Fundamental Study on Rechargeable Reaction of Lithium-Oxygen Battery

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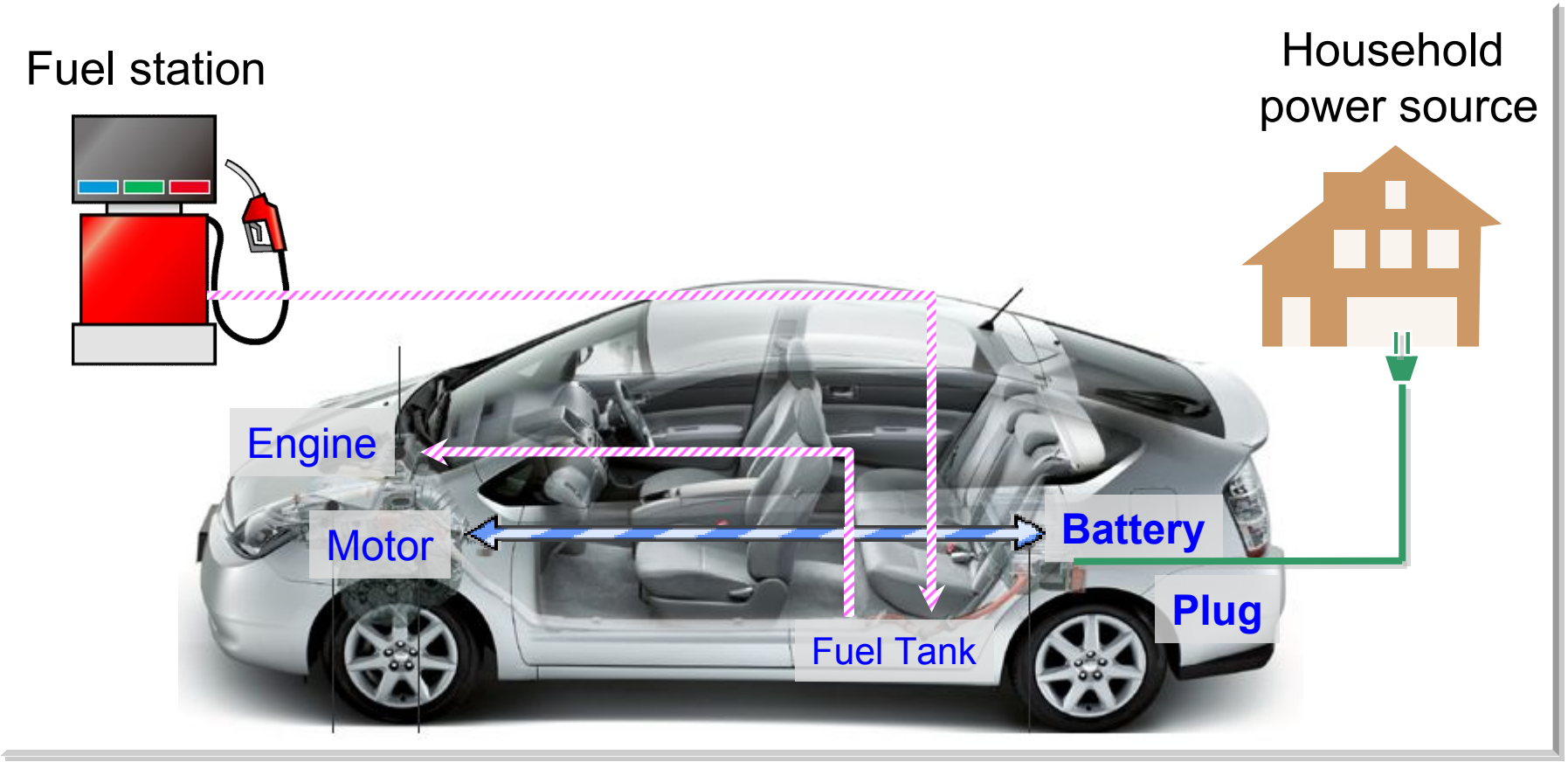
Oct. 7th, 2010
Scalable Energy Storage Beyond Li-Ion: Materials perspectives @ Oak Ridge National Laboratory

Outline

1. Background, our preliminary results and our objective
2. Identification of reaction products and speculation of cathode reaction
3. Selection of electrolytes to control rechargeable reaction
4. Summary

