced batteries. These "superbatteries" improve on the range of standard lead-acid batteries and withstand repeated recharging better—but often at the cost of chemical stability or high peak current. And, says Daniel Sperling, director of the Institute of Transportation Studies at the University of California, Davis, advanced batteries "could be so expensive that they will kill off the market [for EVs] rather than expand it."

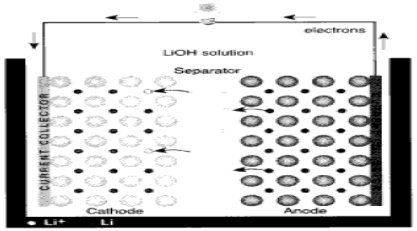
But on page 1115 of this issue, Wu Li and Jeffery Dahn of Simon Fraser University in British Columbia and D.S. Wainwright of Moli Energy report steps toward improving the low current, high cost, and instability of one electric-vehicle contender: the lithium-ion battery. By chemically taming the highly reactive lithium in the battery and replacing the complex electrolyte of earlier versions with a simple water solution, the work "could really simplify the whole field of rechargeable lithium-ion batteries," says George Blomgren, a senior technology fellow at Eveready Battery Company. With further refinement, Dahn and his colleagues believe, aqueous lithium-ion batteries could gain a strong position among EV contenders.

Lithium emerged as a promising material for rechargeable batteries in the mid-1970s, when researchers realized that individual cells based on lithium could produce a higher voltage than nickel-cadmium (NiCad) or lead-acid cells. Higher voltage opened the possibility of lighter batteries for, say, portable electronic equipment, because fewer cells would have to be linked to make a usable battery. What's more, a higher voltage cell can store more energy, which translates to longer operation per charge for a given battery weight.

But these potential benefits came at a high cost. Because lithium reacts violently with moisture, the batteries can burn when in organic compounds. Unfortunately, such electrolytes usually have high resistance to the power-producing flow of current. And their effectiveness rapidly degrades in contact with water and air, which means the batteries must be manufactured with purified materials under carefully controlled conditions, then hermetically sealed.

The first lithium-ion cells made use of lithium metal for the negative electrode and an "intercalation" compound, which usually has a lattice structure, as the positive electrode. As such a cell produces current, lithium atoms give up electrons at the negative electrode, yielding positive ions that travel through the electrolyte to the positive electrode. There they intercalate (reversibly insert themselves) into the other electrode. Because the lithium ions effectively "fall" toward the intercalation compound, which has a much greater affinity for them than does the metal, electrons are driven through the external circuit to the positive electrode, where they are returned to the lithium ions.

The flow can be reversed to recharge the battery when a voltage is applied to the external circuit, pushing the ions back up the electrochemical hill and redepositing them on the lithium metal of the negative electrode. Repeated recharging, however, brought out the flaw in these first lithium lithium ions eventually formed a microscopic "fur" whose high surface area apparently made it unstable enough to burn. In 1989, Moli Energy, a pioneer in the field, had to recall thousands of lithium batteries after several of them began spewing smoke or flames.



The wet look. Lithium and a water electrolyte—ordinarily a reactive mixture—peacefully coexist in the new lithium-ion battery.

Since then, several companies have solved the fur problem by using intercalation compounds at both electrodes. That keeps the batteries safe (providing they aren't ruptured), but lithium's reactivity still forced battery designers to use nonaqueous electrolytes, with attendant high cost and low current. As a result, these batteries are unlikely to power anything larger than camcorders and cellular phones, says Howard Saunders of the Westinghouse Science and Technology Center in Pittsburgh.

Dahn and colleagues' strategy for overcoming this deficiency is to restrain the lithium so it can't react with water, then use a simple electrolyte consisting mainly of distilled water. The feat required two kinds of safeguards: manganese oxide–based intercalation compounds that bind the lithium more tightly than the carbon in earlier lithium-ion batteries, and lithium hydroxide dissolved in the electrolyte. Since lithium hydroxide is exactly what results when lithium reacts with water, loading the electrolyte with the compound in effect saturates the system, ruling out further reactions.

The development is "a big plus as far as safety goes," says Saunders, and it opens the way for the development of lithium batteries that would generate larger currents. The disadvantage is that because water breaks down at the high voltages of earlier lithium cells, Dahn and his colleagues had to lower the cell voltages—and hence their energy densities—to values only slightly better than those of NiCad batteries. But those drawbacks may be offset the new battery's relatively low cost. Its aqueous electrolyte should make it much cheaper to manufacture than nonaqueous systems, and its manganese-based electrodes should reduce materials costs by as much as a factor of 10 over nickel-based cells, Dahn estimates.

Still, the savings may not show up for a while in a practical battery. "It took 10 years for alkaline cells to be perfected, even though the chemistry is fairly straightforward," says Duward Shriver of Northwestern University. And Dahn himself notes that there may not even be a pressing need for a car-sized lithium-ion battery: For his own daily commute of less than 50 miles, he says, a lead-acid–powered car might suffice—"as long as it didn't cost me a hundred thousand." Somewhere down the road, though, his work may mean that EV salesmen won't need to get by on just a shoeshine and a smile anymore.

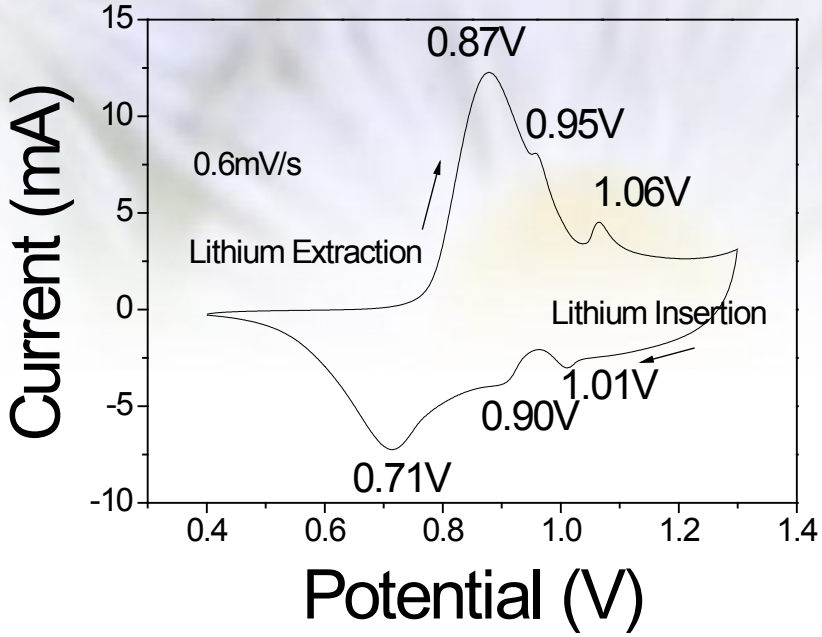
—James Glanz

J. Glanz, Science, 264, 1084 (1994).

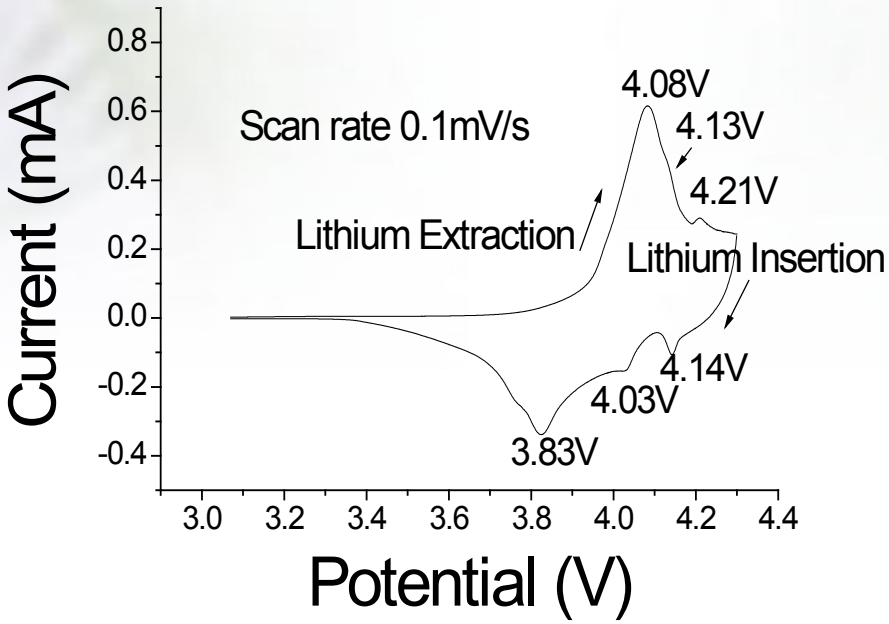
Since our first publication on ARLBs in *Angew. Chem. Int. Edi.* in 2007, Stanford Univ., Kyushu Univ. and the like show great interest.

Our reply: not "maybe" but "sure".

2.1 Cathode: $LiCoO_2$



(a) In saturated Li_2SO_4 aqueous



(b) In organic LIB 315

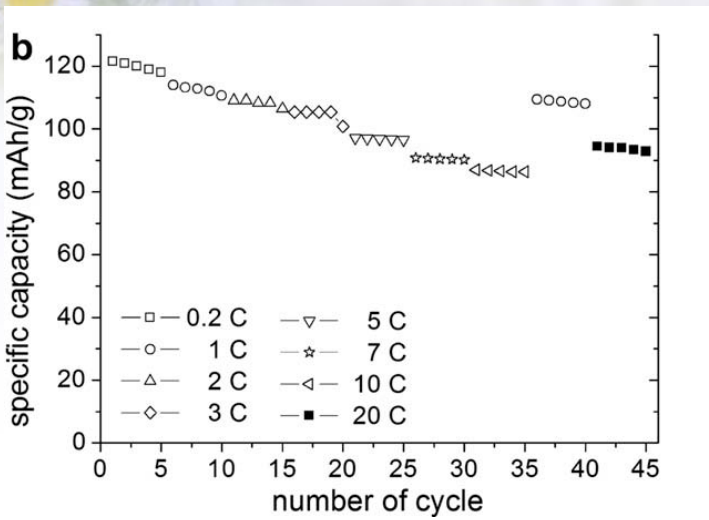
De-intercalation and intercalation of $LiCoO_2$ in aqueous and organic solutions.

Similar behavior including phase transitions.

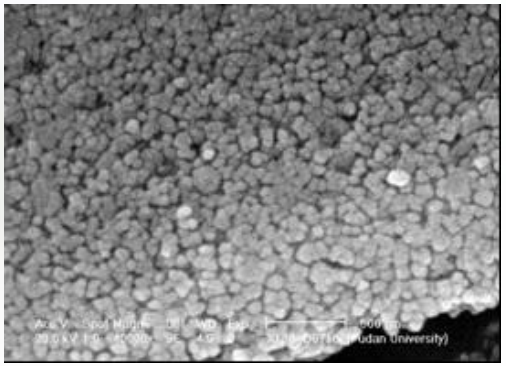
$D_{Li+} = 1.649 \times 10^{-10}$ cm²/s

Wu et al., *Angew. Chem. Int. Ed.*, 46, 295 (2007); *Electrochim. Acta*, 52, 4911 (2007).

