

Water Stable Lithium Metal Electrode for Lithium-Air Rechargeable Batteries

O.Yamamoto, T.Zhang, N.Imanishi, and Y.Takeda

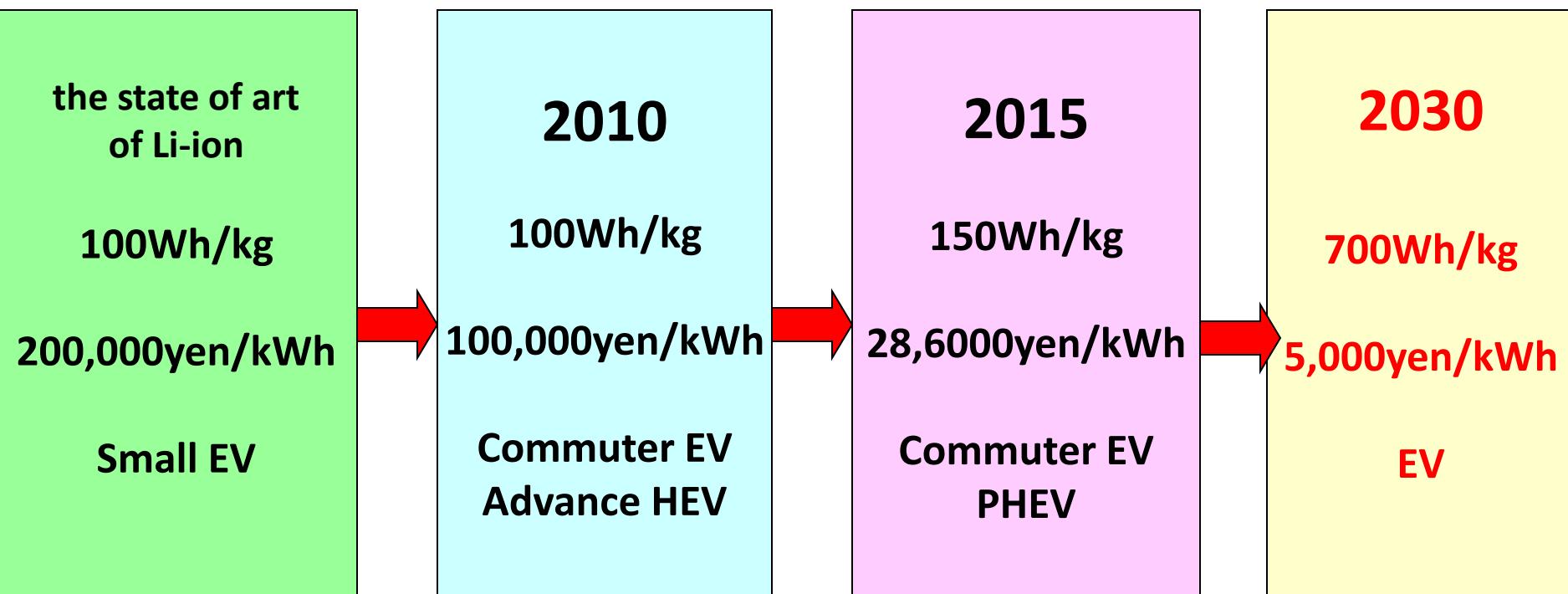
*Advanced Battery Research Center, Mie University
Tsu, 514-8017, Japan*

yamamoto@chem.mie-u.ac.jp

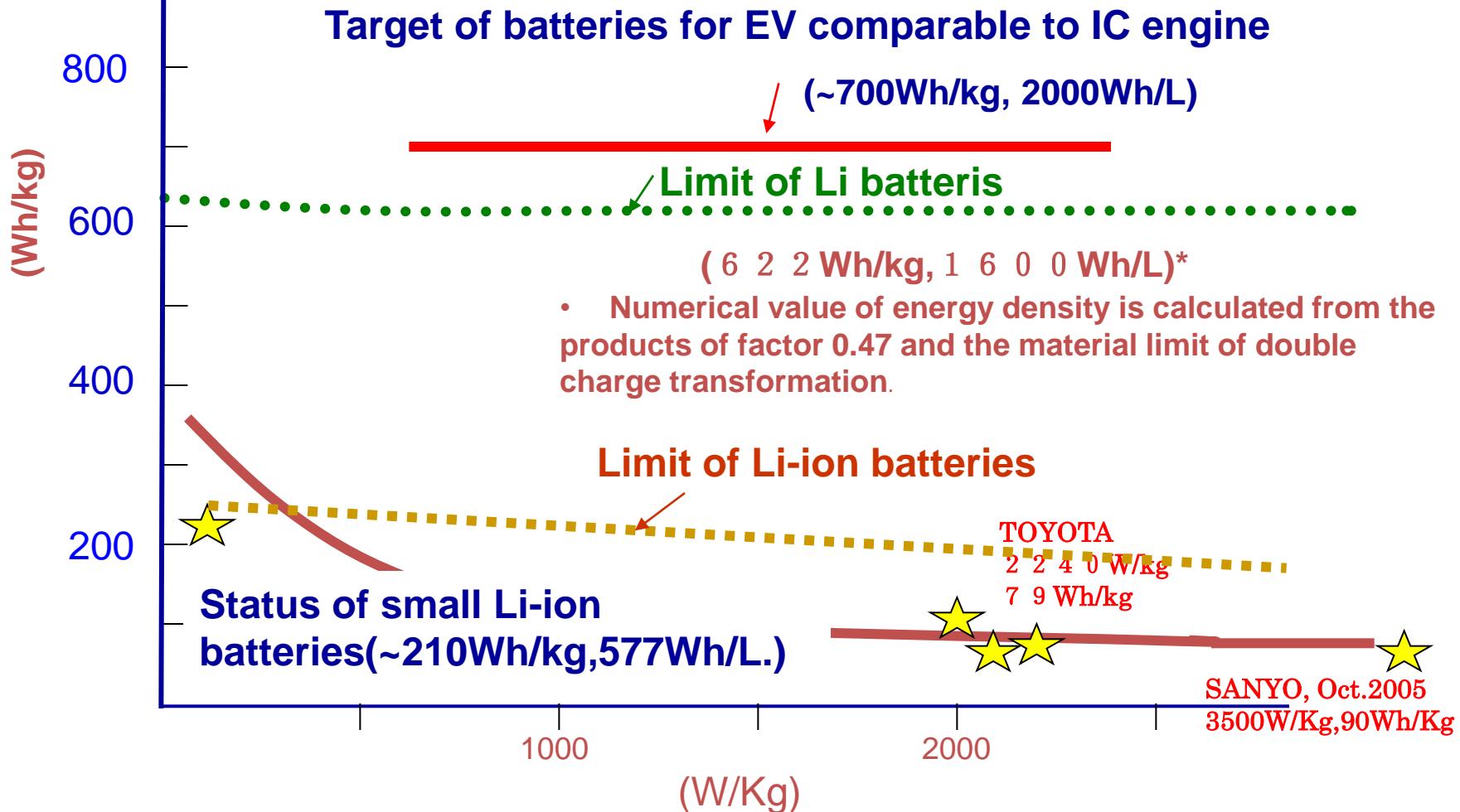
Ishe Shrine, Mie: 8th century style building

Strategy for Battery R&D for EV in Japan

Aug. 2006 by NEDO

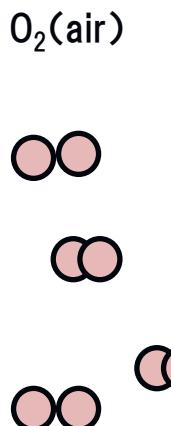
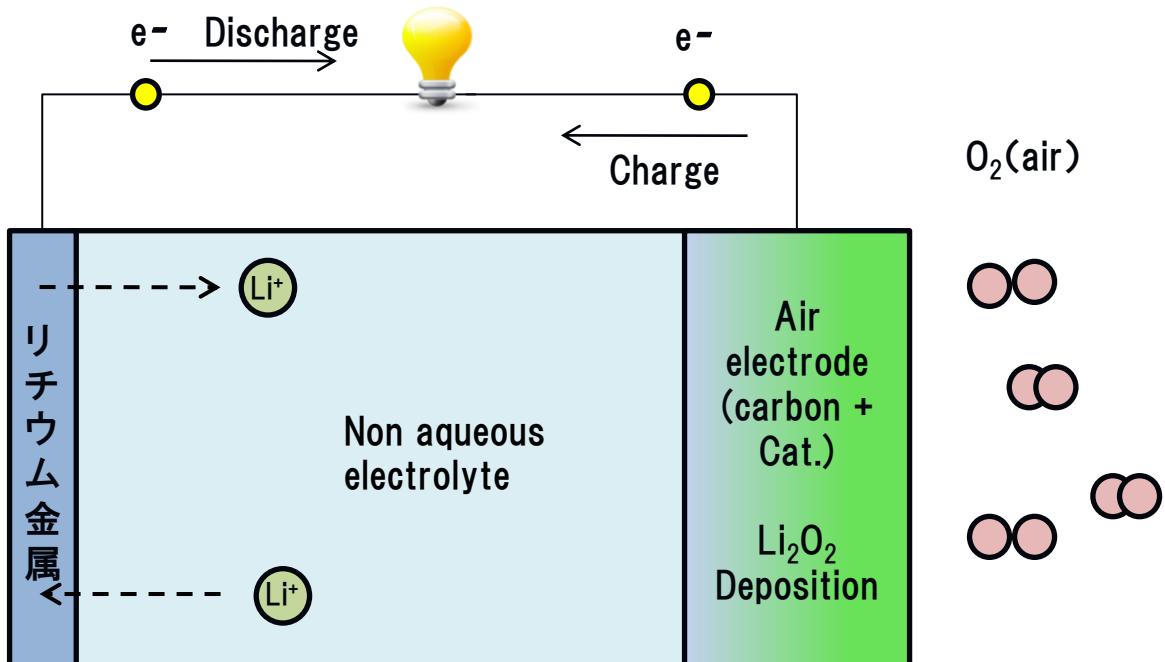


The state of art of Lithium ion batteries and the target



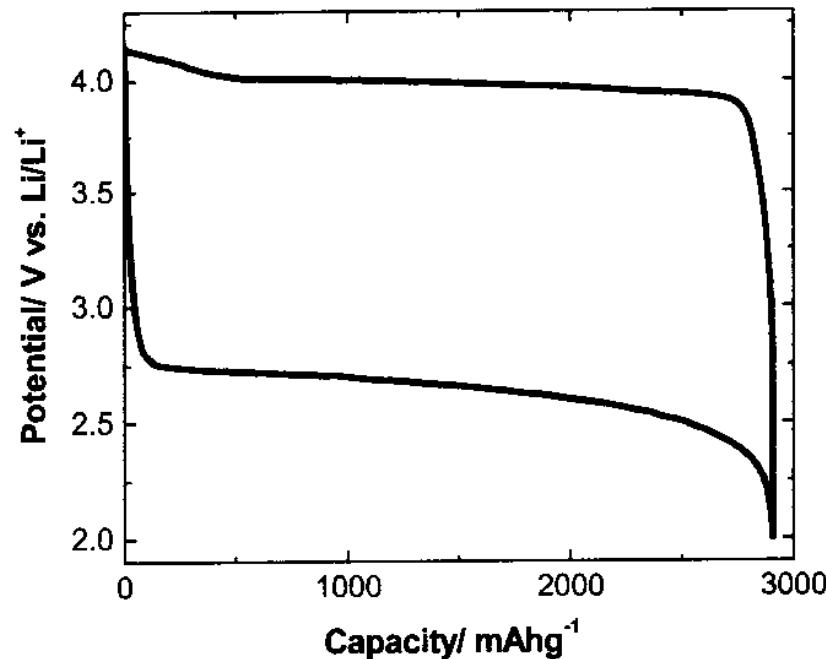
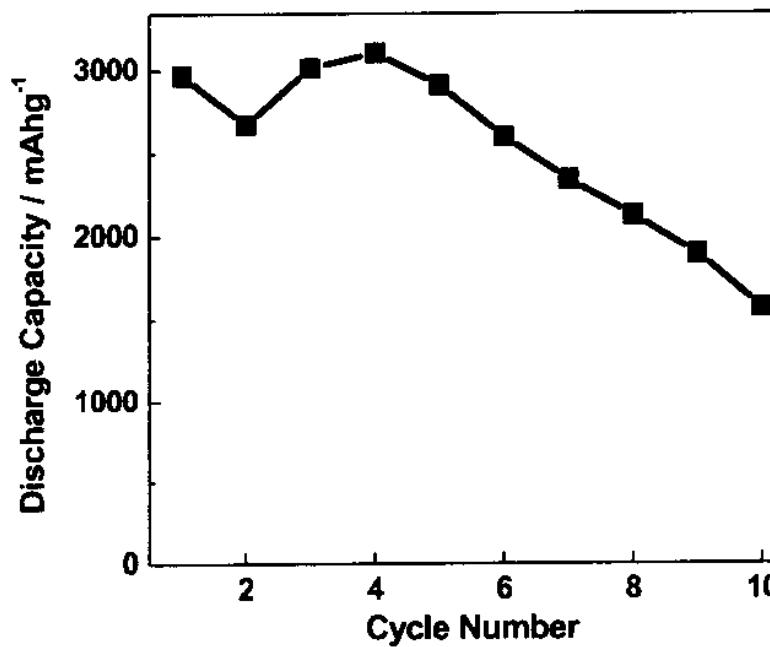
Li/air battery with non-aqueous electrolyte

Proposed by K.M. Abraham on 1996



Non-aqueous electrolyte
 $\text{O}_2 + 2\text{Li} = \text{Li}_2\text{O}_2$ $E \sim 3.0\text{V}$
 $\text{O}_2 + 4\text{Li} = 2\text{Li}_2\text{O}$
Energy density $11,000$ Wh/kg; same to that of gasoline