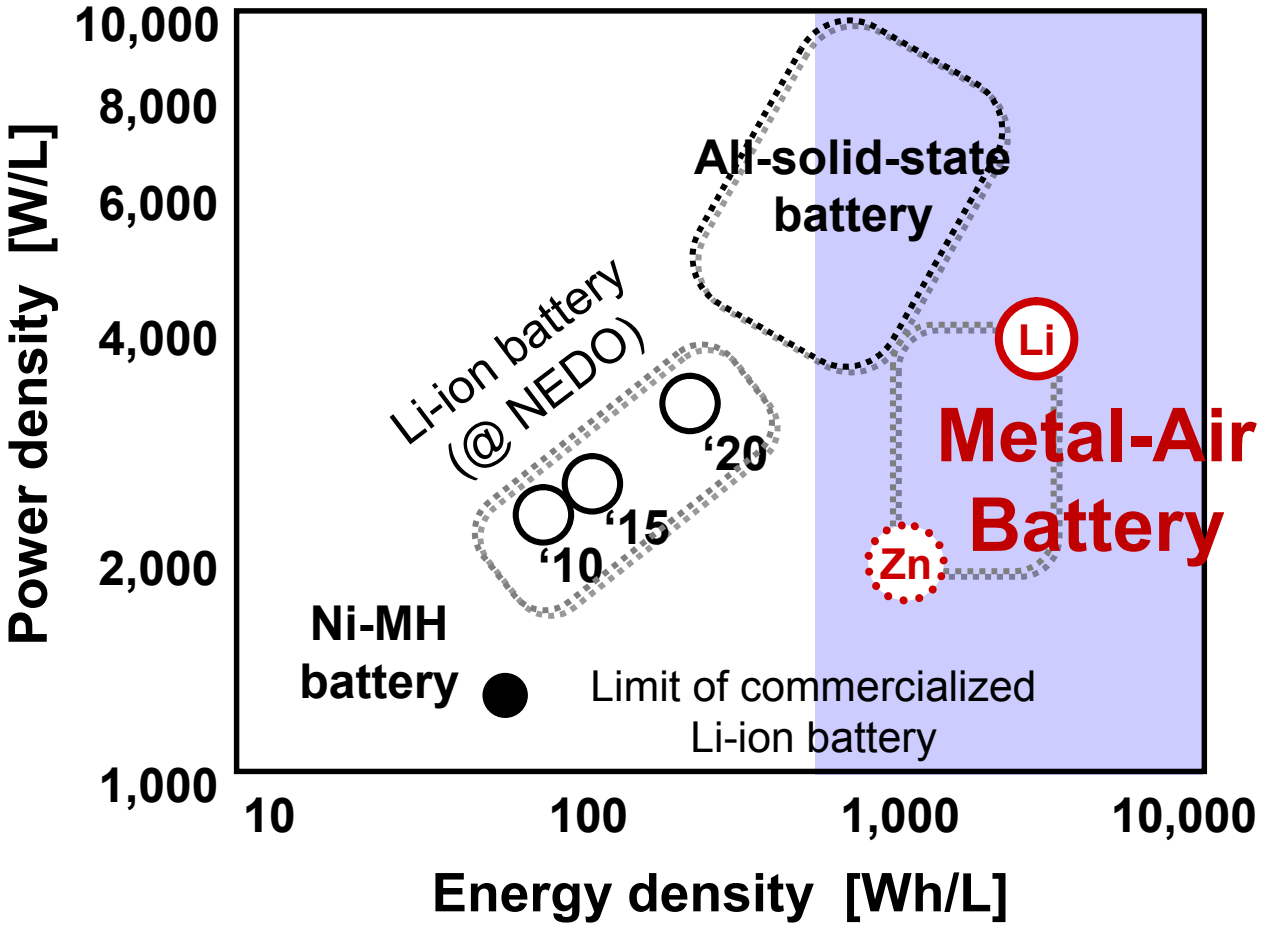
Plug-in hybrid vehicles



Use of external electric source to charge batteries

Short Distance＝EV　Long Distance＝HV

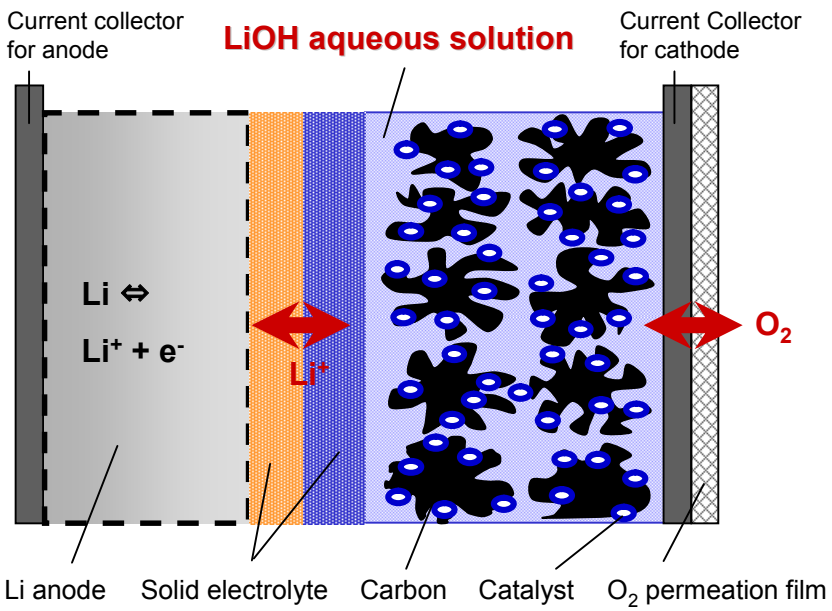
Battery research @ TOYOTA



Li-Air batteries with Li metal and O_2 gas