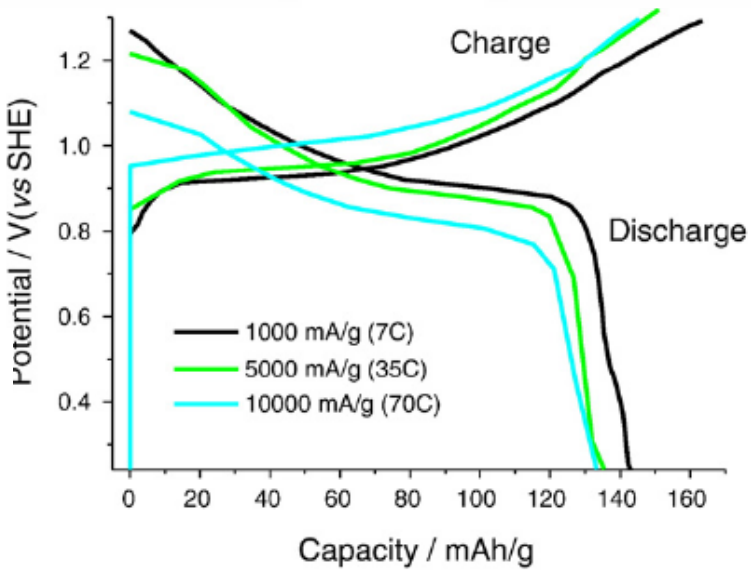
Nanostructured $LiCoO_2$



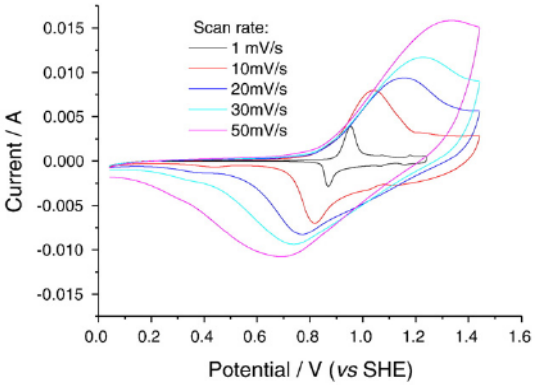
Our nano $LiCoO_2$



$LiCoO_2$ from traditional solid-state reaction in aqueous electrolytes: Results from Stanford University.



Fast kinetics



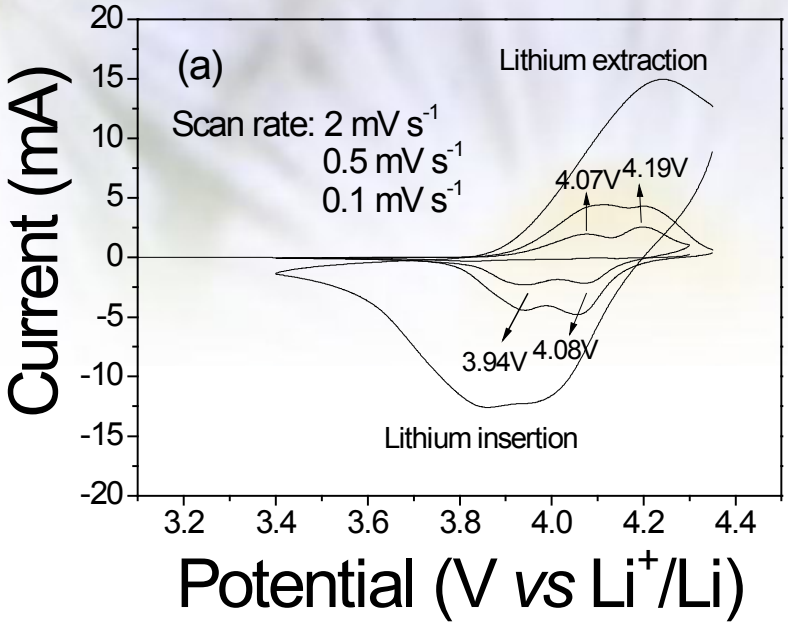
Very good charge-discharge behavior for high power density.

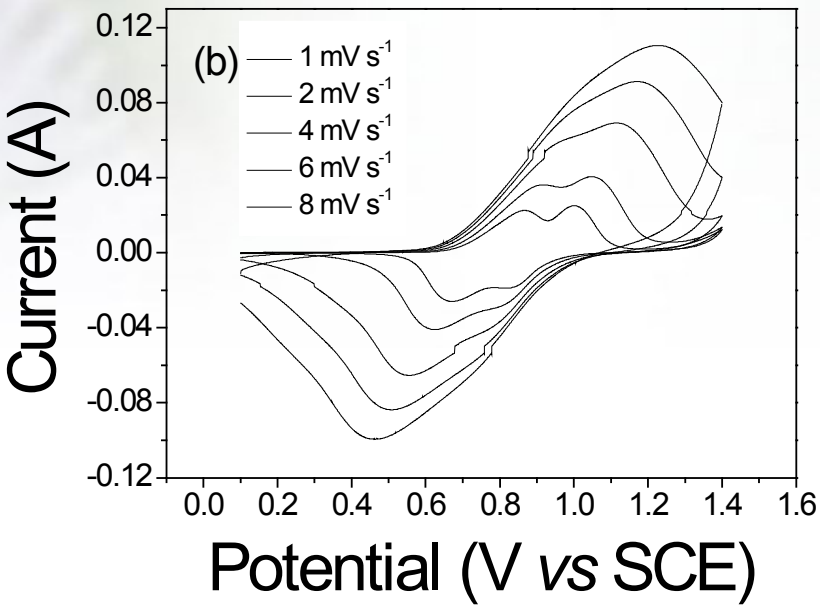
Full charge: < 1 min.

Wu et al., *Electrochem. Commun.* 11 (2010) 1524.

$LiMn_2O_4$: cheap

Fast kinetics





(a)In organic LIB 315

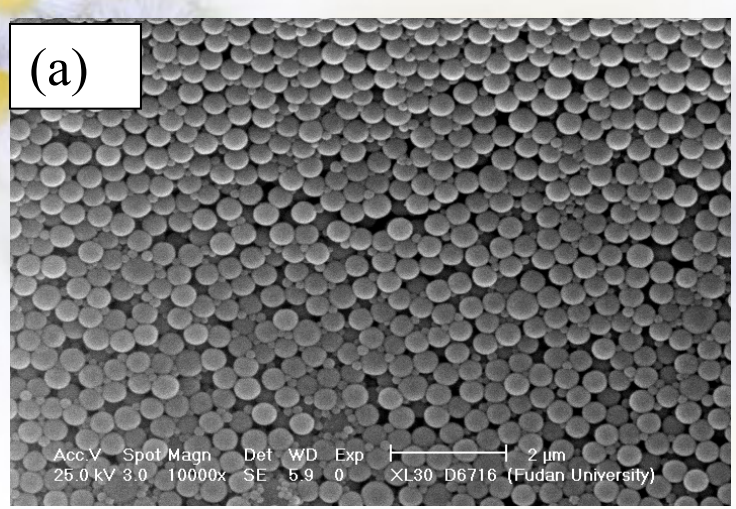
(b) In 2 M Li_2SO_4 aqueous

Similar intercalation and deintercalation behavior in organic and aqueous electrolytes.

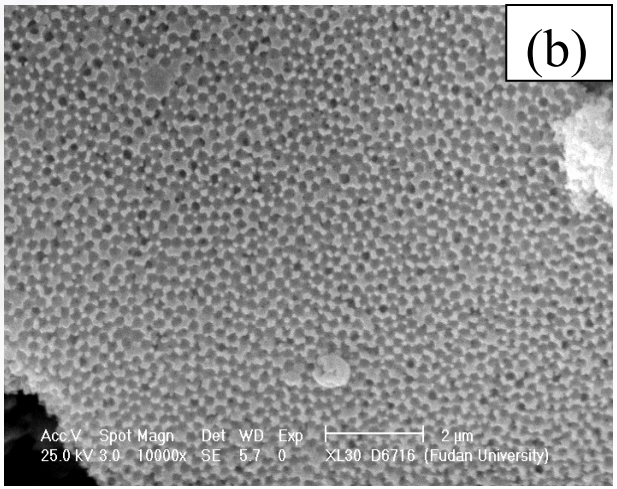
Satisfactory at high scan rate, indicating great promise for application at high current density for aqueous electrolyte.

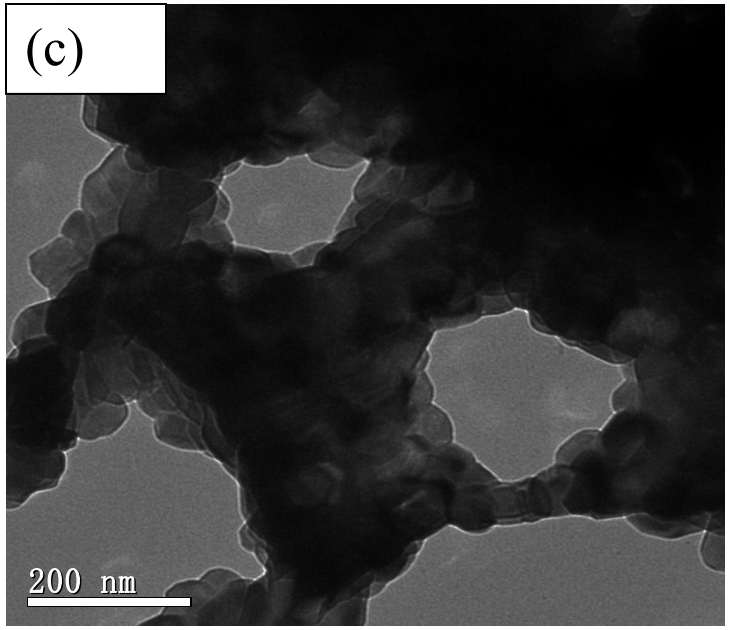
Wu et al., *Funt. Mater. Lett.*, 3 (2010) 151.