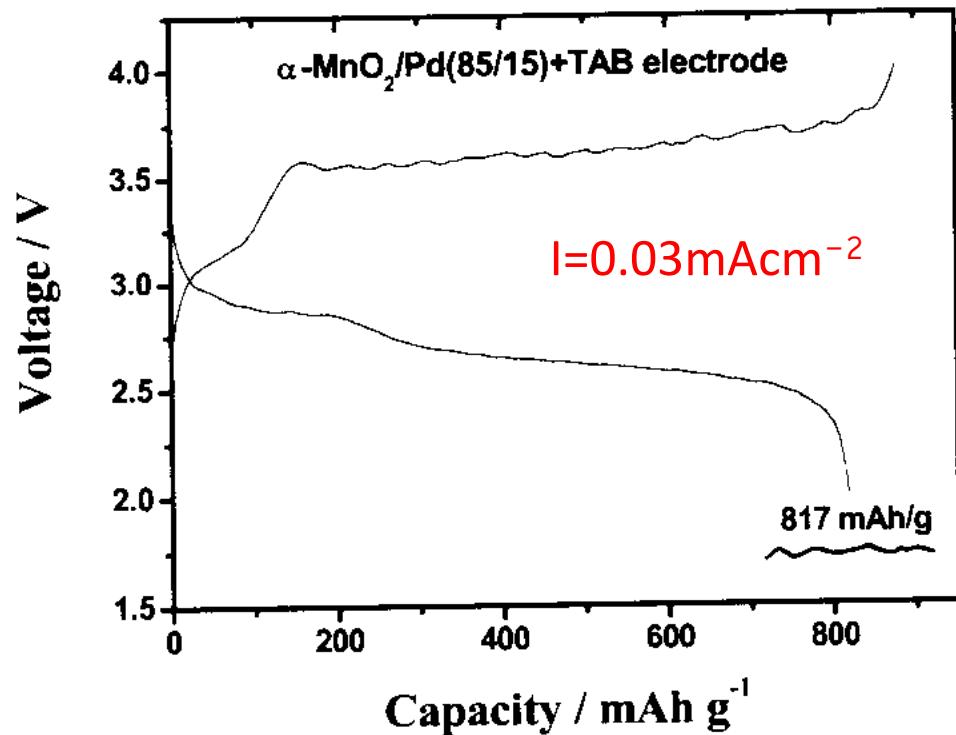




Li/0.1M TBAPF₆ in PC/
MnO₂ Nano-tube, O₂

By P.Bruce et al.
ECS Meeting at Vienna
Oct. 2009

High polarization
Poor cyclic performance

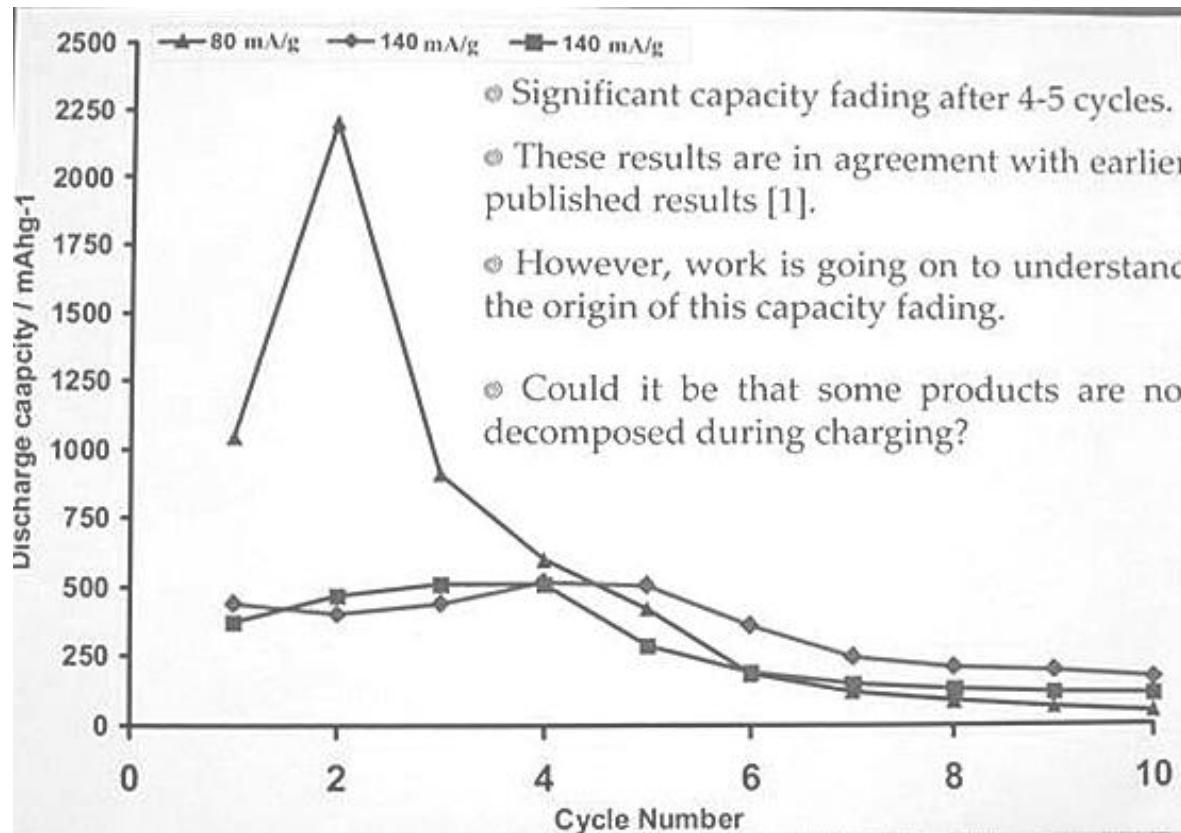


A high charge and
discharge
polarization at a
low current density

Figure2. Charge discharge curves of $\alpha\text{-MnO}_2/\text{Pd}(85/15)$ + TAB electrode for Li-air battery at the voltage range of 4.0V-2.0V.

By Ishihara et al. ECS Meeting 2010

Stability of Li/non-aqueous solution/air cell



**Li / 1M LiPF₆ in PC / C+ α -MnO₂
under air**

Seyed Reza Younesi et al.,
Lithium oxygen batteries; challenges and possibility, Abs. 465,
PRiME 2008 Meeting, Honolulu, ECS

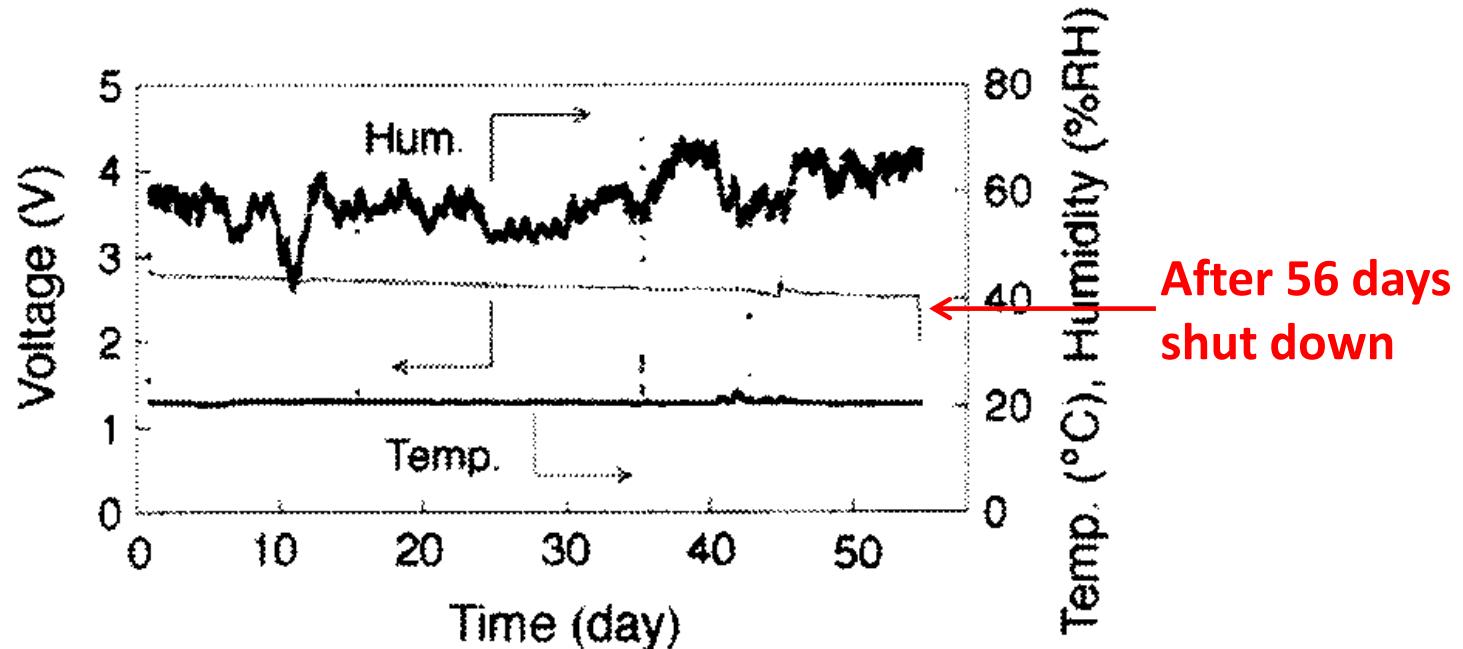


Fig. 5. The effect of humidity on discharge profile. Electrolyte: 0.5 M LiTFSI-EMITFSI; I: 0.01 mA cm^{-2} ; in air.

By Kuboki et al Toshiba J.Power Sources, 146, 766 (2005)

Strategy of our research on Li/air batteries at Mie University

- 1. Energy density is more than 700 Wh/kg
Calculated energy density >1,500 Wh/kg**

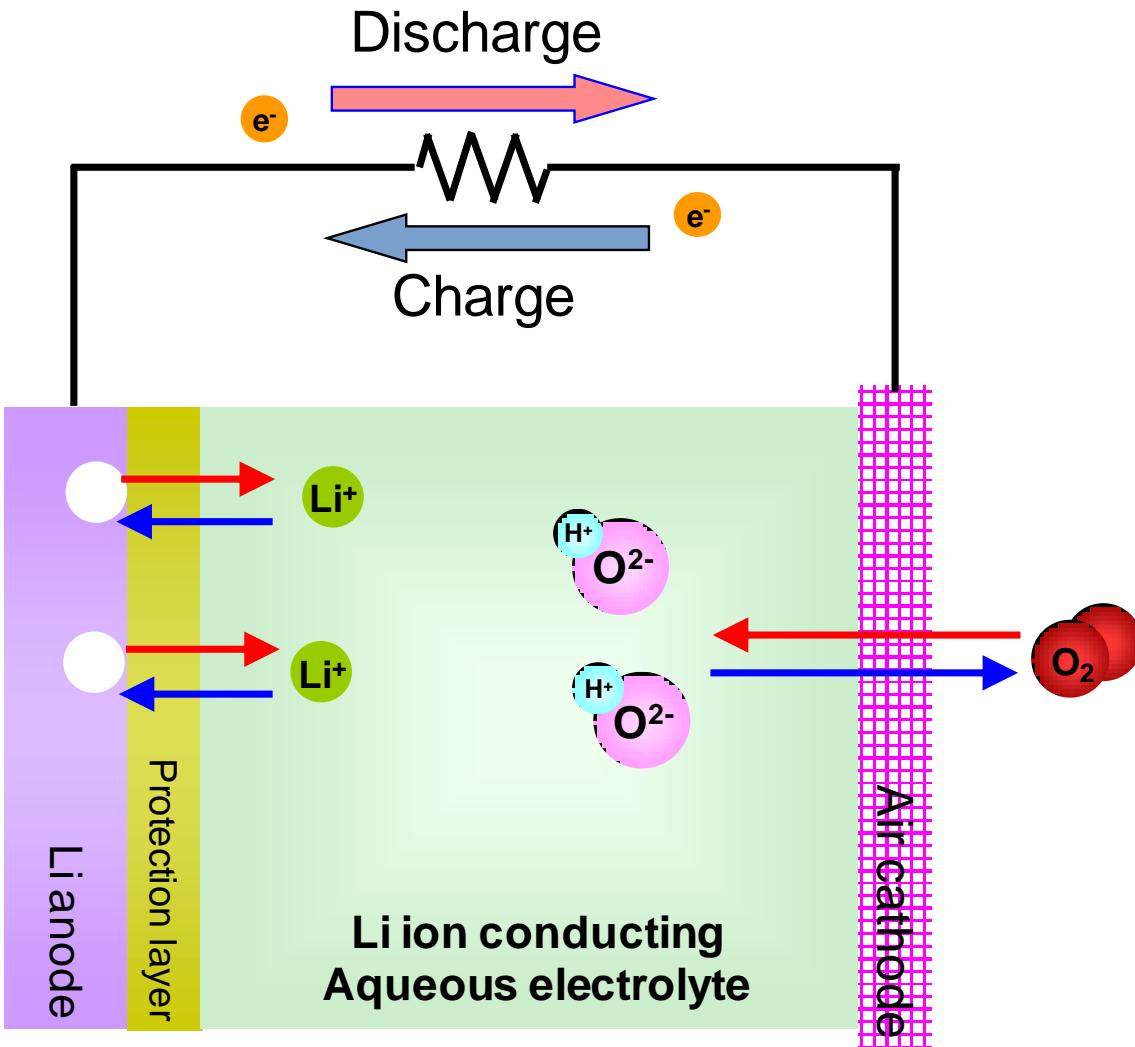
- 2. Cell energy efficiency is more than 80 %
Charge and discharge polarizations <0.7 V**