are highly promising to achieve long cruising range of electric vehicles.

Li-air battery

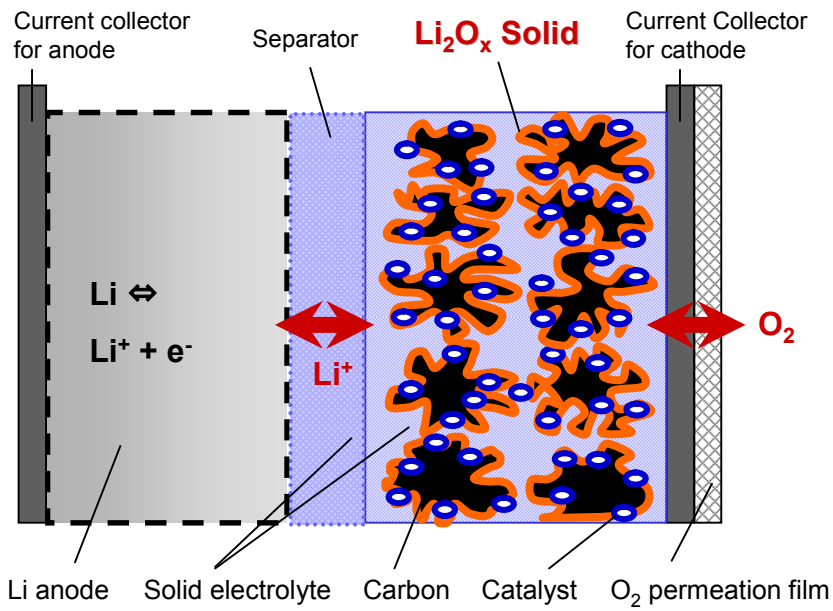
Aqueous system



Cathode reaction mechanism

$$4Li^+ + 4e^- + O_2 + 2H_2O \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} 4LiOH$$