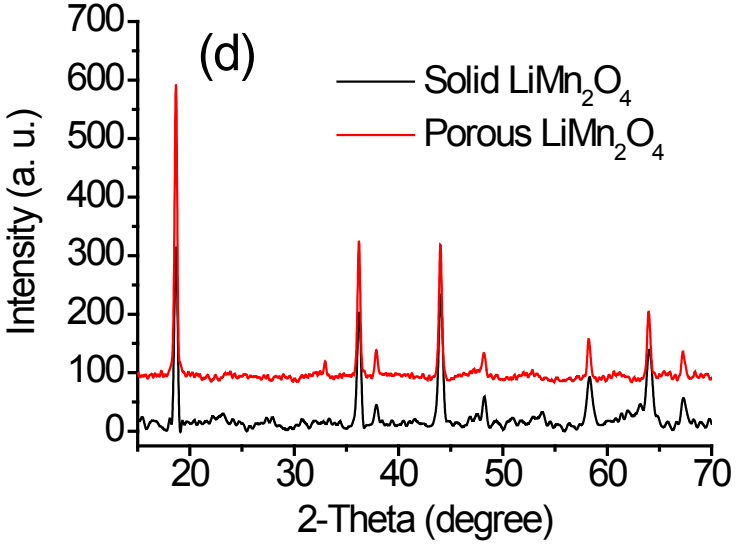
PS template



(1) Macroporous







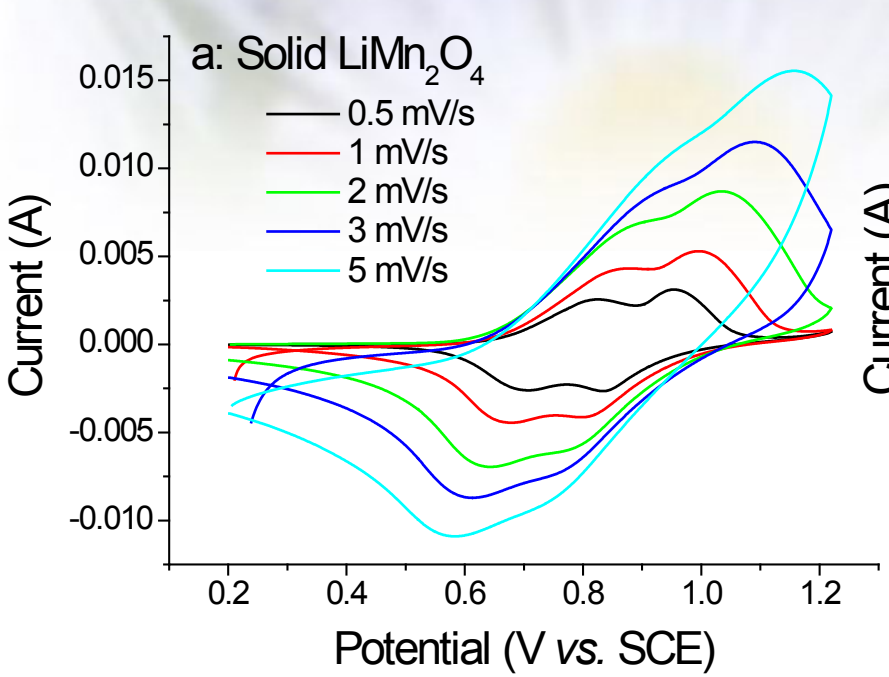
(2) Nanograin

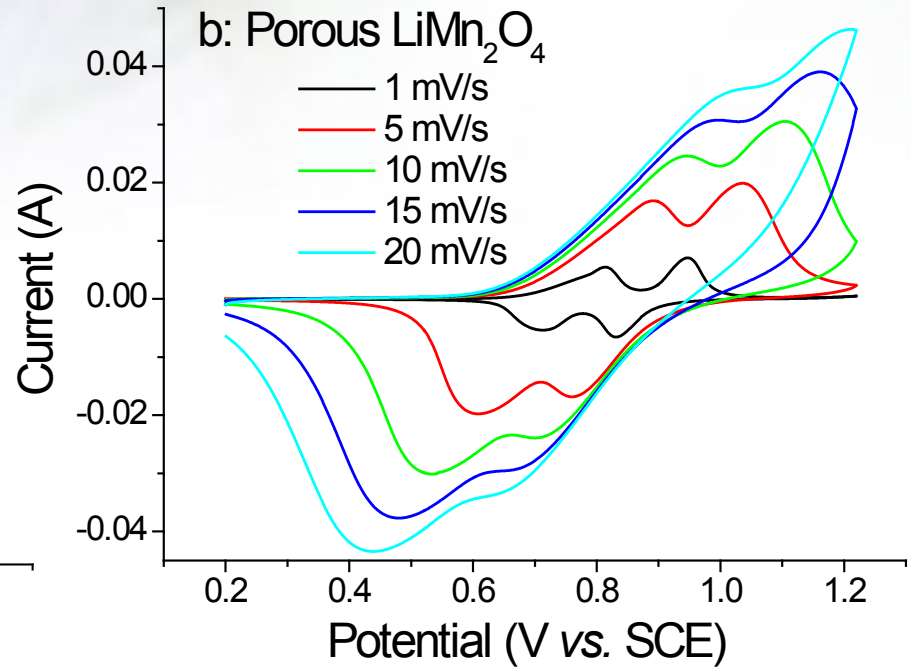
(3) High crystallinity

Wu et al., *Energ. Environ. Sci.*, 2011, 43985 (**Feature article**).

CVs in 0.5 mol l^{-1} Li_2SO_4 aqueous solution.

Ultra-fast kinetics





(a) Solid-$LiMn_2O_4$

(b) Porous-$LiMn_2O_4$

Electrode: 80% active material, 10% conductive agent and 10% binder.

The transportation process in porous $LiMn_2O_4$ electrode will be more facile.

Porous $LiMn_2O_4$: 118 mAh/g

Solid $LiMn_2O_4$: 85 mAh/g

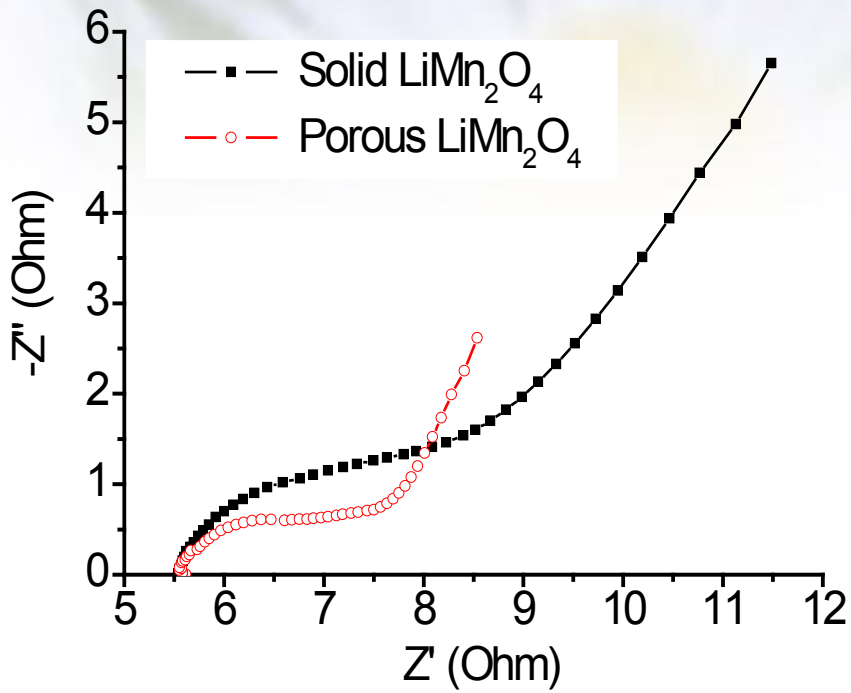


Fig. Nyquist plots by using Ni mesh as the counter electrodes.

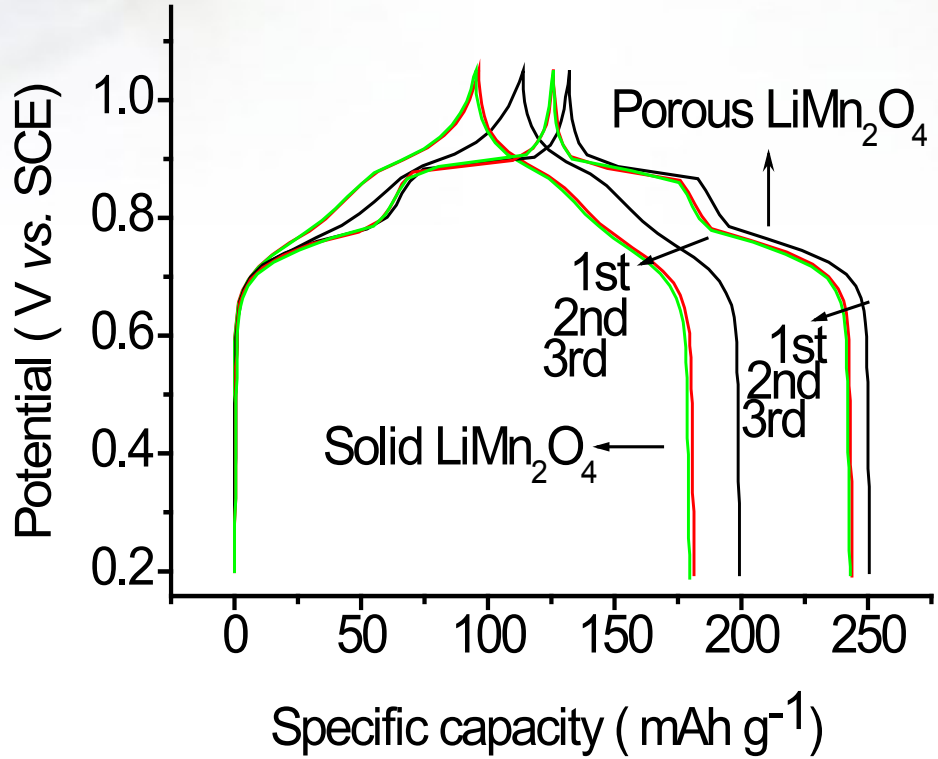
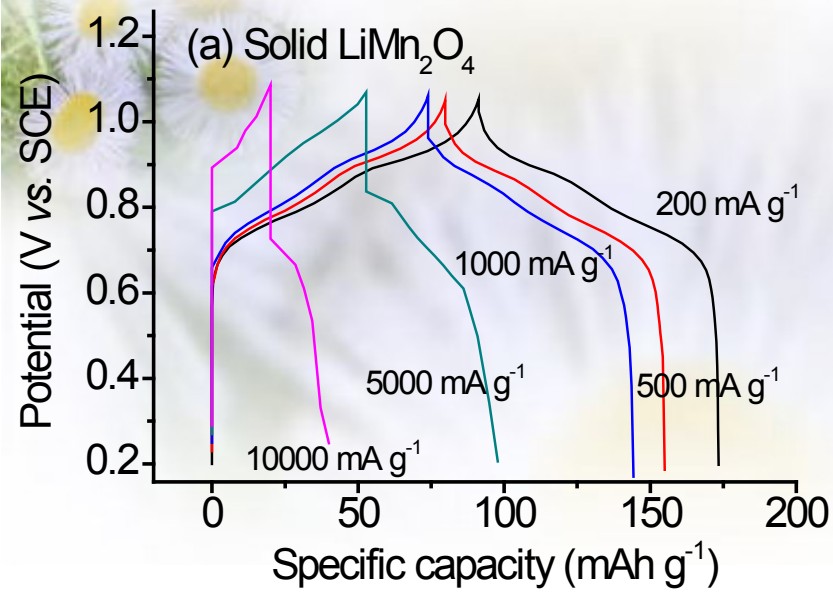


Fig. Charge-discharge curves at 100 mA/g for the initial 3 cycles.



In the case of porous $LiMn_2O_4$, capacity retention is 76% at the charge current density of 10000 mA/g.

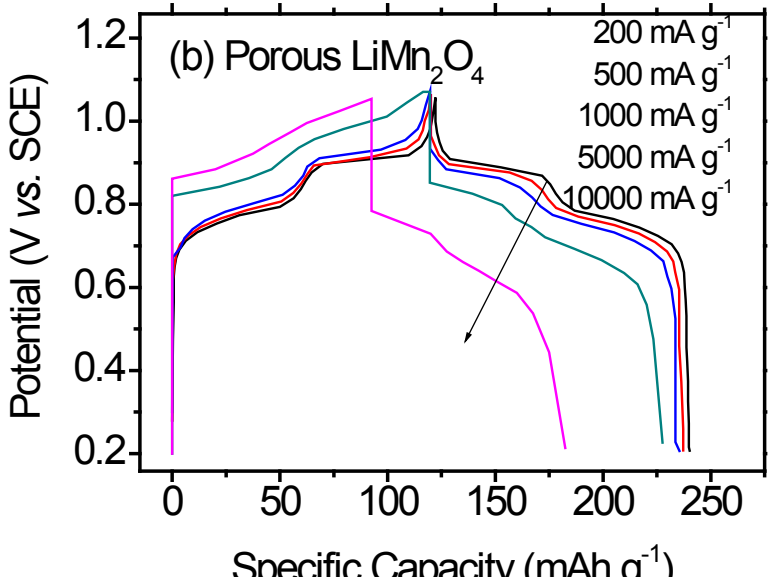


Fig. Charge-discharge at different current density.