Our research subjects

- A water stable lithium metal electrode
To prevent a contamination with water
- Li/air secondary batteries with a water electrolyte
To reduce a electrode polarization
- A low interface resistance between Li and SEI
To improve a lithium dendrite formation

Li/air battery with aqueous electrolyte

Proposed by S.J.Visco on 2006



Aqueous electrolyte



E 3.5~4.3V

Energy density ~5,000Wh/kg

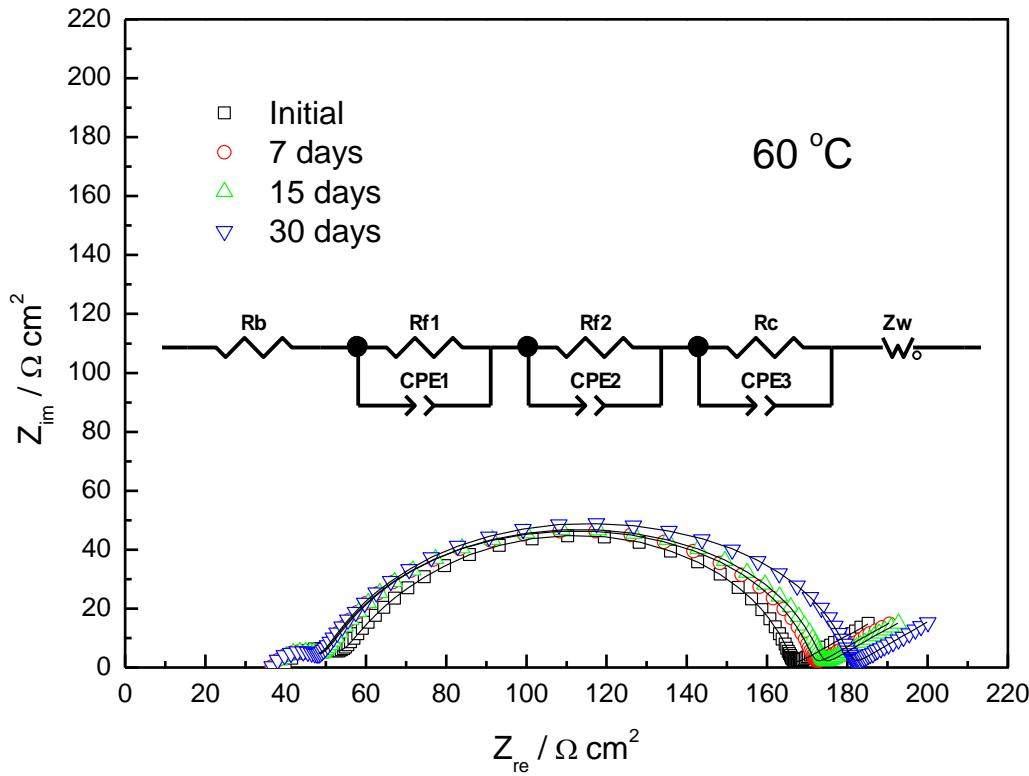
Non-aqueous electrolyte



Energy density 11,000

Wh/kg; same to that of gasoline

Resistance of Li/PEO₁₈LiTFSI-BaTiO₃/LTAP in aqueous 1 M LiCl solution by O.Yamamoto et al. Electrochem. Solid State Lett. 12, A132 (2009)

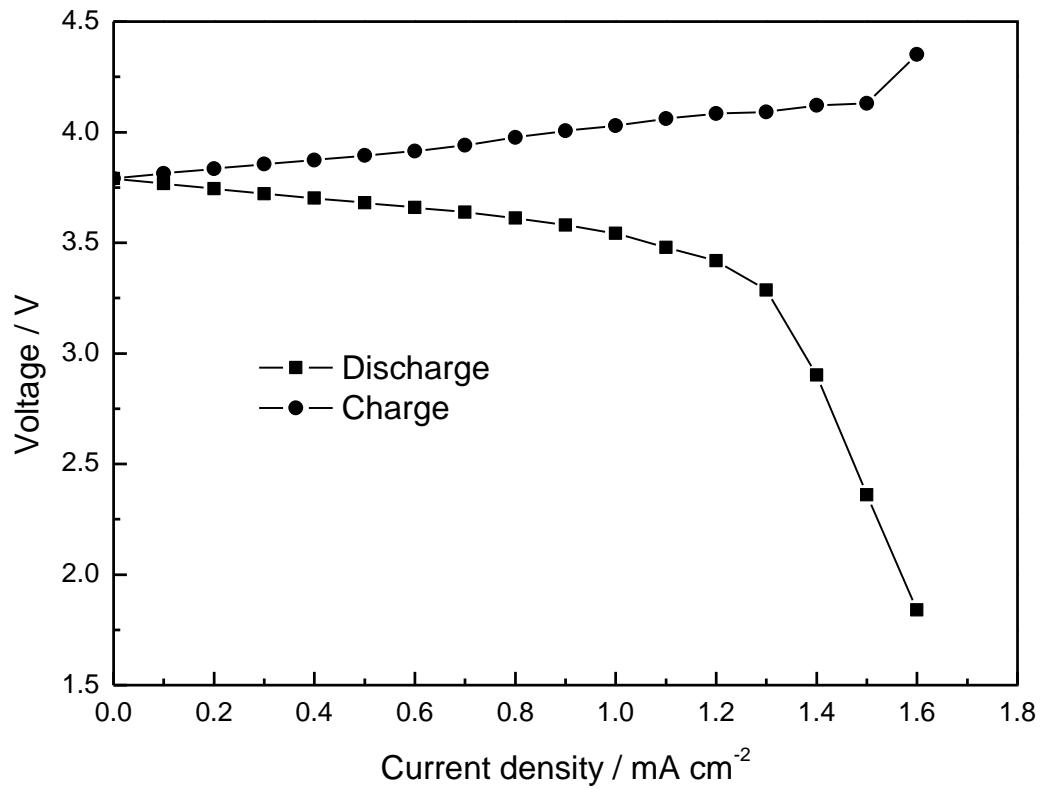


The total cell resistance of 171 $\Omega \text{ cm}^2$ is lower than that of that of the Li/PEO₁₈LiTFSI/LTAP/aqueous 1 M LiCl cell of 539 $\Omega \text{ cm}^2$ reported previously. , and increased only 10% over one month, suggesting an excellent stability of such a multilayer Li anode construction in the aqueous solution.

Li/PEO₁₈LiTFSI-10%BaTiO₃/LTAP/aqueous 1 M LiCl/Pt, air cell

- The better electrochemical performance could be expected for the multilayer Li anode with BaTiO₃ nanoparticles in the PEO₁₈LiTFSI interlayer.

Lithium dissolution and deposition polarization curves

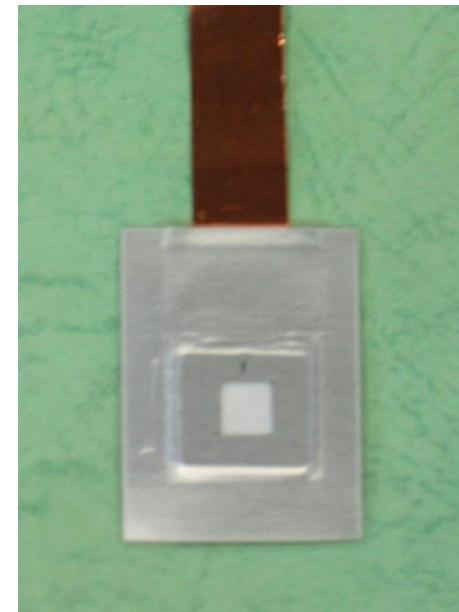
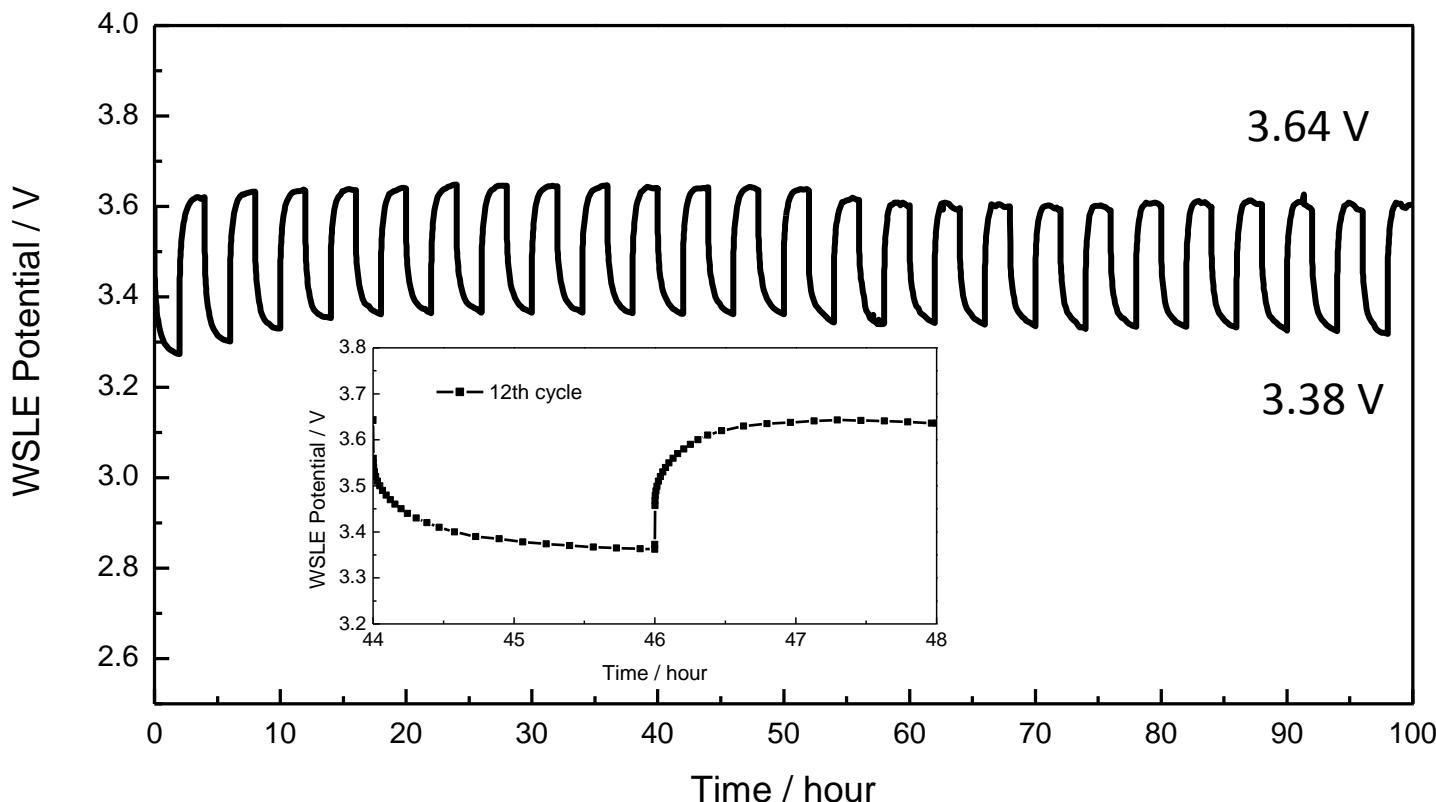


The calculated polarization resistance is approximately $170 \Omega \text{ cm}^2$ for the discharge curve in the current range 0 to 1.0 mA/cm^2 , which is comparable to the total cell resistance estimated by the impedance method.

In the high current density region ($>1.3 \text{ mA/cm}^2$), an appreciable polarization was observed in the discharge process. This polarization could be postulated as being from the lithium ion diffusion process in the electrode.

Anodic polarization curves of the Li/PEO₁₈LiTFSI-10 wt.% BaTiO₃/LTAP/aqueous 1M LiCl/Pt, air cell at 60 °C.