Nonaqueous system



Cathode reaction mechanism

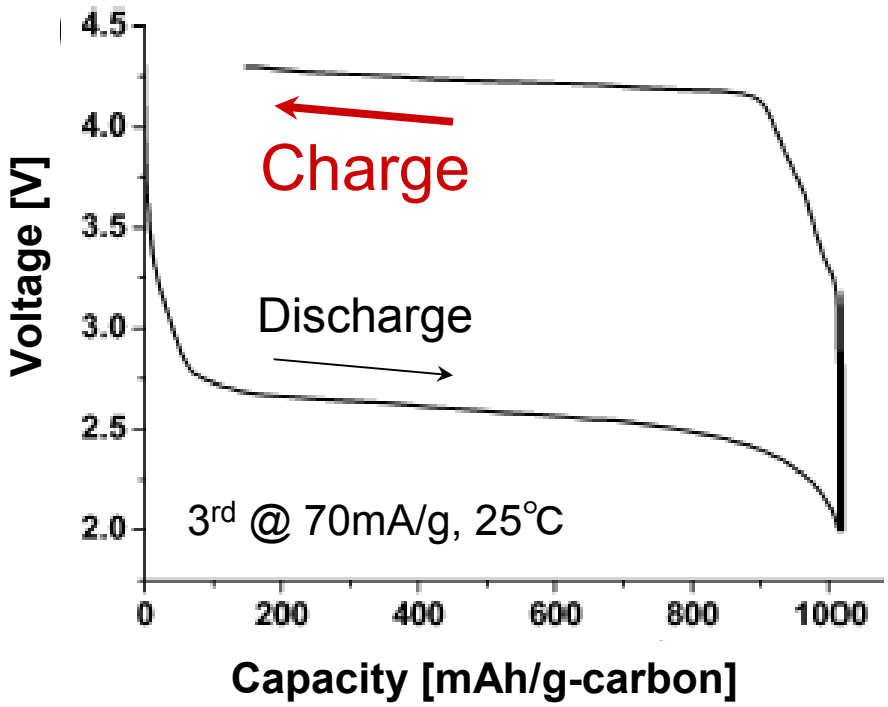
$$2Li^+ + 2e^- + O_2 \underset{\text{Charge}}{\overset{\text{Discharge}}{\rightleftharpoons}} Li_2O_2$$

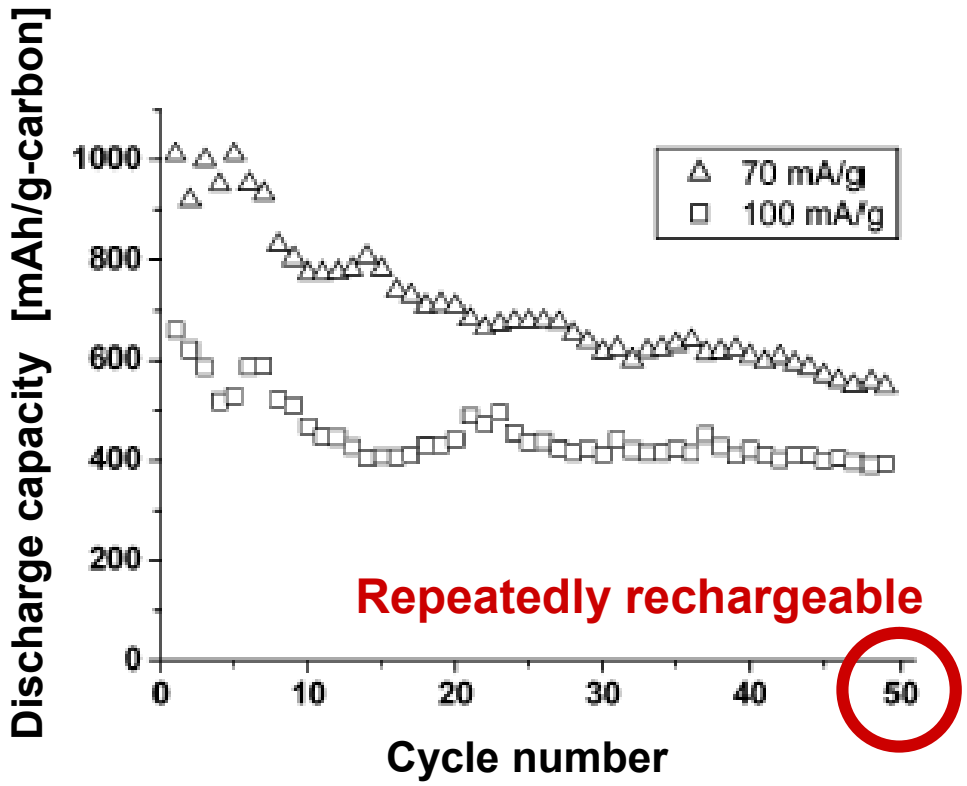
Li_2O_x solid on a cathode is formed and decomposed.

Rechargeability

Prof. Bruce et al., *J. Am. Chem. Soc.*, 128 (**2006**) 1390.