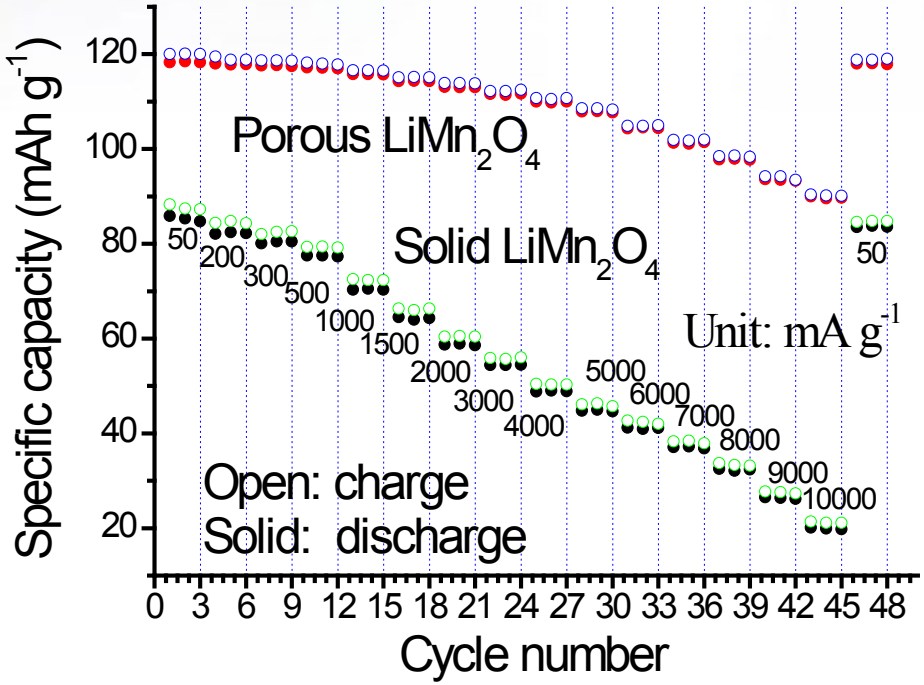
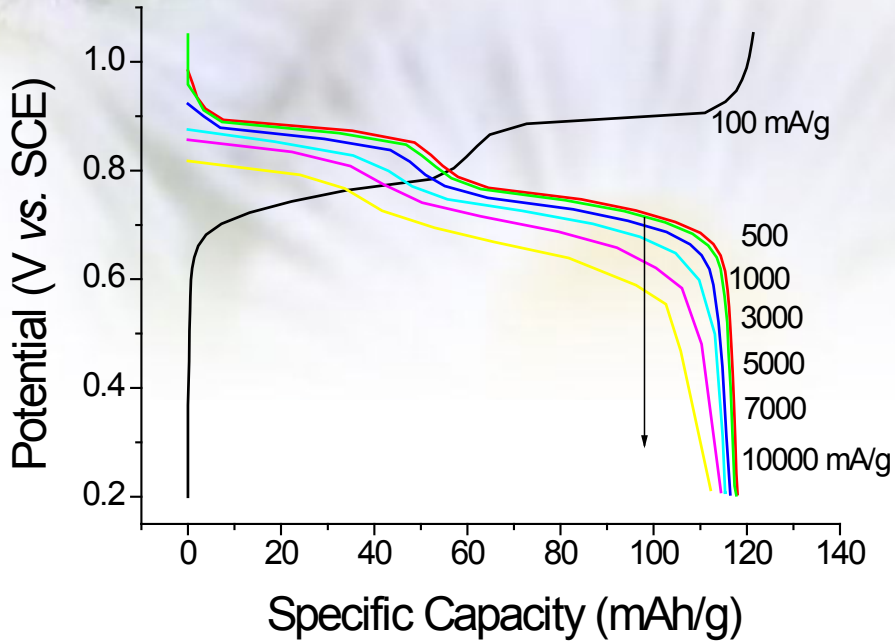
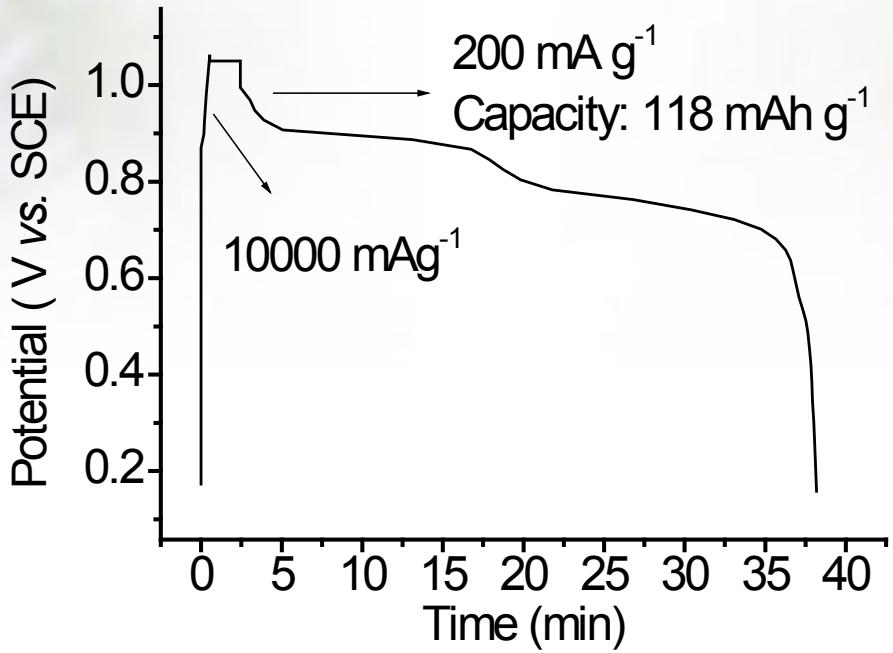


Fig. Capacity at different current density.

Porous $LiMn_2O_4$





The discharge curves of porous when it was fully charged at 100 mA/g): Capacity retention of 95% at 10000 mA/g.

Charge at 10000 mA/g and then kept at 1.29 V (NHE) until current goes to 100 mA/g.

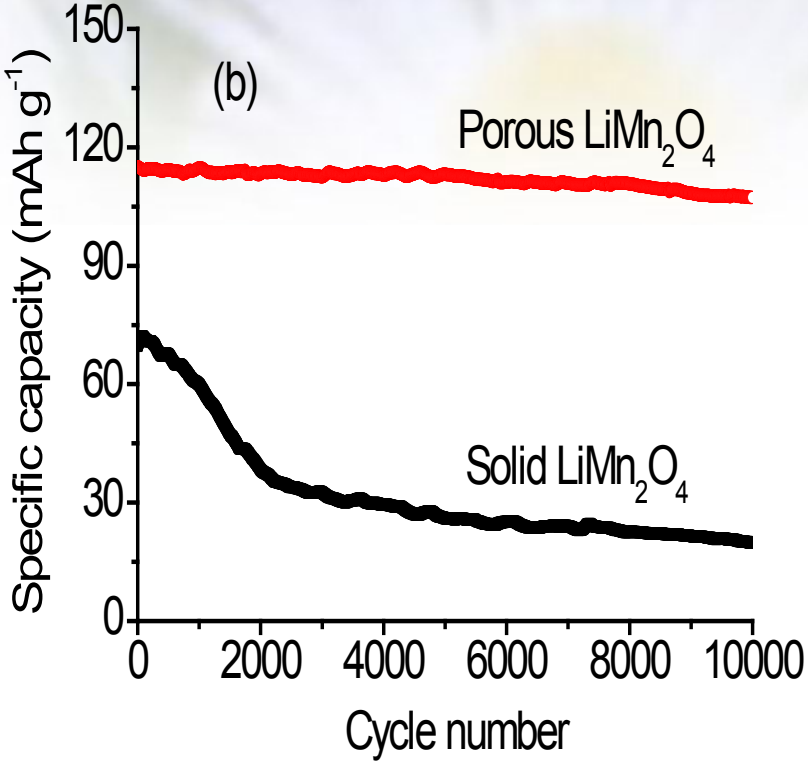
Full charge: < 2.4 mins.

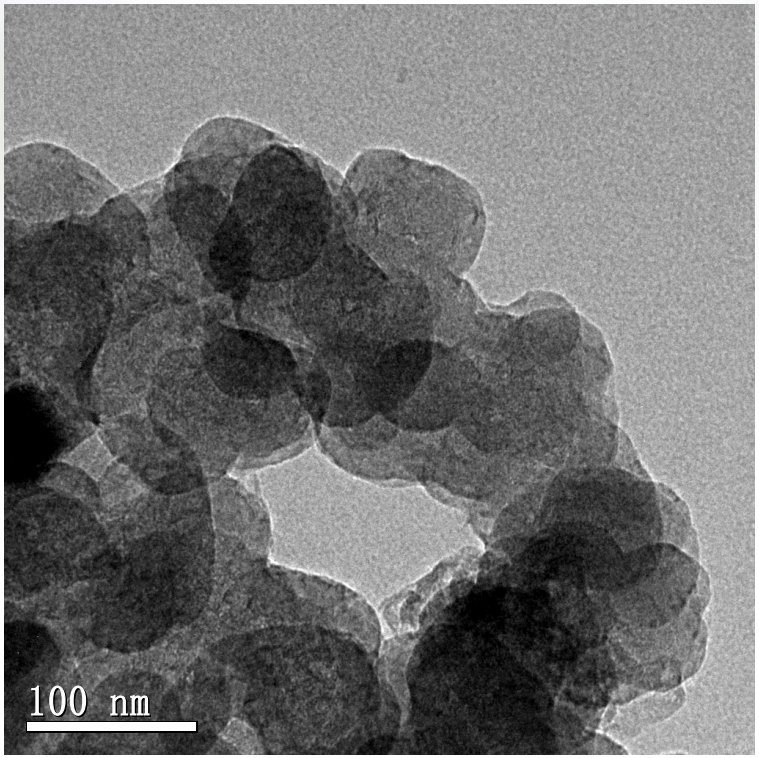
Ultra-fast kinetics: much faster than in organic electrolytes.

Good crystal, nano grain and porous structure

No acid: pH ~7

Excellent cycling behavior



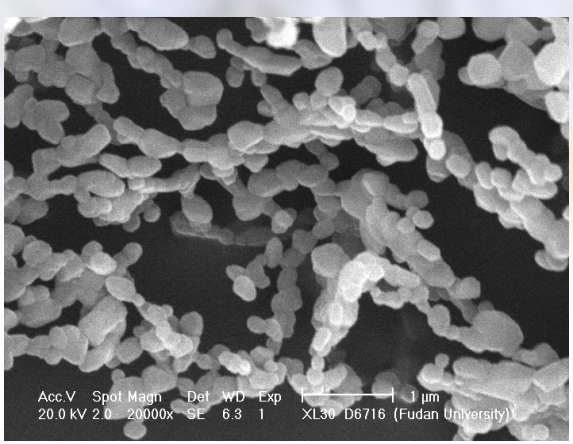


TEM of porous $LiMn_2O_4$ after 10000 cycles.