Cyclic performance of Li/PEO₁₈Li(CF₃SO₂)₂N-BaTiO₃/aqueous LiCl/Pt



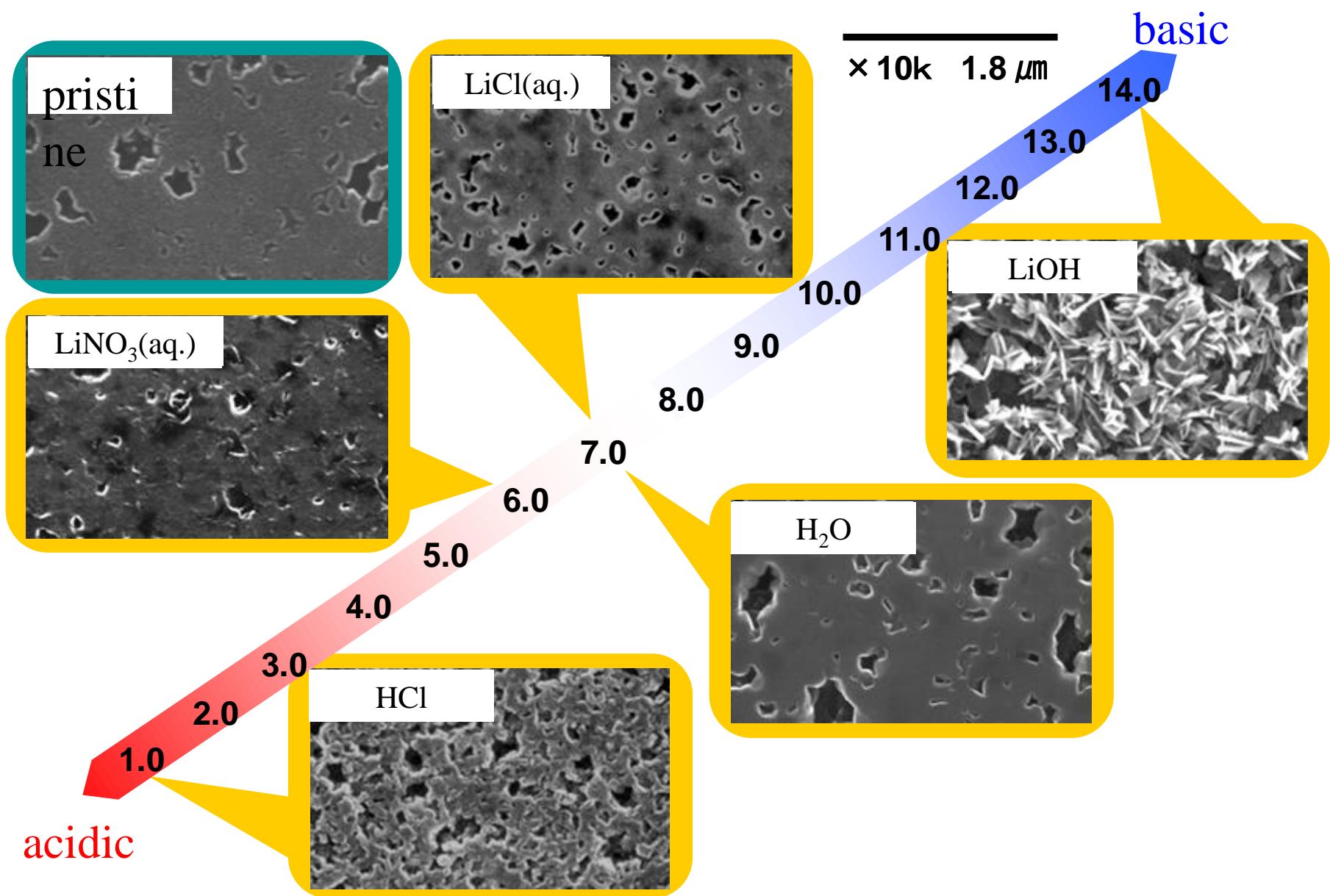
WSLE/1 M LiCl + 0.002 M LiOH/Pt black, air beaker cell at 0.3 mA cm⁻² and 60 °C

- Small polarization and good cyclic performance for the lithium ions dissolution and deposition on the lithium anode.
- The three layer lithium anode and the lithium-ion conducting framework of the LTAP are stable during the lithium deposition and dissolution cycling.

Problems for Li/air batteries with water

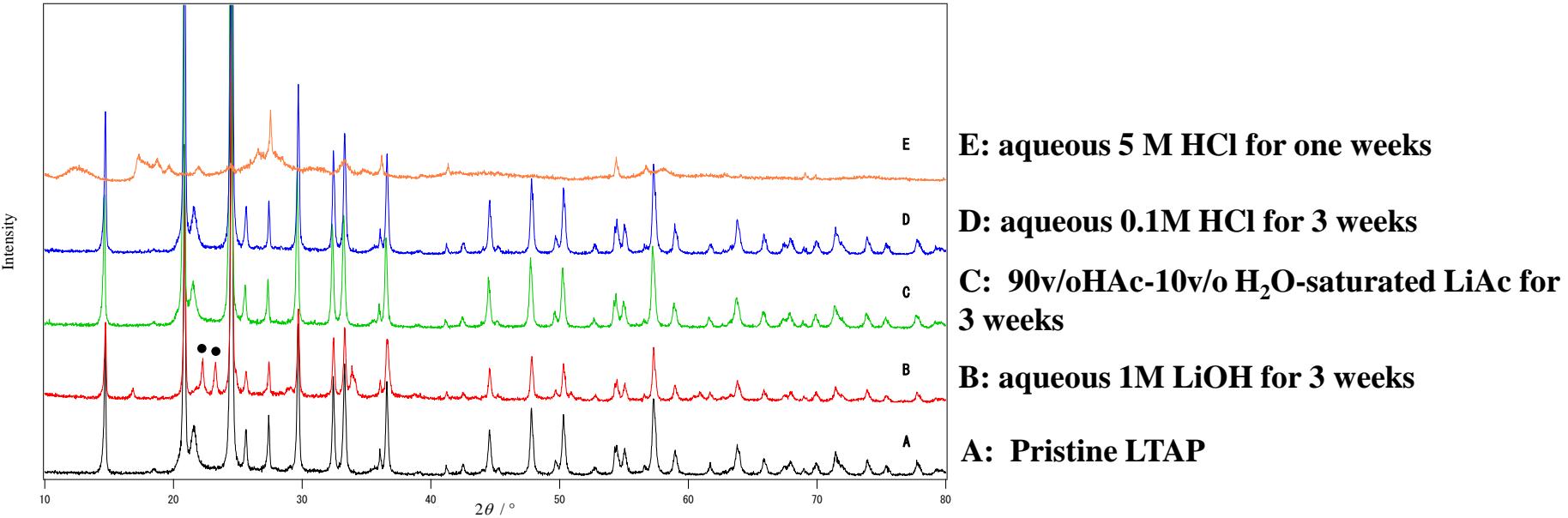
- 1. Stability of LATP in alkaline solutions**
- 2. Deposition of reaction product on the carbon electrode**
- 3. Evaporation of water**
- 4. Dendrite formation on lithium metal anode**

Stability of LTAP vs. pH



Stability of LTAP in acid and alkaline solutions

by O.Yamamoto et al. J.Power Source, 185 (2008) 1393, 189 (2009) 371,

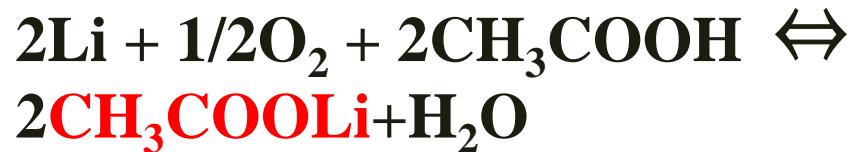


Solution	Immersed	Conductivity (S cm ⁻¹ , 25 °C)
Pristine LTAP		1.63×10^{-4}
0.1 M HCl	3 weeks at 25°C	2.98×10^{-6}
1M LiOH	1 weeks at 25 °C	1.06×10^{-5}
1M LiCl	3 weeks at 25 °C	9.44×10^{-5}
HAc + H ₂ O +LiAc	5 months at 50 °C	1.30×10^{-4}

Acetic acid as a new electrolyte

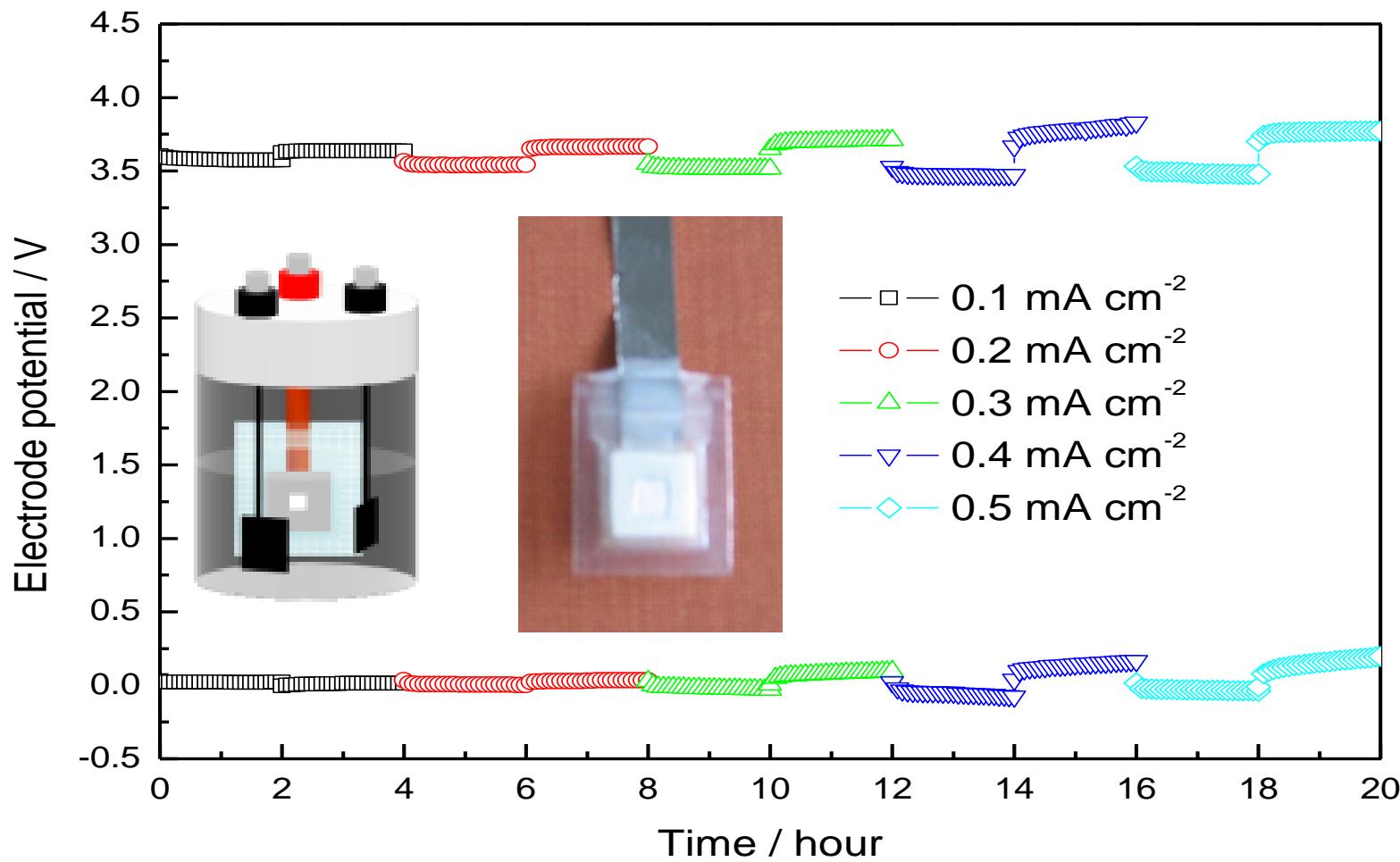
by O.Yamamoto et al. Chem. Commun., 46 (2010)
1661