Li / PC, $LiPF_6$(1M) / MnO_2-loaded cathode / O_2

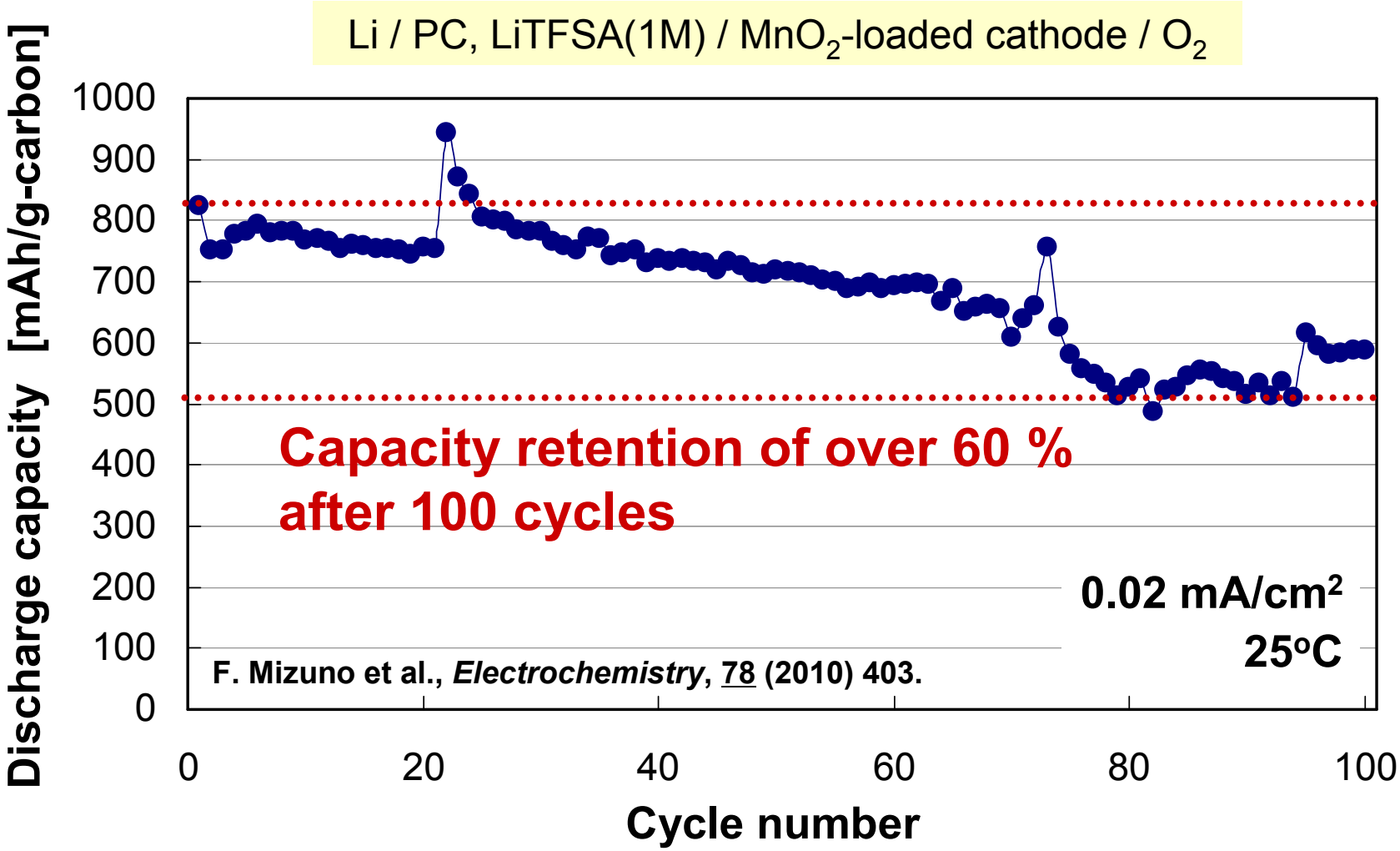




Rechargeability of over 50 cycles was confirmed.