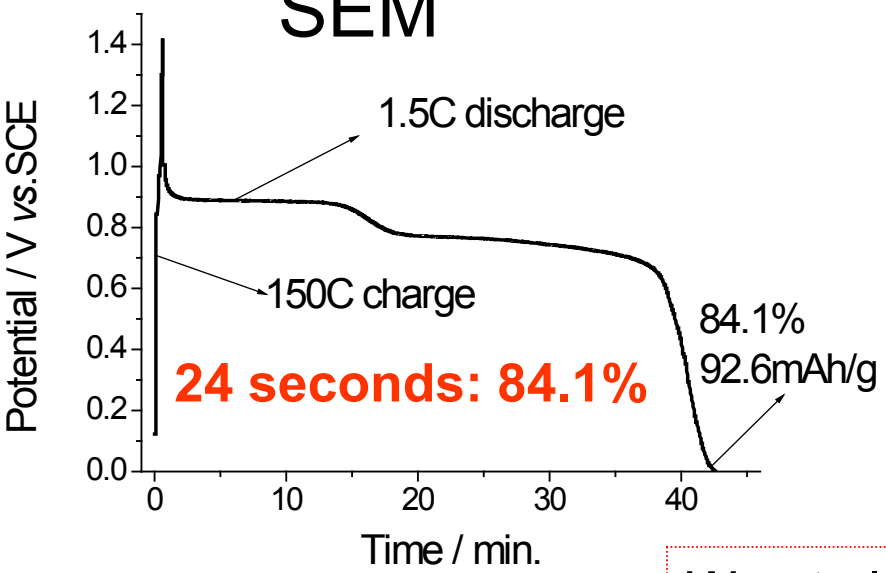
Stable morphology and crystal structure after 10000 cycles.

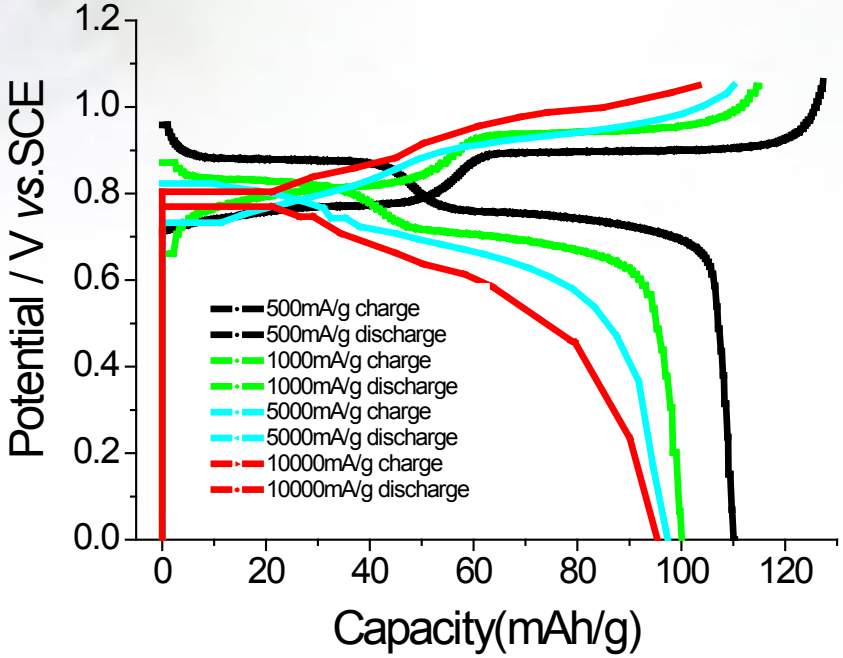
Oxygen: not removed

Nanochain $LiMn_2O_4$: **Super-fast** charge capability



SEM



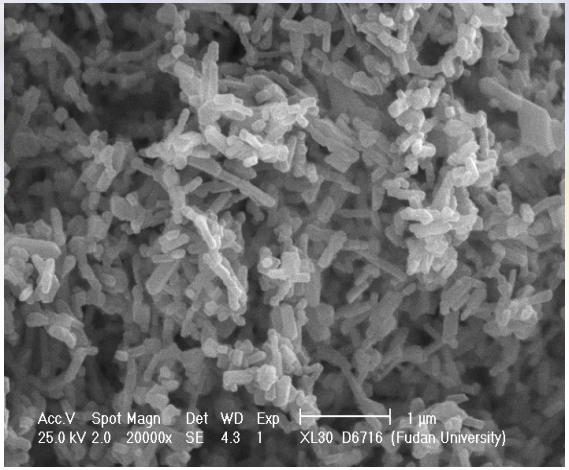


Charge/discharge curves at different current densities

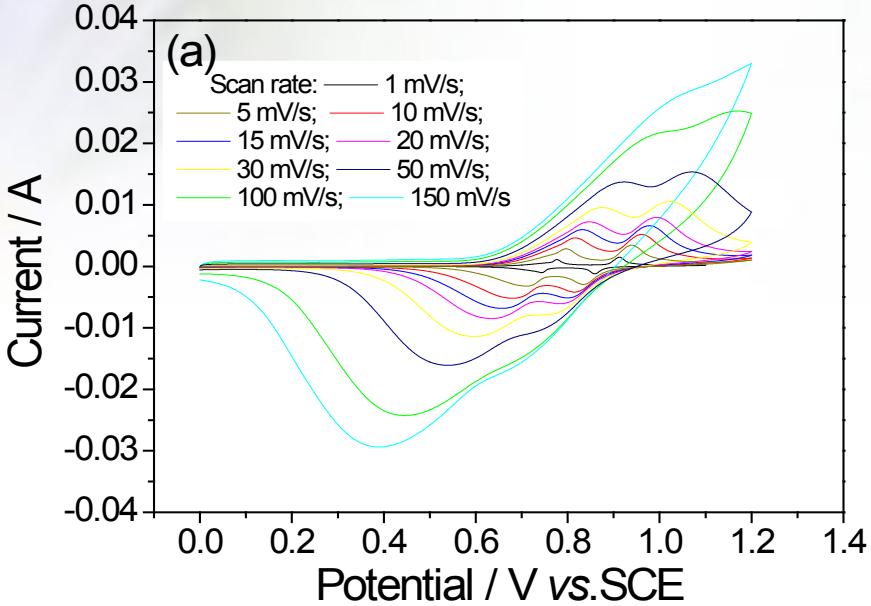
Super-fast charge performance

Wu et al., *Electrochem. Commun.*, 13 (2011) 205.

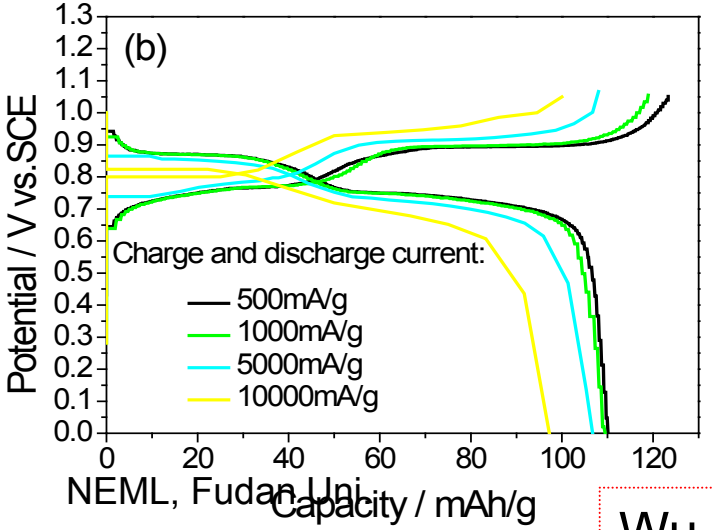
$LiMn_2O_4$ nanorod : **Super-fast** charge capability



SEM



CVs at different scan rate



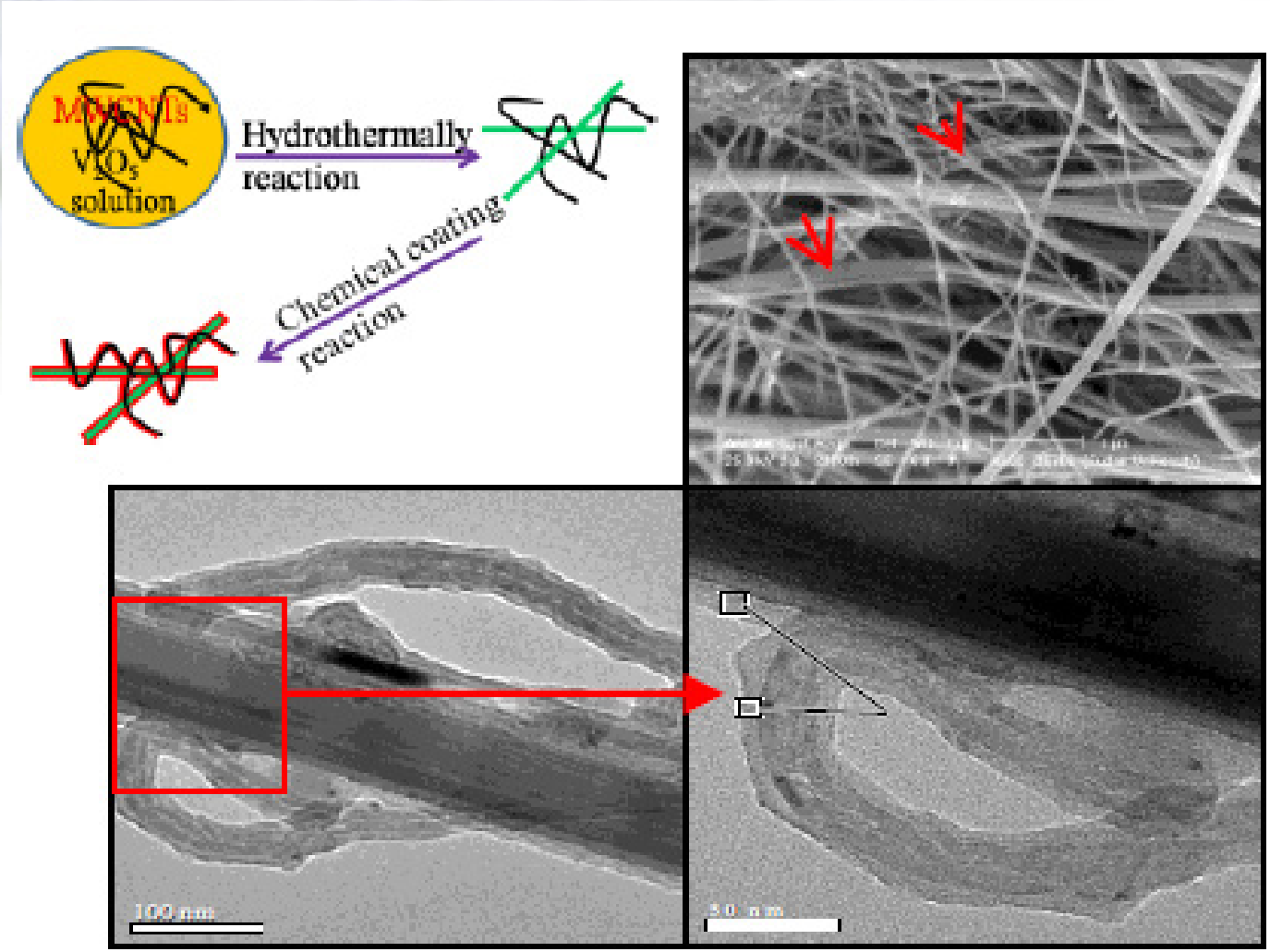
Charge/discharge curves at different current densities

Super-fast charge kinetics: 40 sec (90%)