Cell Reaction

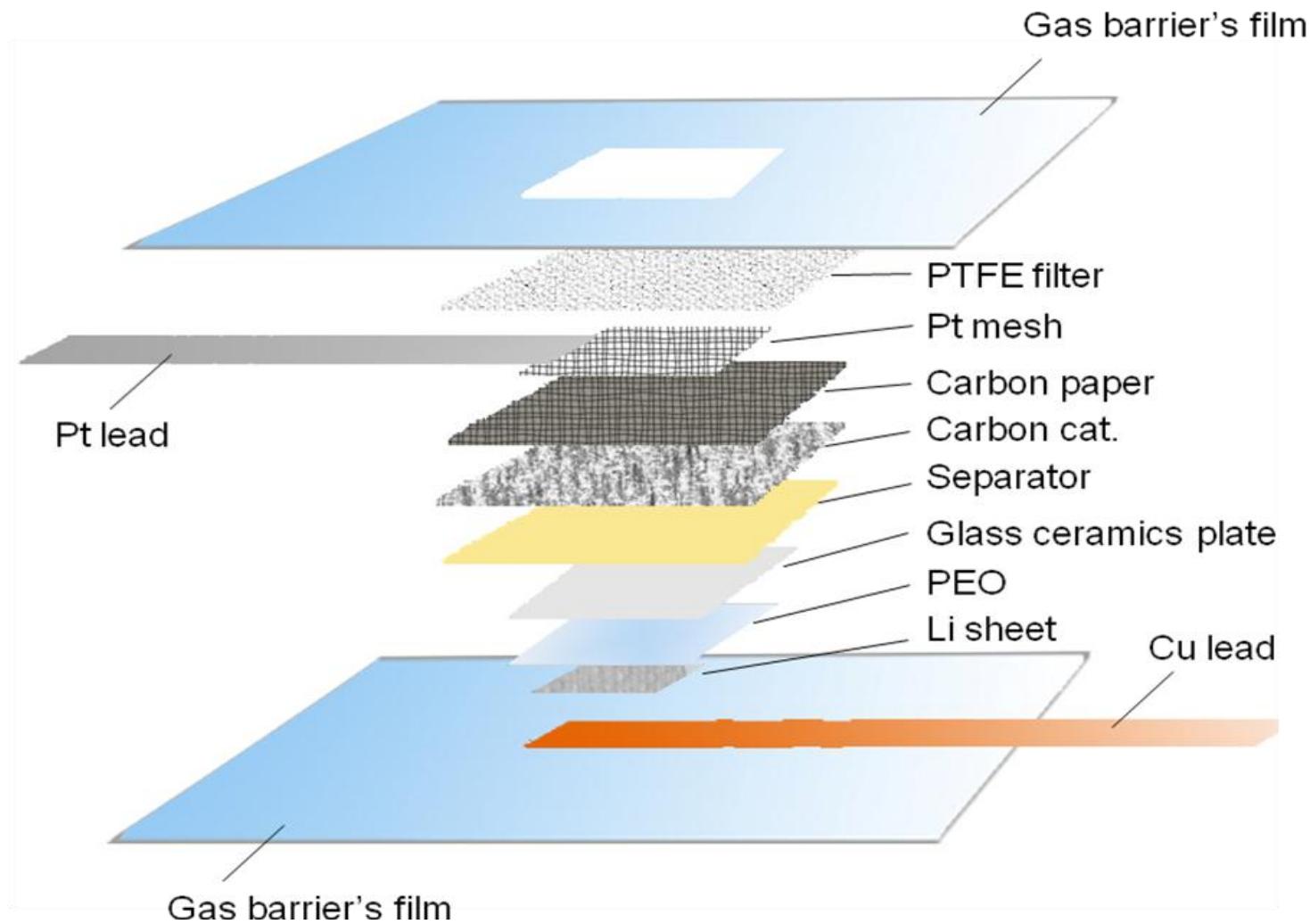


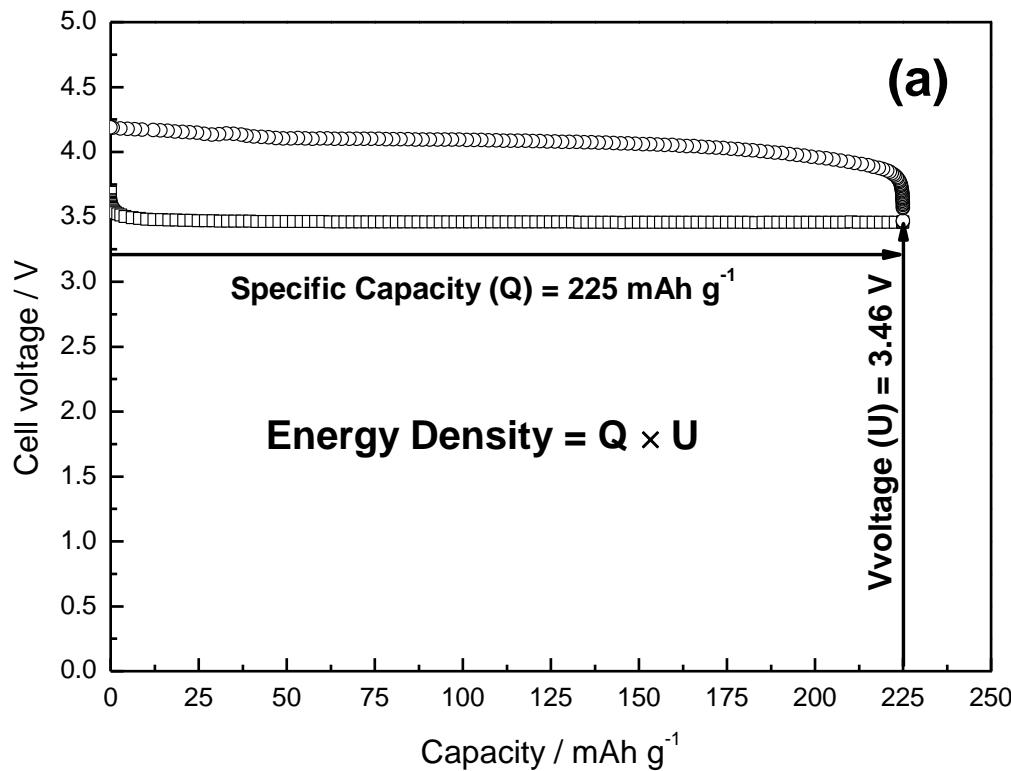
Energy density

$$400\text{mAh/g} \times 3.4\text{V} = 1360 \text{ Wh/kg} > 700\text{Wh/kg}$$

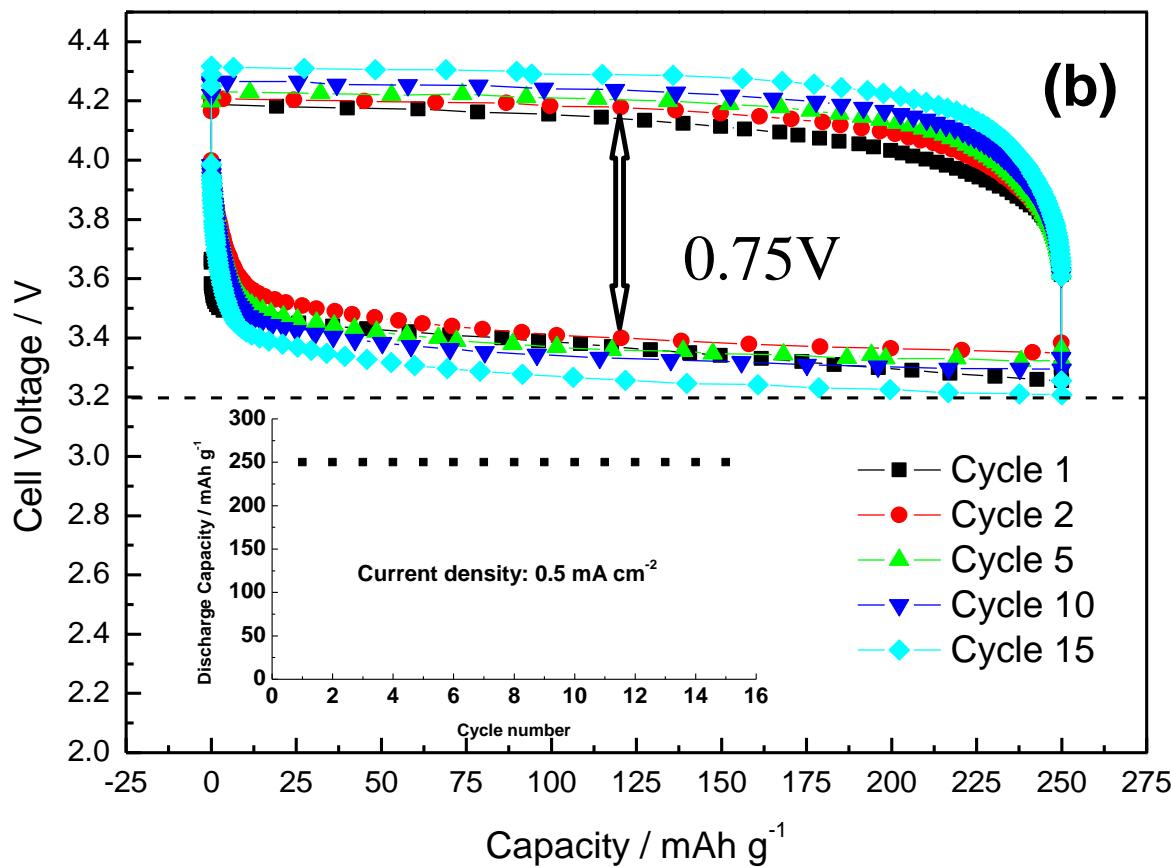


Anode and cathode potentials for Li/PEO/LTAP/HAc solution/Pt, air
at 60°C by O.Yamamoto et al. Chem. Commun., 46 (2010) 1661

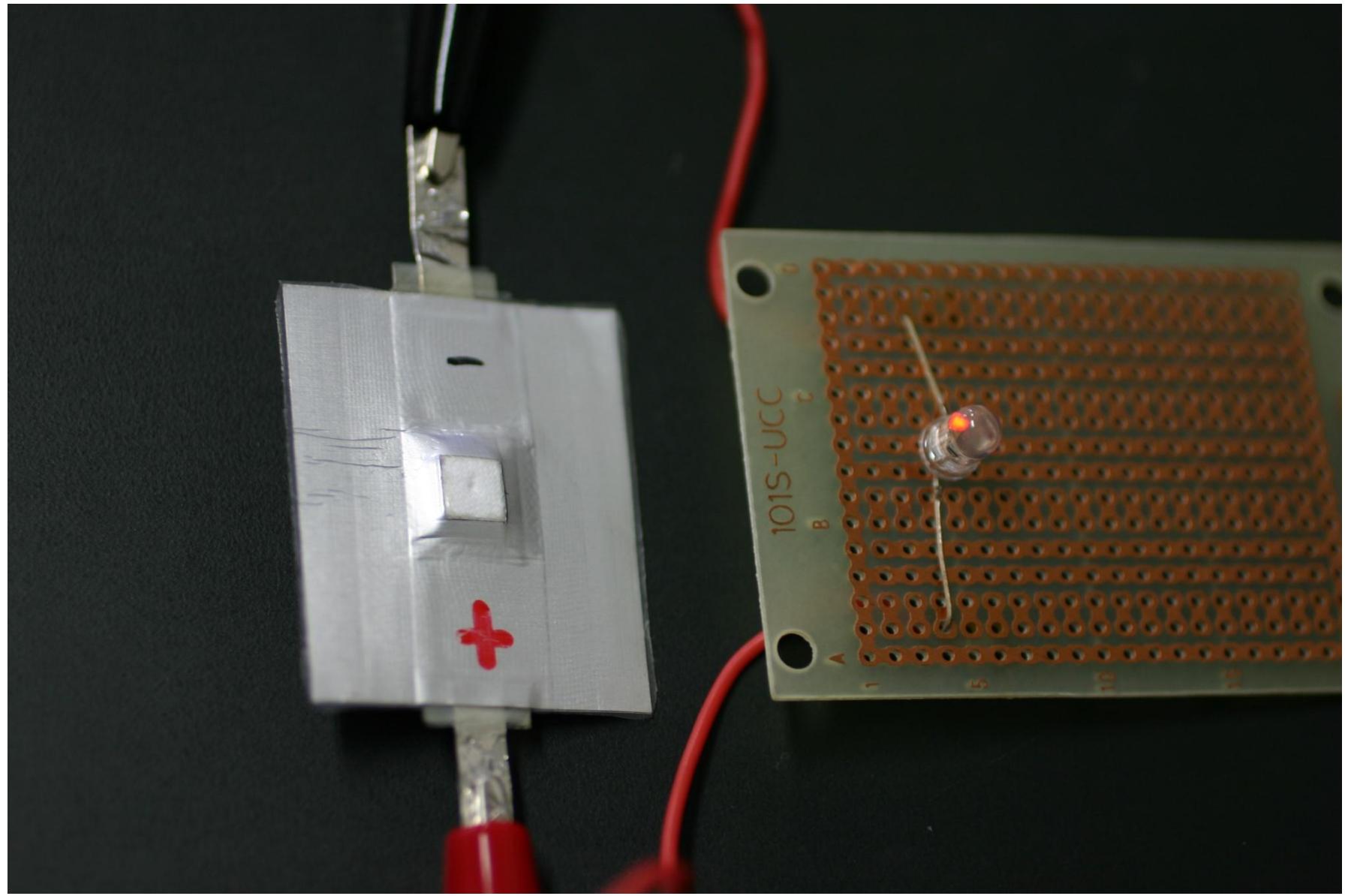




Charge-discharge performance of Li/PEO/LTAP/HAc-H₂O-LiAc(saturated)/carbon air cell at 0.5 mA cm⁻² and 60 ° C. (a) The volume ratio of the electrolyte was 90/10 HAc/H₂O. The cell was sealed in a high pressure vessel with 3 atm of air to suppress evaporation of the electrolyte.



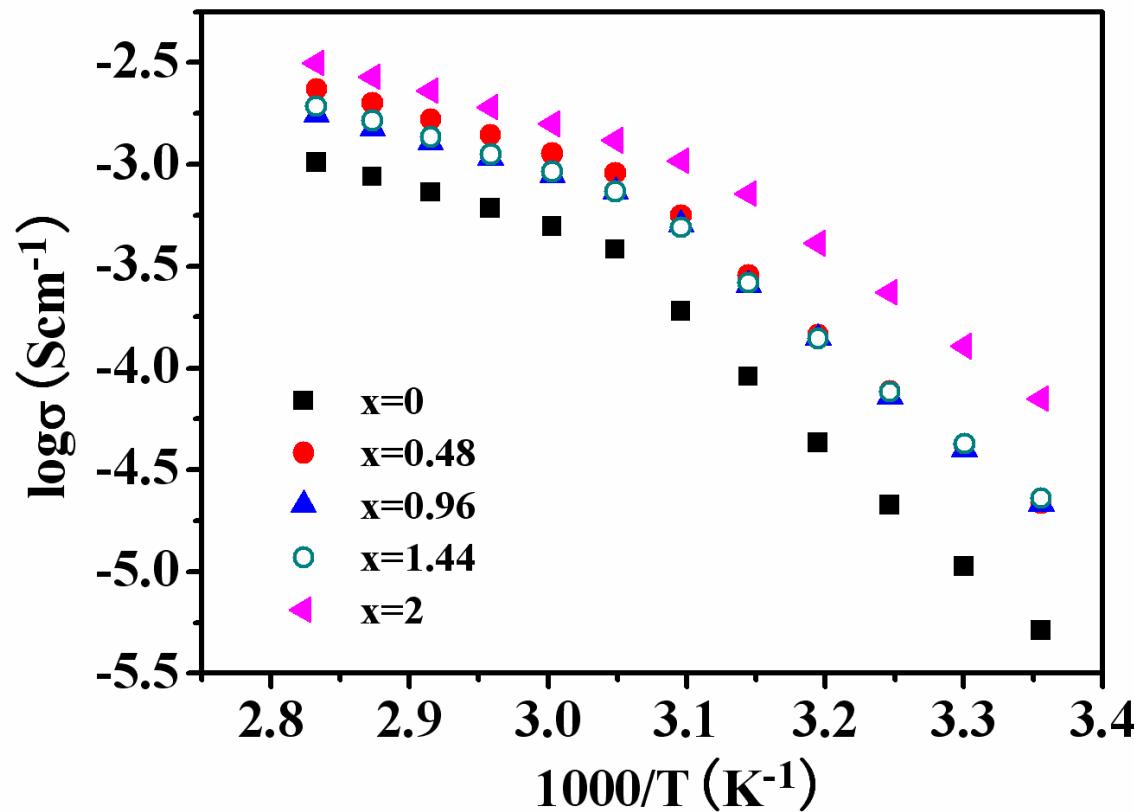
Charge-discharge performance of Li/PEO/LTAP/HAc- H_2O -LiAc(saturated)/carbon air cell at 0.5 mA cm^{-2} and 60° C . The amount of HAc in the electrolyte was defined as 1 mg. The cell was sealed in a high pressure vessel with 3 atm of air to suppress evaporation of the electrolyte.



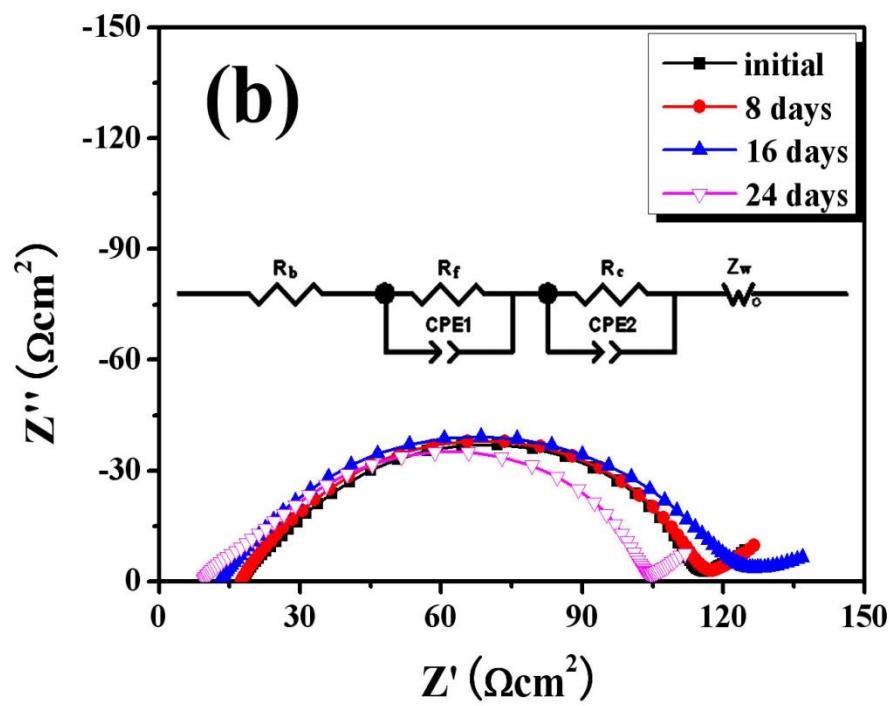
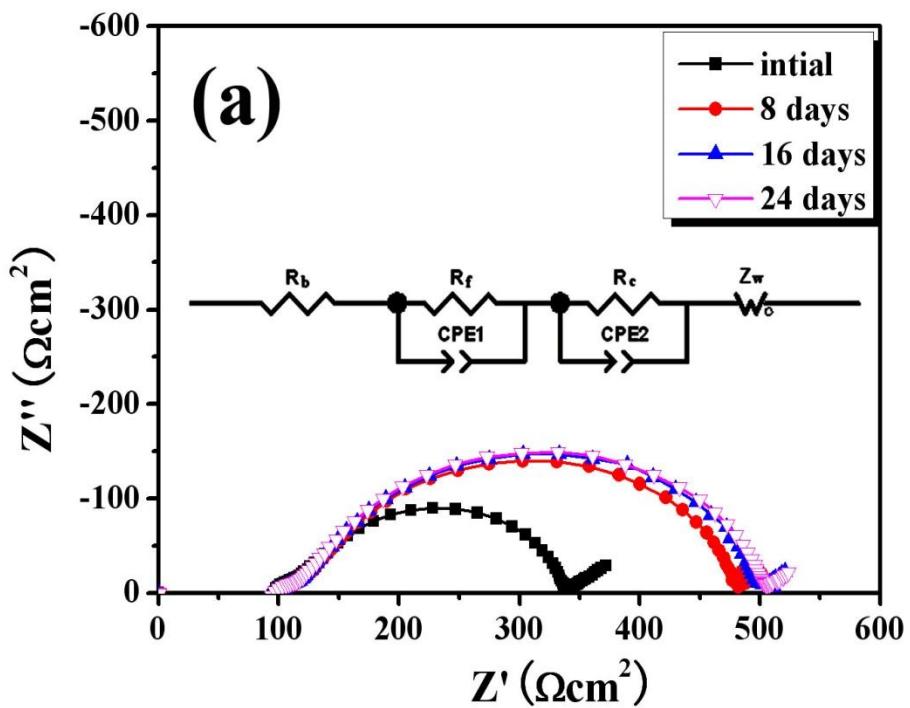
Dendrite formation on Li metal electrodes at Li/PEO-Ionic Liquid composite

**O.Yamamaoto et al. J.Electrochem. Soc.,
157 (2010) A1098**

Lithium Dendrite Formation in Li/poly(ethylene oxide)-Li(CF_3SO_2)₂N and N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imid /Li Cells



Temperature dependence of the electrical conductivity
for $\text{PEO}_{18}\text{LiTFSI}-x\text{PP}_{13}\text{TFSI}$ as a function of x

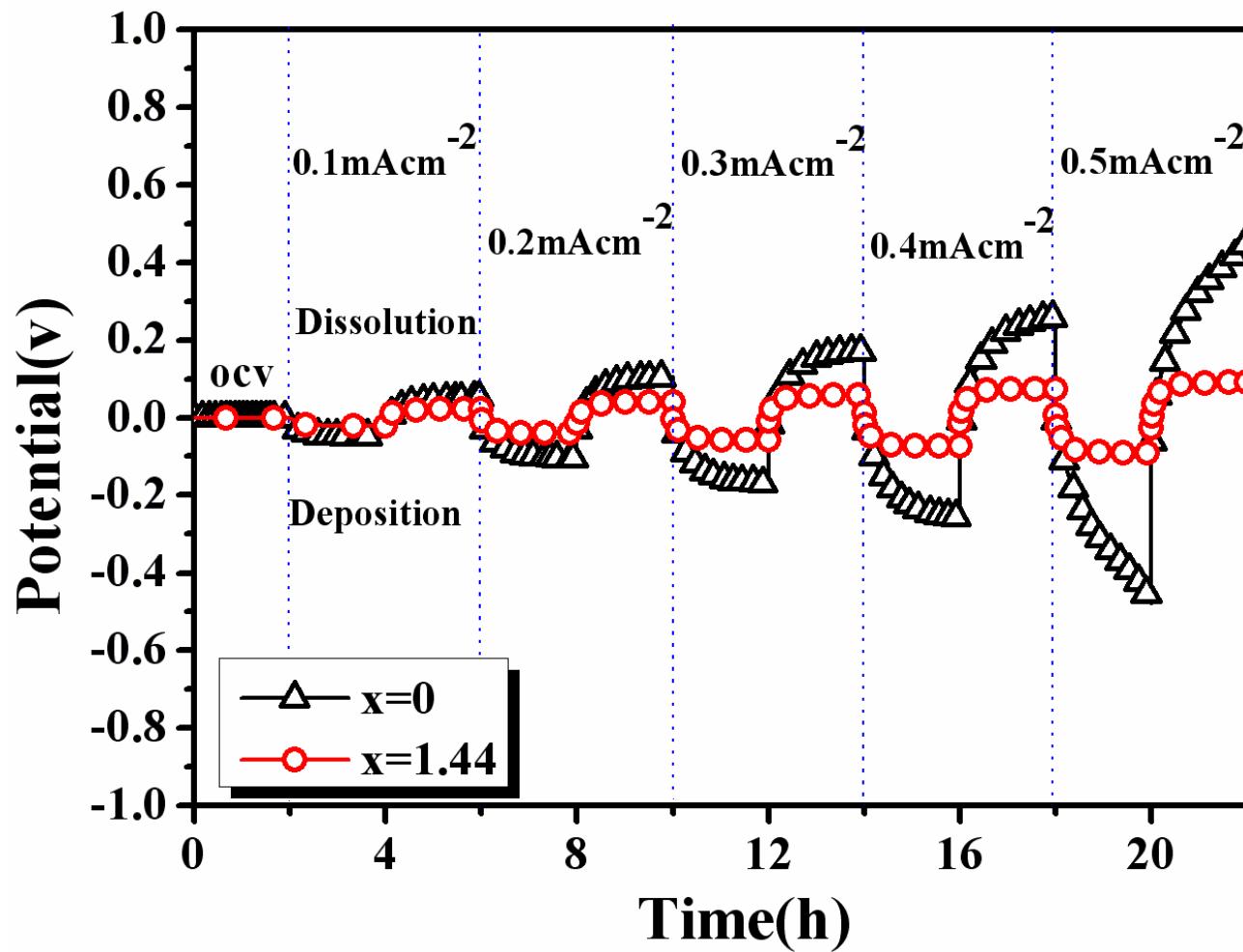


Time dependence of the impedance spectra of

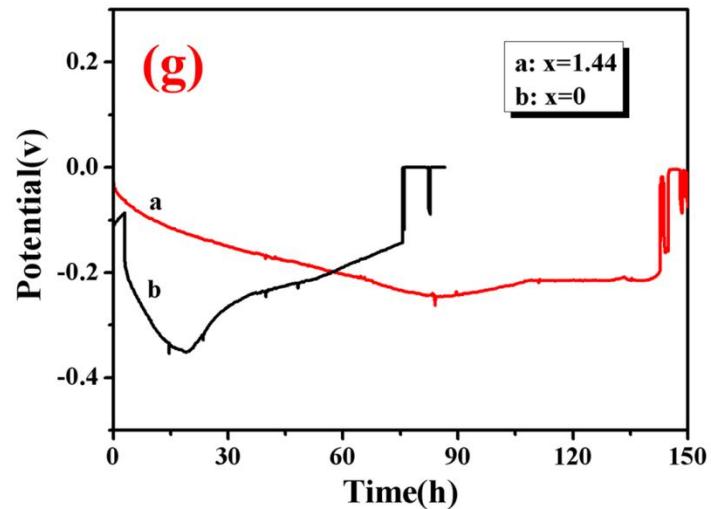
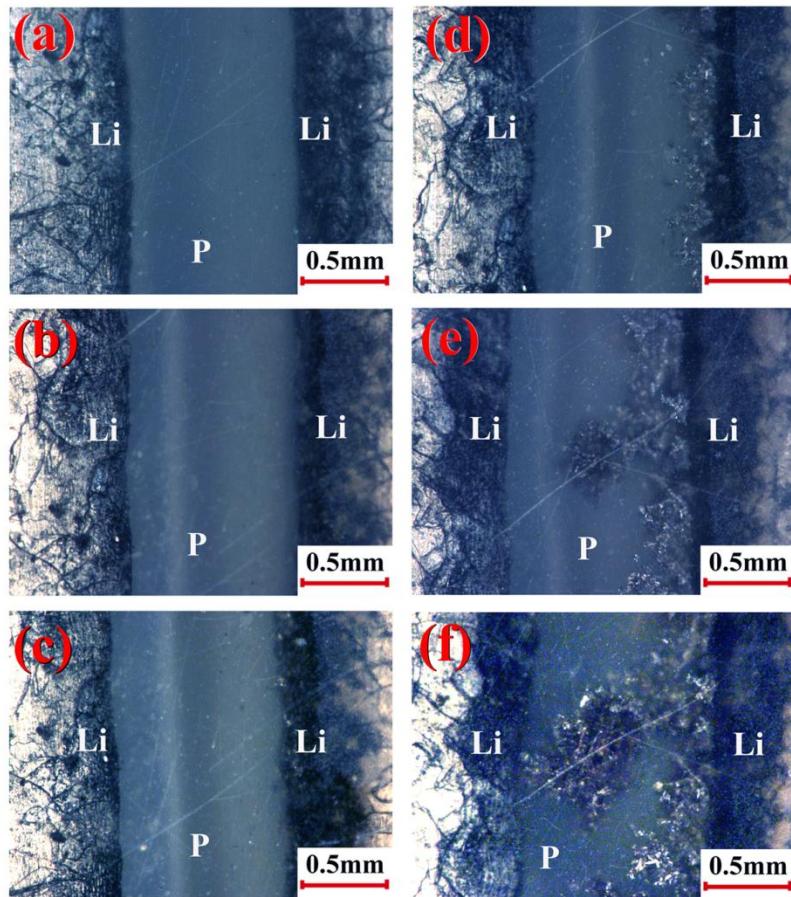
(a) Li/PEO₁₈LiTFSI/Li

(b) Li/PEO₁₈LiTFSI-1.44PP₁₃TFSI/Li

at 60 °C.