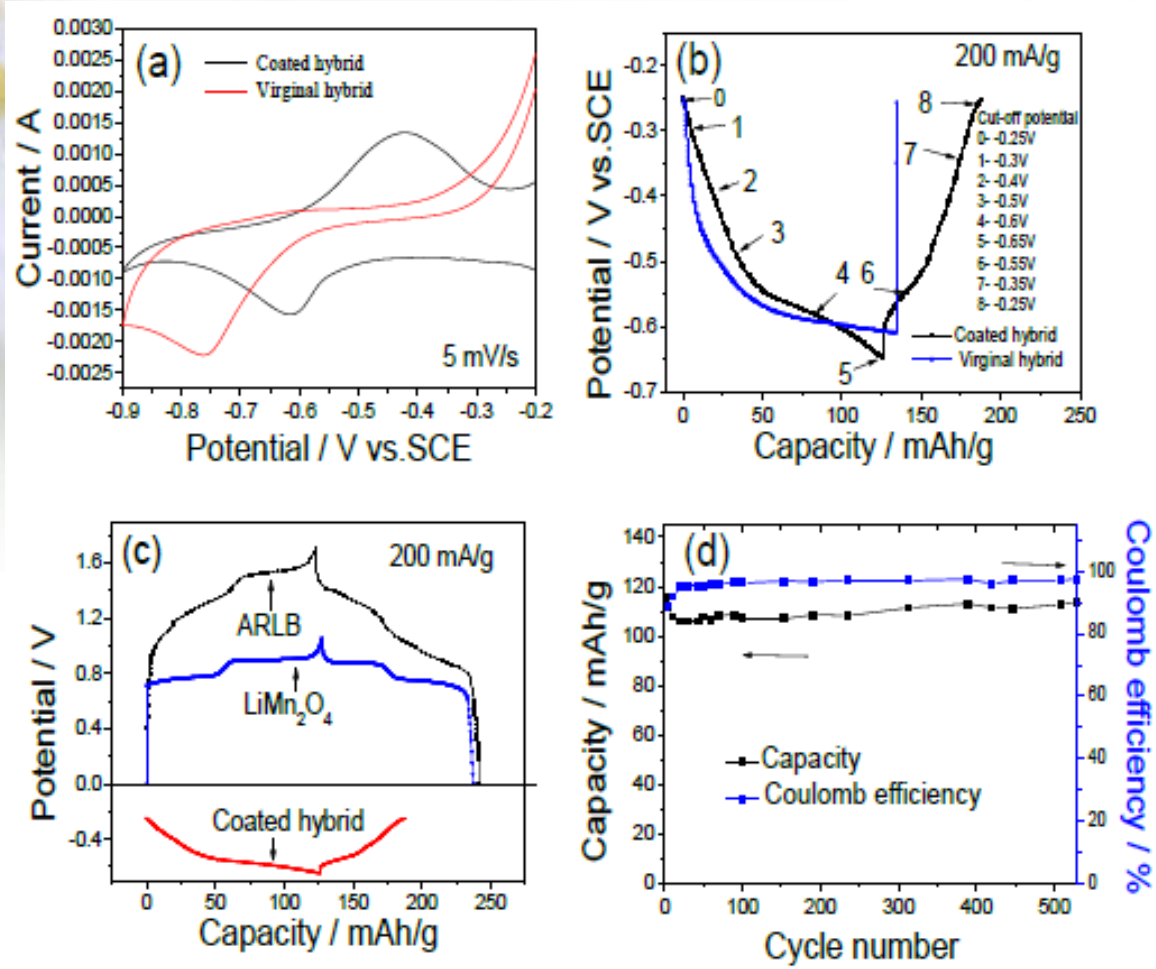
NEML, Fudan Uni.

Wu et al., *Electrochem. Commun.*, 13, 1159 (2011).

2.2 Anode: PPy@(V_2O_5+CNTs)



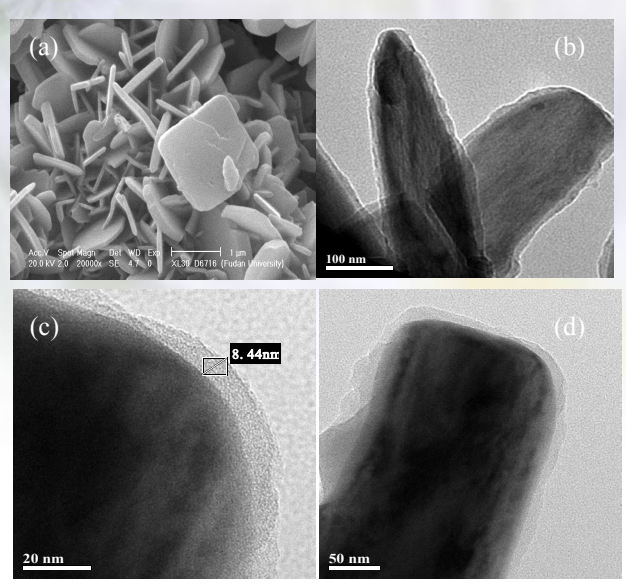
SEM micrograph of the virginal hybrid of V_2O_5 with MWCNTs and TEM micrographs of the coated hybrid.

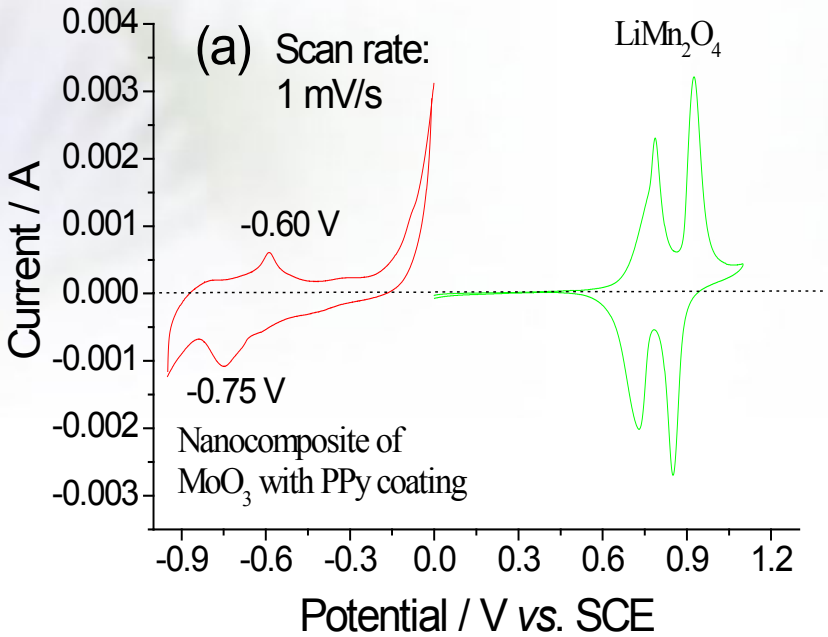


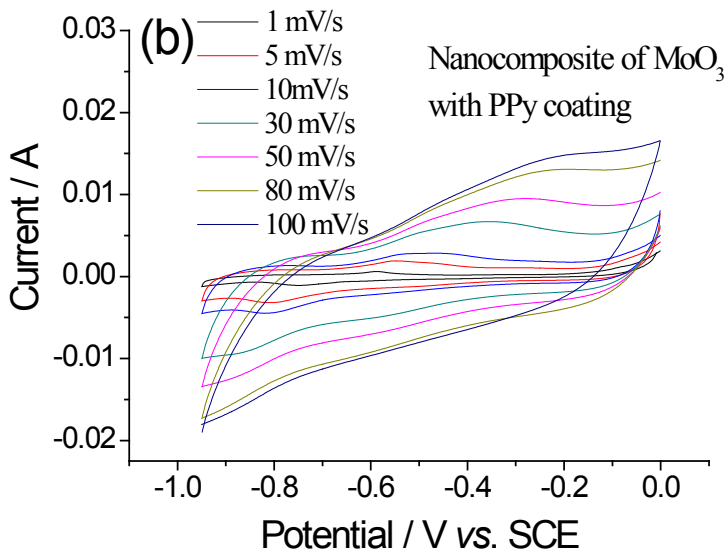
Wu et al., *J. Mater. Chem.*, 2012, 22, in press

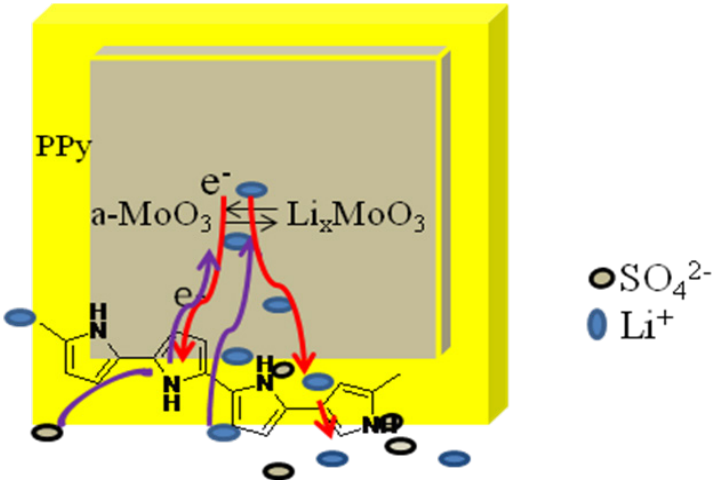
Electrochemical performance of the virginal and the coated hybrids and the prepared ARLB: (a) cyclic voltammograms, (b) charge and discharge curves, (c) charge and discharge curves of the ARLB together with those of $LiMn_2O_4$ and the coated hybrid, and (d) cycling behavior.