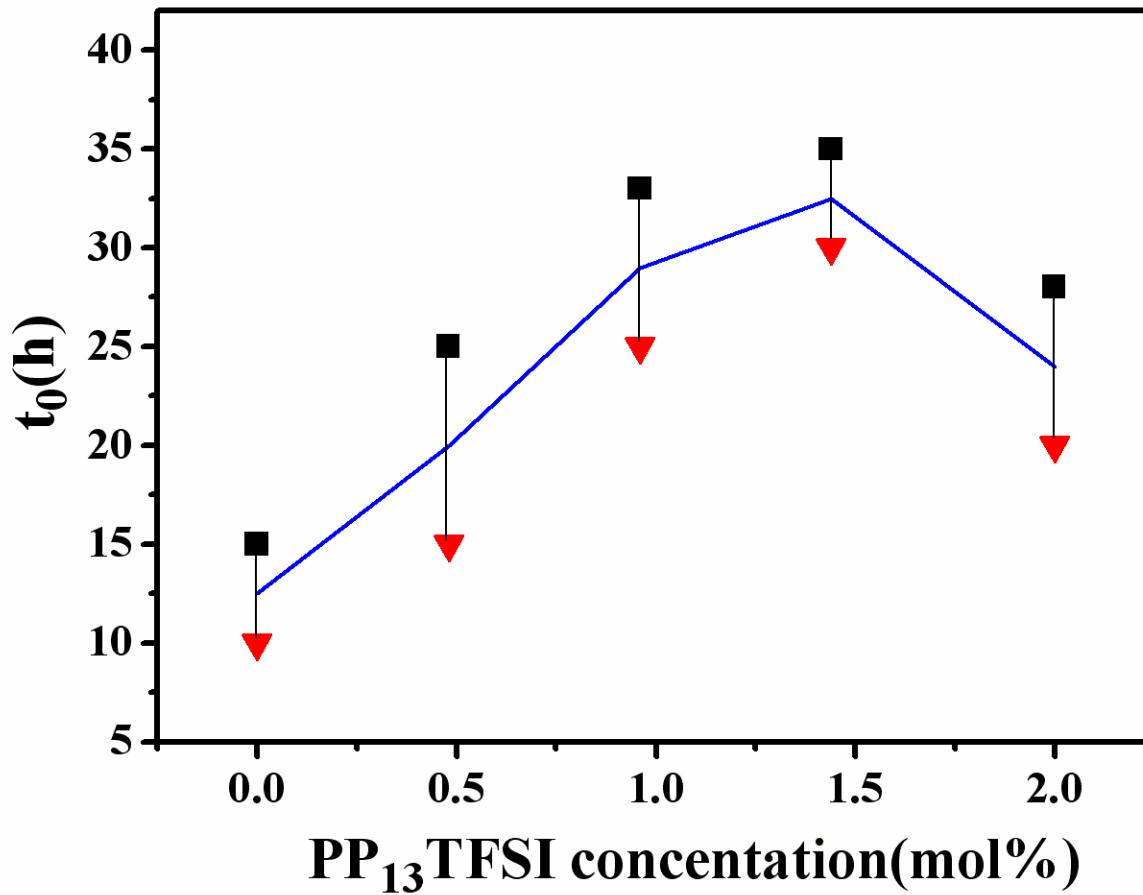


**Constant current polarization curves of
Li/PEO₁₈LiTFSI-xPP₁₃TFSI/Li at 60 °C.**

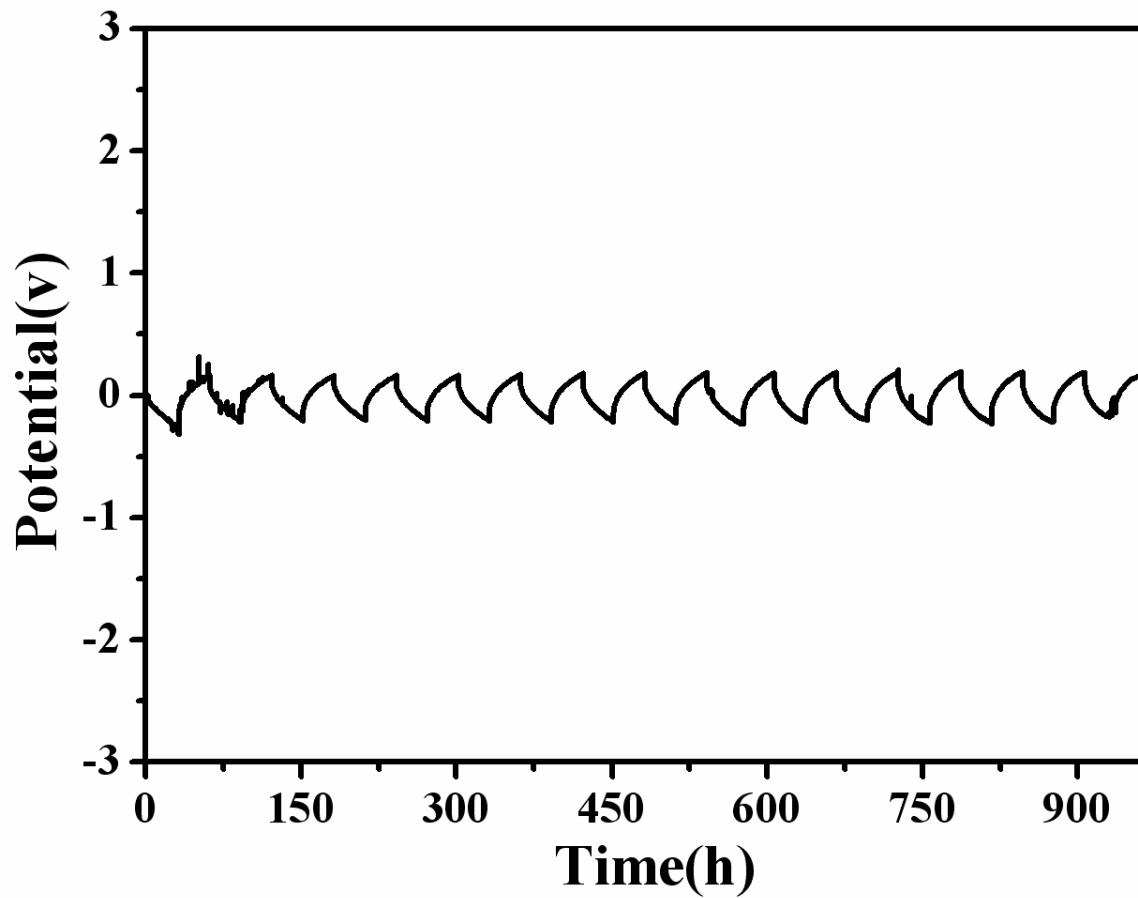


**Dendrite growth in a Li/PEO₁₈LiTFSI-1.44PP₁₃TFSI/Li visualization cell
and the cell potential vs. polarization time curves
at 60 °C and 0.3 mAc⁻².**

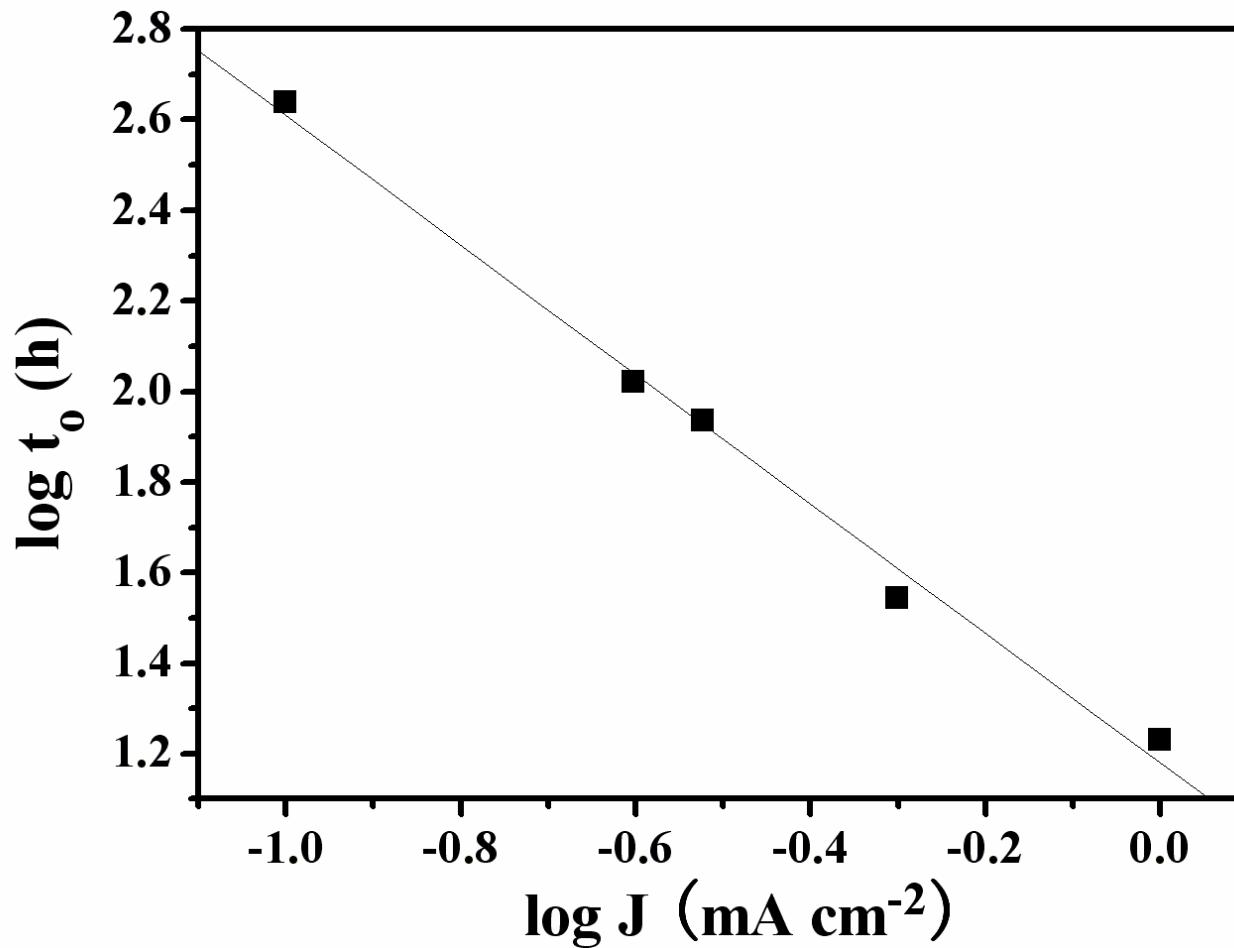
(a)t=0h, (b) t=78 h, (c) t=85 h, (d) t=100 h,
(e) t=130, (f) t=145, and (g) the polarization curve.



Dendrite formation onset time (t_0) vs x in a
 $\text{Li}/\text{PEO}_{18}\text{LiTFSI}-x\text{PP}_{13}\text{TFSI}/\text{Li}$ visualization cell
at 60°C and 0.5 mAcm^{-2} .
▼: no dendrite and ■: dendrite



Cycling performance for Li/ PEO₁₈LiTFSI-1.44PP₁₃TFSI/Li
at 60 °C and 0.3 mAcm⁻².



**Log current density (J) vs. log dendrite formation
onset time (t_0) curves for
Li/PEO₁₈LiTFSI-1.44PP₁₃TFSI/Li at 60 °C**

Dendrite formation onset time (t_o) and short-circuit time (t_s) at different polarization current densities for Li/PEO₁₈LiTFSI/Li and Li/PEO₁₈LiTFSI-1.44PP₁₃TFSI/Li at 60 °C

Sample	Current density (mA cm⁻²)	t_o (h)	t_s (h)
PEO₁₈LiTFSI	0.1	125	225
	0.25	60	76
	0.5	15	20
	1.0	10	15
PEO₁₈LiTFSI-1.44PP₁₃TFSI	0.1	434	594
	0.25	105	135
	0.3	86	145
	0.5	35	75
	1.0	17	35

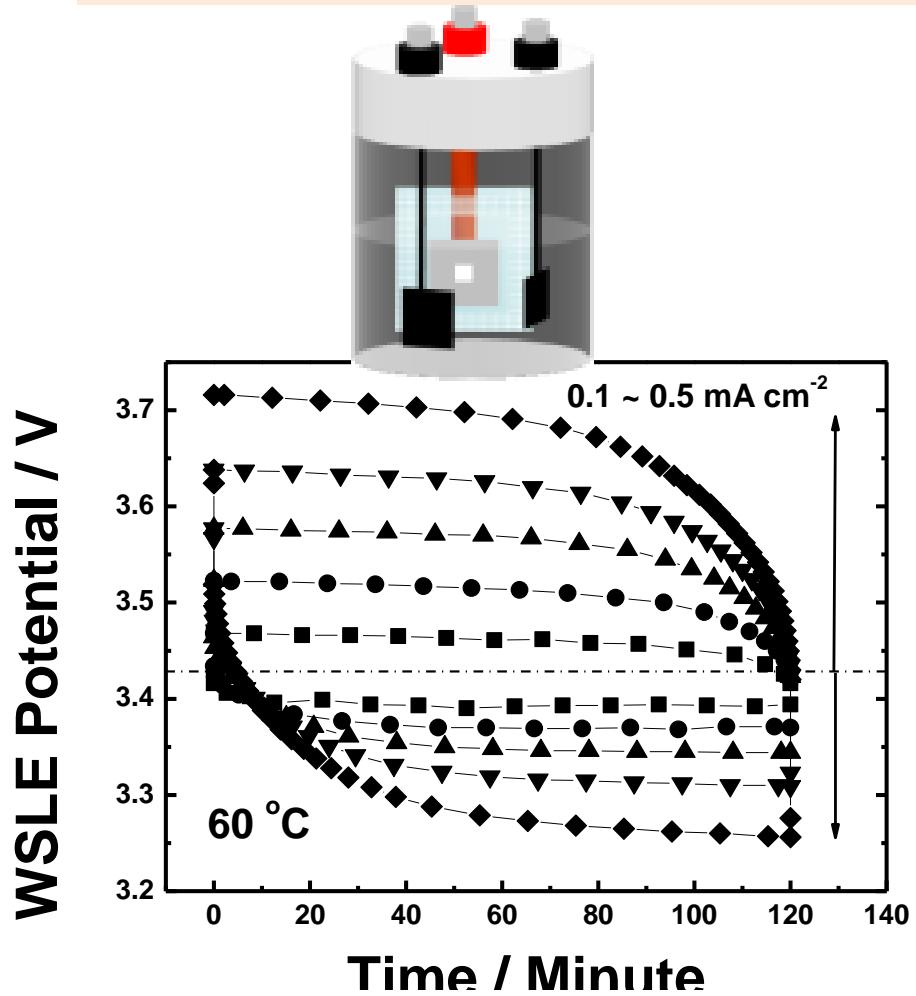
Specific capacitance of Li-metal anode

Electrolyte	Temp. (°C)	Current density (mA cm ⁻²)	Onset Time (h)	Capacity* (mAh g ⁻¹)
PEO ₁₈ LiTFSI	60	1.0	10	870
		0.5	15	688
		0.1	125	1025
PEO ₁₈ LiTFSI- acid modified SiO ₂	60	1.0	15	1167
		0.5	32	1225
		0.1	250	1624
PEO ₁₈ LiTFSI- 1.44PP13TFSI	60	1.0	17	1270
		0.5	35	1300
		0.1	434	2148
EC-DMC-EMC-LiPF ₆	25	1.0	0.2	22

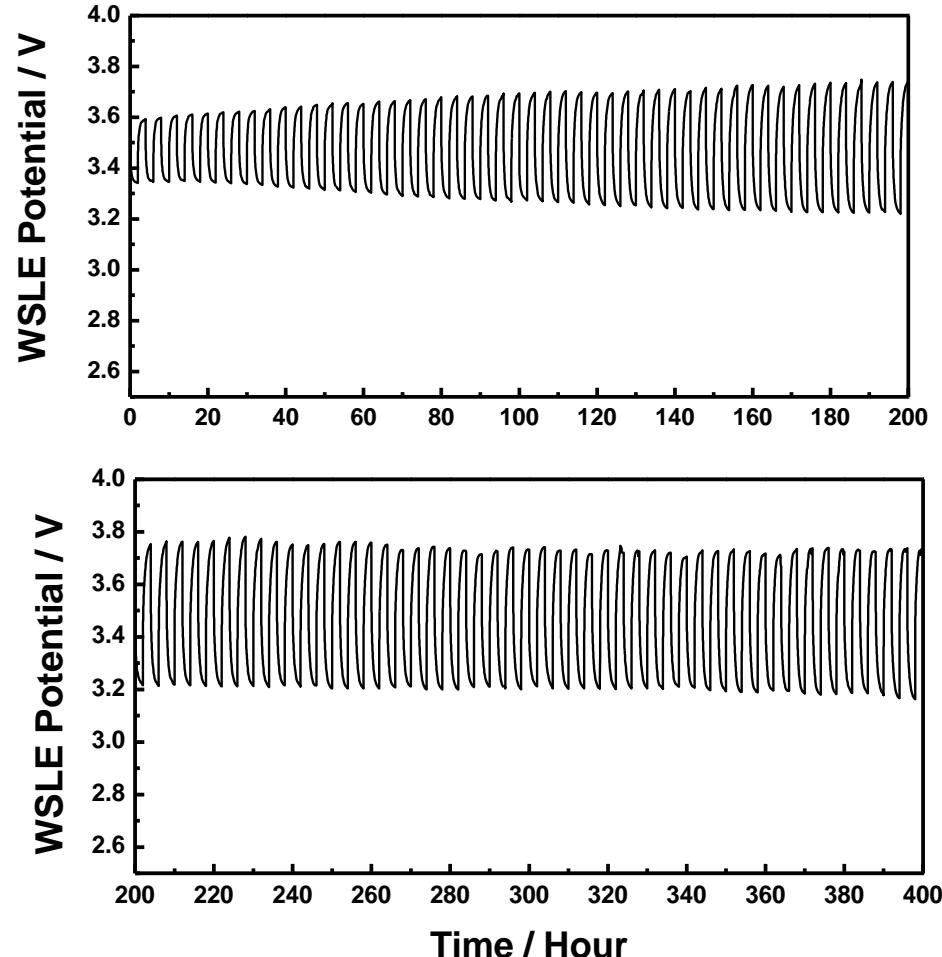
* Capacity during t=0 ~ t_{onset} including Cu substrate with a thickness of 10µm.

We have found a possibility of lithium/air rechargeable batteries with water electrolyte by using a LiCl saturated aqueous electrolyte, because the water stable lithium conducting solid electrolyte LTAP is stable in a **saturated LiCl and LiOH aqueous solution**

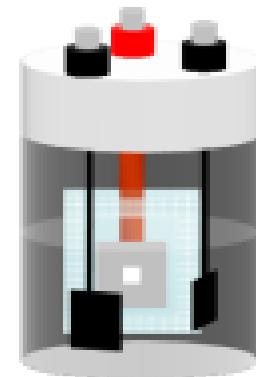
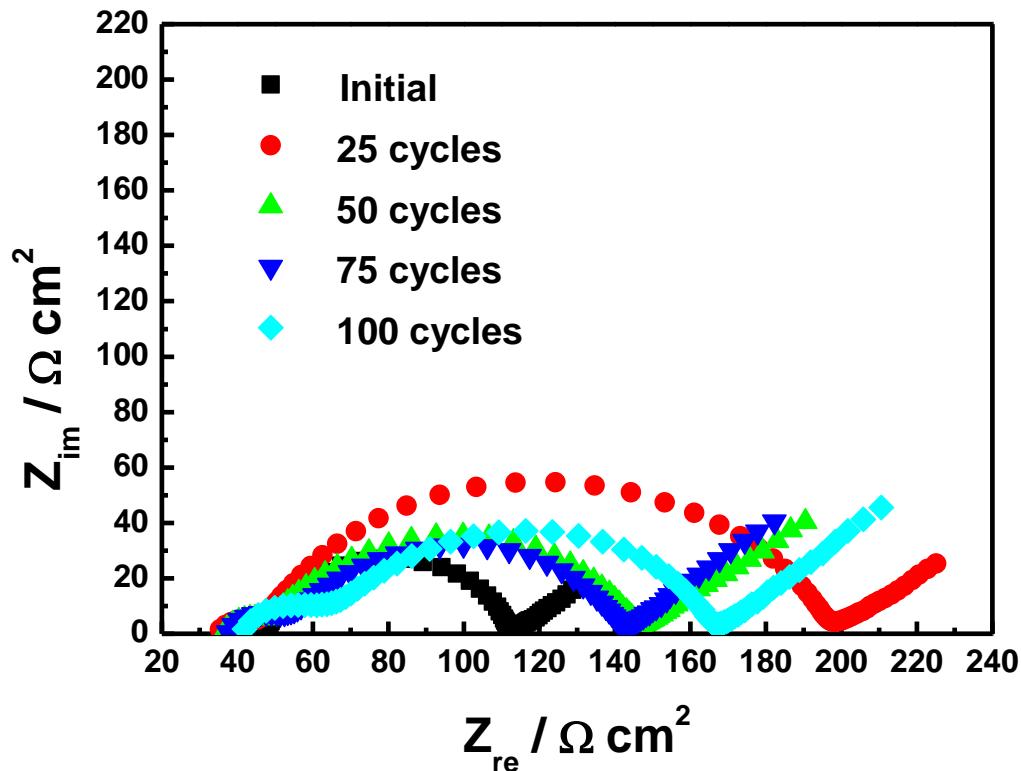
Discharge/Charge performance of Li/PEO₁₈LiTFSI-PP₁₃TFSI/aqueous LiCl/Pt, air cell at 60 °C

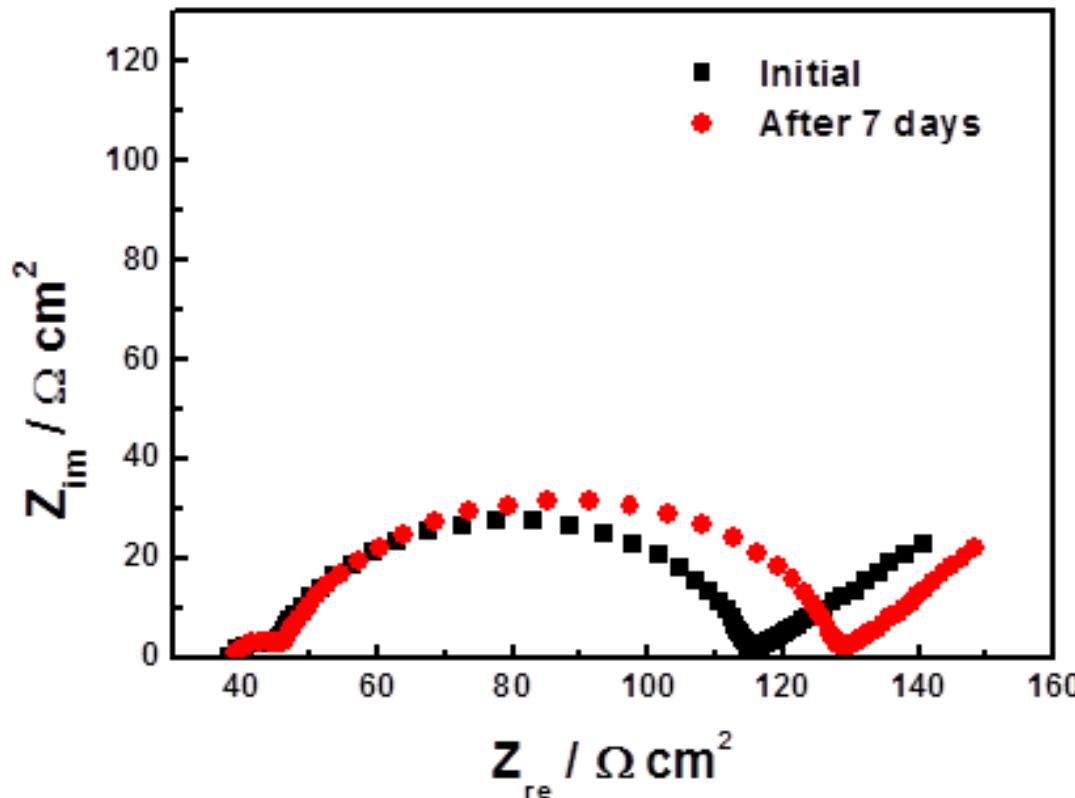


Variation of potential with time for the lithium electrode in the WSLE/aqueous 1 M LiCl + 0.004 M LiOH/Pt beaker cell at different current densities.



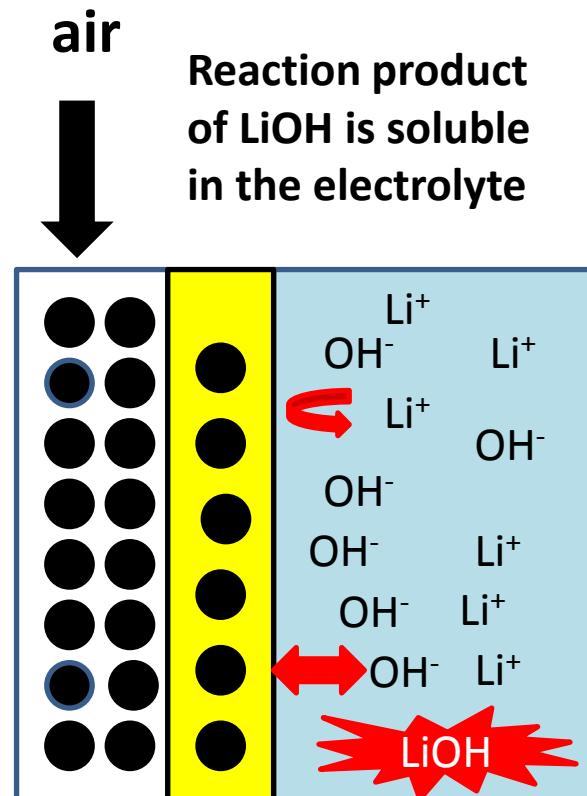
Impedance change of Li/PEO₁₈LiTFSI-PP₁₃TFSI/ aqueous LiCl/Pt, air at 60 °C during cycling





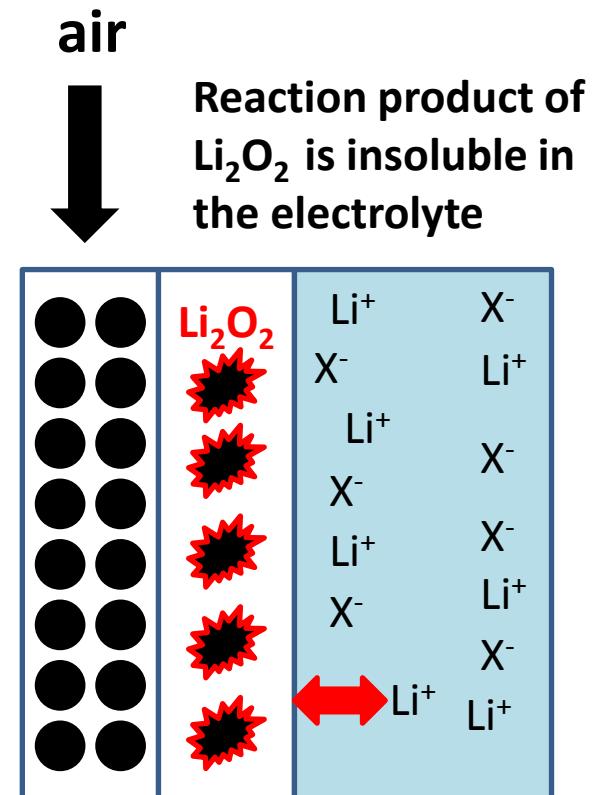
Time dependence of Impedance spectra for Li/PEO₁₈LiTFSI-ionic liquid/LTAP/sat. LiCl and sat. LiOH aqueous solution at 60 °C

This result suggests that Li/air secondary batteries with water electrolyte will be successfully developed, which show a low polarization for oxygen reduction and evolution and a high specific energy density as high as 700 Wh/g



Gas diffusion layer Reaction layer Aqueous Electrolyte

Anion exchange membrane



Gas diffusion layer Reaction layer Non-aqueous Electrolyte

Further study for aqueous electrolyte Li/air batteries

1. Improve the electrical conductivity of LTAP and the interface resistance between lithium metal and the polymer electrolyte.
2. Search of a new water stable lithium ion conducting solid electrolyte like the Garnet-type solid electrolyte by Weppner.
Recently, we have found the Garnet-type electrolyte is stable in water (ECS Fall Meeting 2010)
3. Search of a catalyst with a high oxygen reduction and oxygen evolution catalytic activity.
For a aqueous electrolyte system, we can use the results of Zn/air and fuel cells
4. Control the formation site of solid LiOH
A place in the electrolyte using an anion exchange ionic membrane proposed by EDF