Anode: PPy@MoO_3

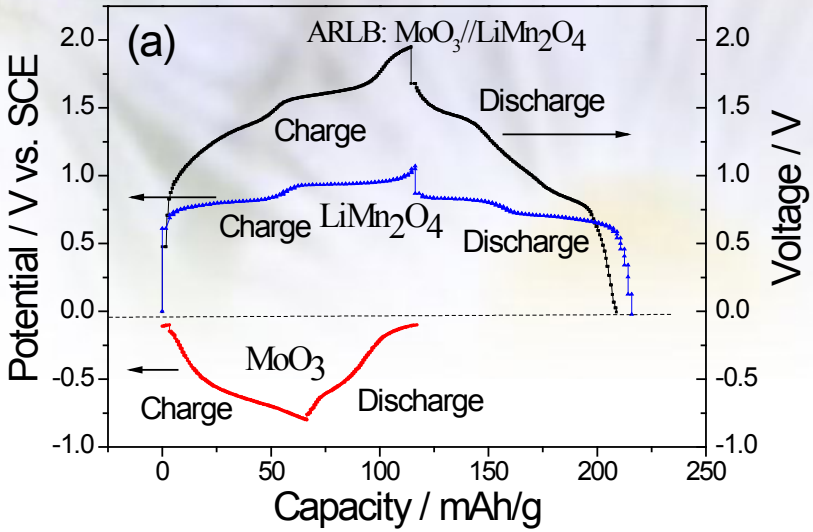


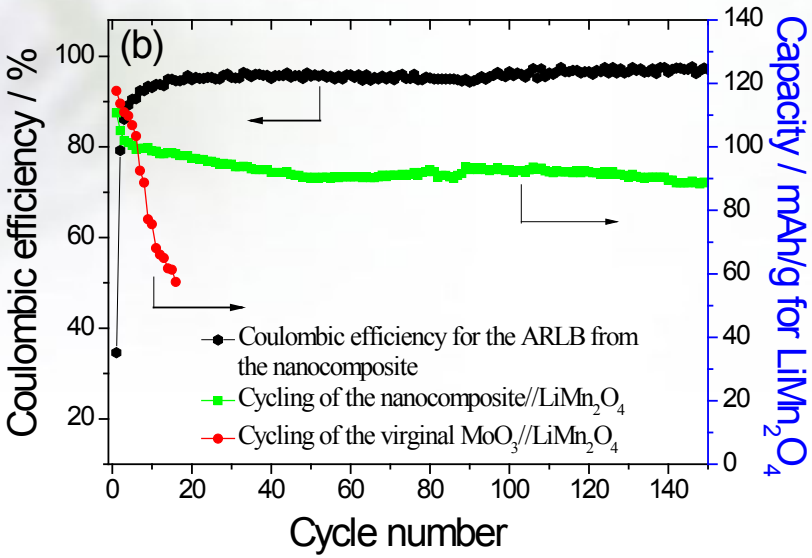


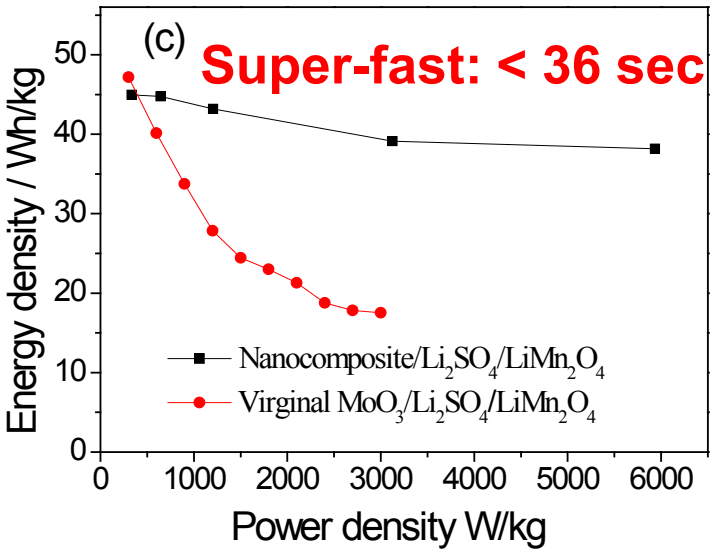




PPy@MoO_3//$LiMn_2O_4$







The energy density of this ARLB is 45 Wh/kg (lower than the estimated value, about **55 Wh/kg**) at 350 W/kg and even maintains at 38 Wh/kg at 6 kW/kg. This kind of excellent rate capability can be compared with supercapacitors.

Wu et al., *Energy Environ. Sci.*, 5, 6909 (2012).

(Top 10 most-read EES article)

Comparison of Filling (charge) Time

Filling gasoline	**1-3 mins (Full)**
Filling natural gas	3-5 mins (full, fast)
Lithium ion batteries	> 10 min (<80%)
ARLBs	< 1 min (>90%)

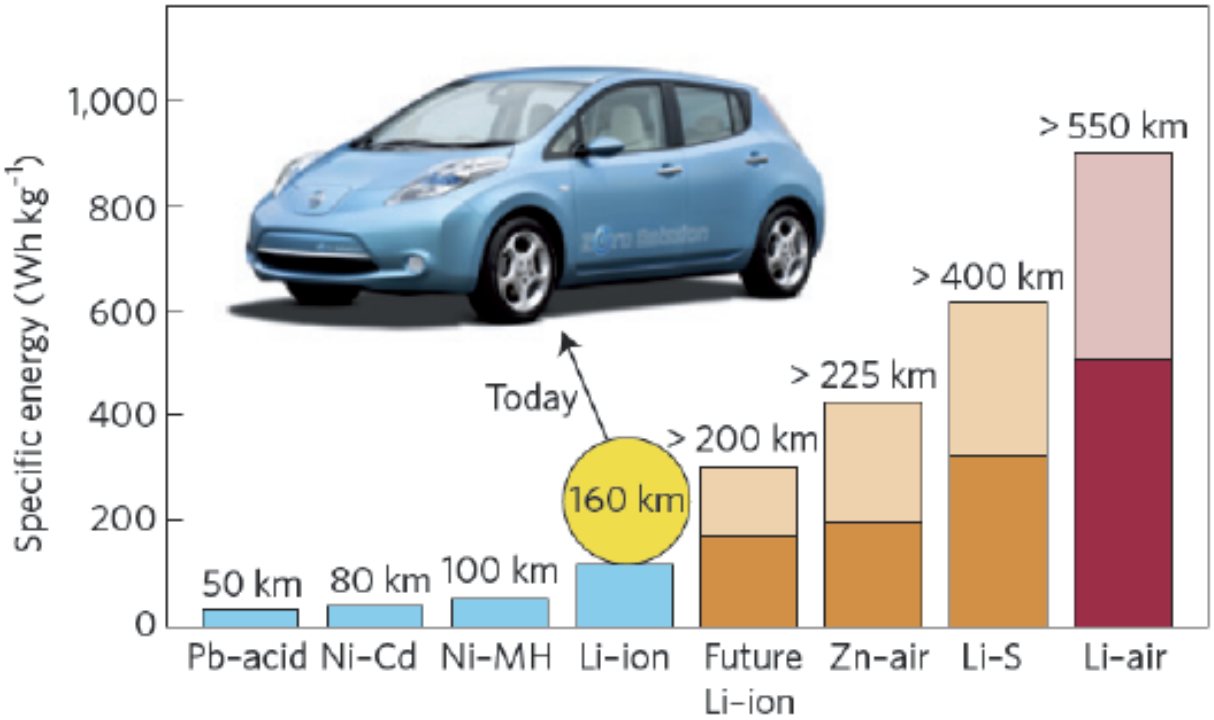
Note: For average size vehicle.

2.3 Advantages of ARLBs

- **Easy to produce**
- **Good availability of lithium salts**
- **High ionic conductivity, about 1-2 orders of magnitude higher than organic electrolyte, suitable for charge and discharge at high rate**
- **High power density**
- **Good safety, no combustibility or explosion**
- **Low cost for production due to no requirements on the content of moisture**
- **Low requirements on separators especially the shut-down performance**
- **Friendly to environment, completely GREEN**
- **Satisfactory energy density 40- 90 Wh/kg for the total electrodes**
- **Super-fast charge capability**
- **Excellent cycling behavior**

Good promising for energy storage, HEVs, assistance for EVs and range-extenders.

3. New ARLBs: EVs for long distance



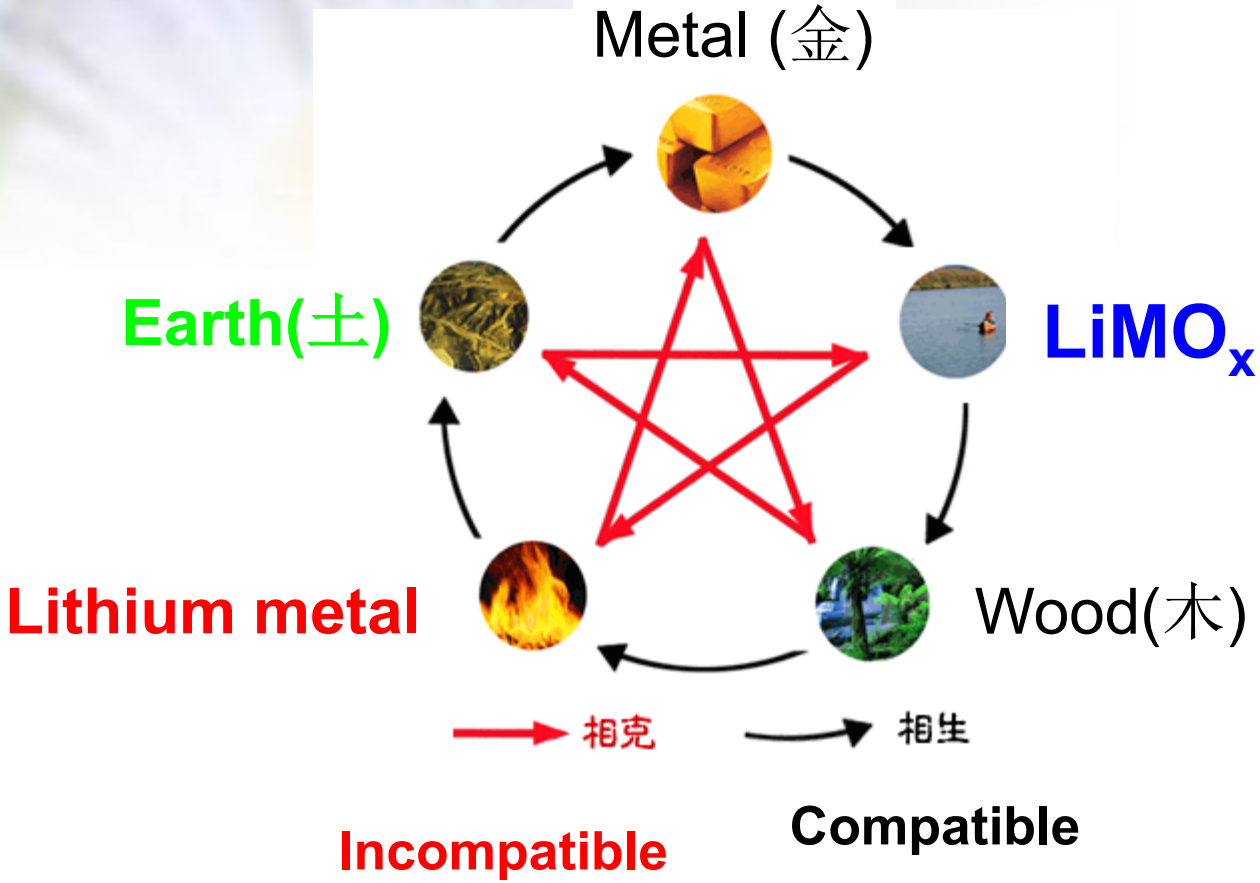
High voltage cathode ???
Li-rich cathode ???
Si anode ???

??? No idea so far

P.G. Bruce et al., *Nat. Mater.*, 11, 19 (2012).

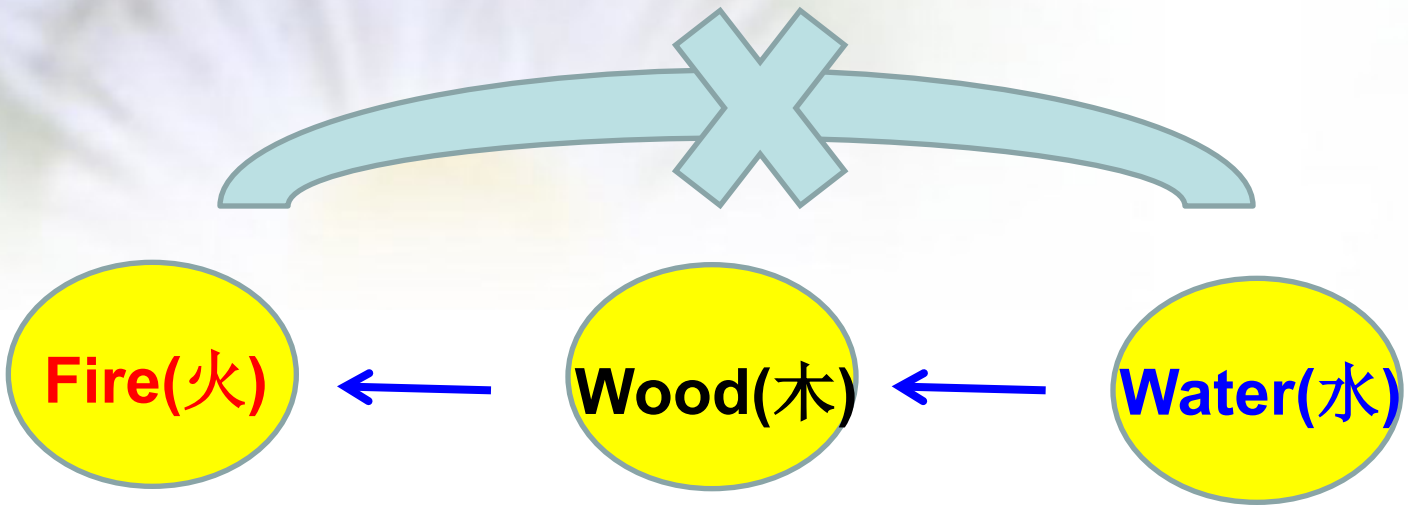
Li metal is not stable in water !!!

$$Li + H_2O = LiOH + H_2$$



Traditional Theory of the Five Elements

To make fire compatible with water

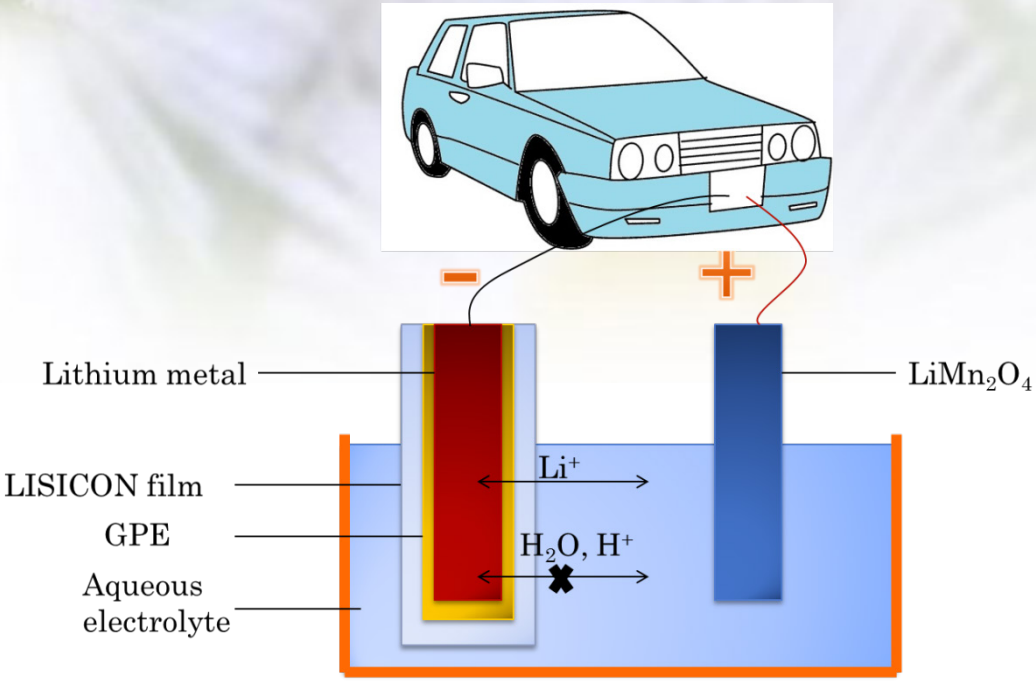


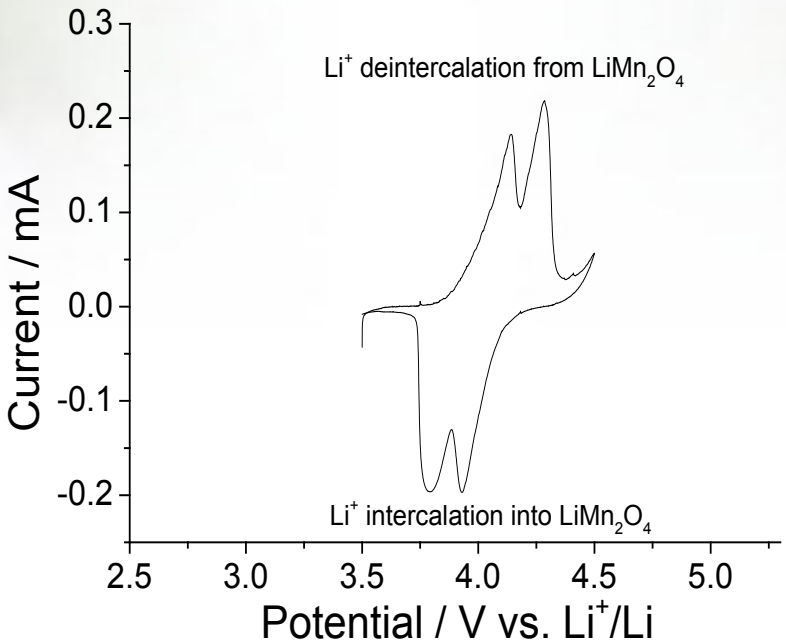
Lithium metal GPE + LISICON $LiMn_2O_4$

Target: Polymers

No LISICON (earth)

ARLBs of High Energy Density





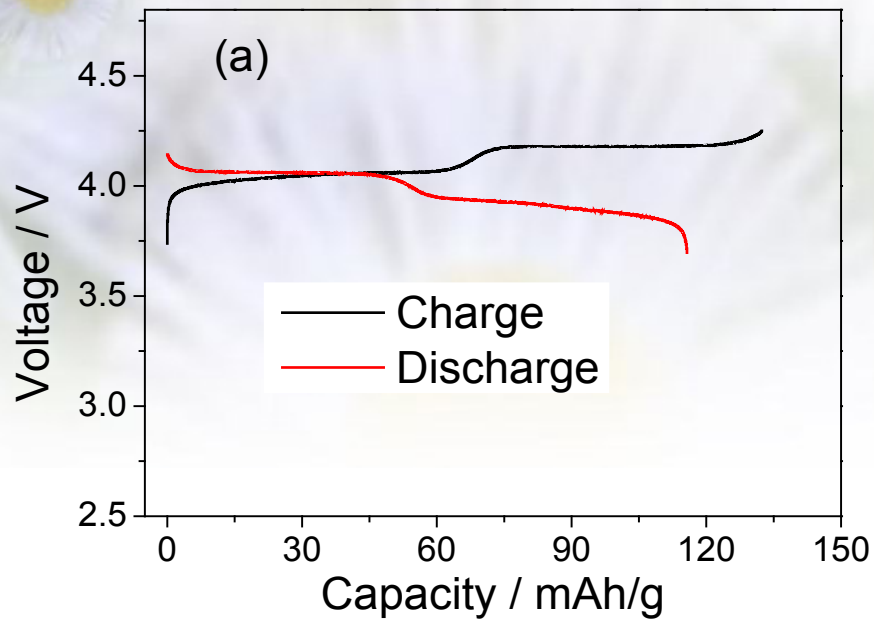
Anode reaction: $Li^+ + e^- \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li$ (1)

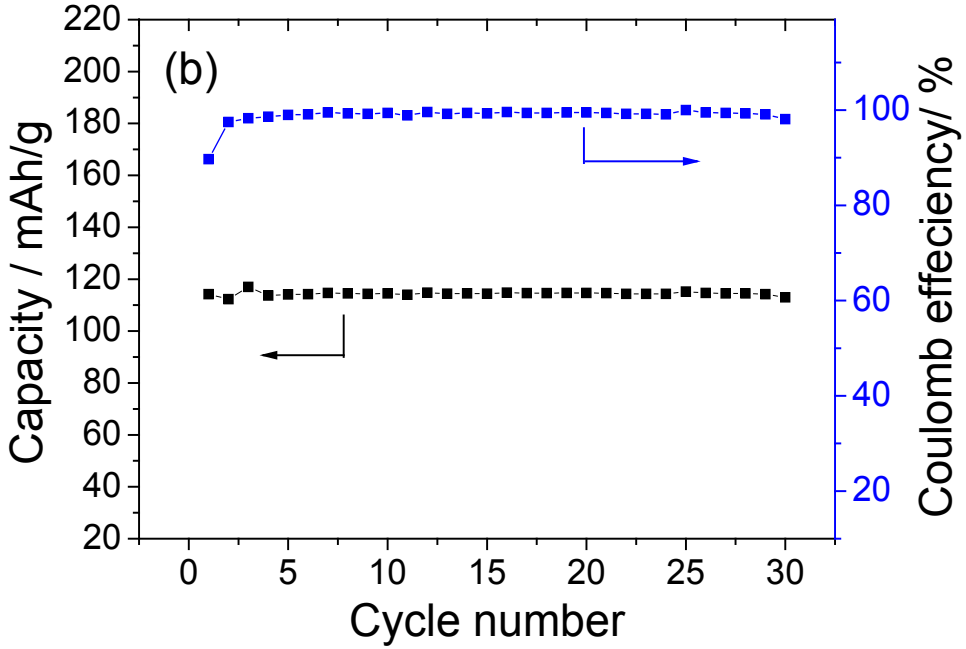
Cathode reaction: $LiMn_2O_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}Mn_2O_4 + x\,Li^+ + x\,e^-$ (2)

Total reaction: $LiMn_2O_4 \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Li_{1-x}Mn_2O_4 + x\,Li$ (3)

CN Patent Application No: 201210195152.2, PCT is under way.

ARLB of $Li//LiMn_2O_4$





- **Fast kinetics:**
  Small overpotential
- **High energy/power efficiency:**
  >95% (very rare)
- **Good cycling:**
  No evident capacity fading
- **Stable lithium metal:**
  No chance of lithium dendrite

High energy density

ARLB	Calculated energy density	50% utilization based on LIBs	Possible practical energy density
$Li//LiMn_2O_4$	446 Wh/kg	50%	> 220 Wh/kg
Li//NCM	> 600 Wh/g	50%	> 300 Wh/kg

In aqueous electrolyte: **At least 3 times thicker electrode pellets.**

Advantage of the New ARLBs

- **Good safety and reliability**: an effective (**close contact with the anode**) cooling system (**aqueous**)
- **Benign to environment**: much green (**no $LiPF_6$**)
- **High energy density**: > **600 Wh/kg** based on the mass of the electrode materials, and > 300 Wh/kg for practical value
- **High coulomb efficiency**: **near 100%** except for the initial cycles
- **Fast redox kinetics** for the electrodes: small overpotentials & superfast charge
- **High energy/power efficiency**: **> 95%**
- **No memory effects**
- **Excellent cycling life: > 10000 cycles**
- **Low cost** … …

4. Summary

- **Nanomaterials greatly promote the development of ARLBs (aqueous rechargeable lithium batteries) including reversible capacity, rate capability and cycling behavior.**

- **New designed ARLBs open a great future for energy storage including EVs and smart grids in the near future.**

- **Social sciences are good to develop natural sciences: life enjoyment can lead to new ideas.**

We are developing new rechargeable aqueous battery systems with energy density > 500 Wh/kg (estimated practical value).

Acknowledgment

Financial sponsors and collaborators:

- National Basic Research Program of China (973 Program No: 2007CB209702)
- Natural Science Foundation Committee of China
- Ministry of Science and Technology of China
- Science and Technology Commission of Shanghai Municipality
- Alexander von Humboldt Foundation (Partnership Program)
- Sanyo Chemical

Study Tour to Xi'An (2011)
(The top of Hua Mountain to watch sunrise)

Thanks for your kind attention !