⇒ Important property to use as a rechargeable battery

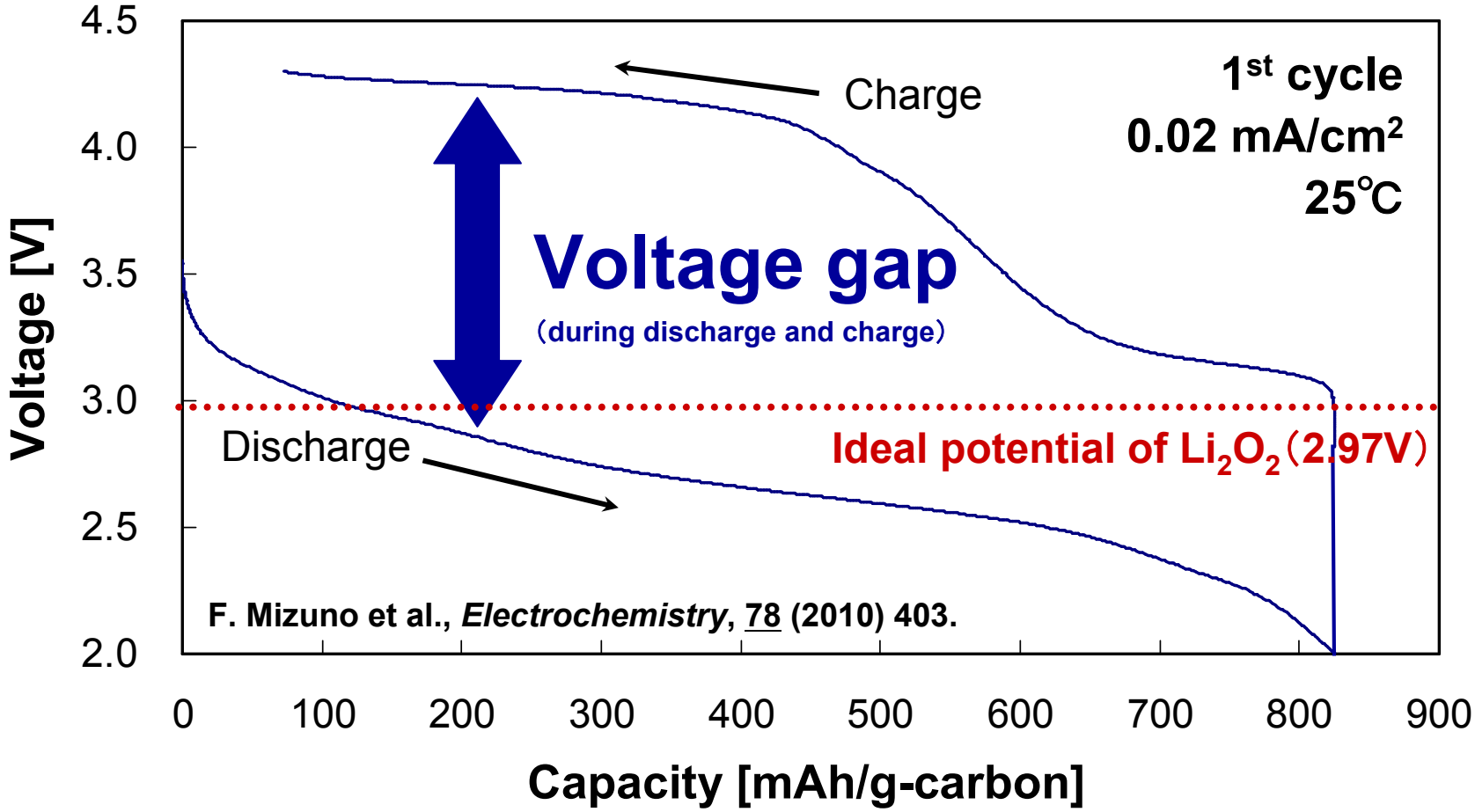
Preliminary result @ TOYOTA



Rechargeability of over 100 cycles was reproduced.

Preliminary result @ TOYOTA

Li / PC, LiTFSA(1M) / MnO_2-loaded cathode / O_2



Large voltage gap (1.4 V) results in low energy efficiency.

In this study

Li-Air batteries with carbonate-based liquid electrolytes

1. Rechargeability of over 100 cycles
2. Large voltage gap of 1.4 V
   (More energy for charging is needed.)

Objectives

Understanding of cathode reaction mechanism

to clarify the reason for large voltage gap

1. Identification of discharged product and charged gas
2. Speculation of reaction route

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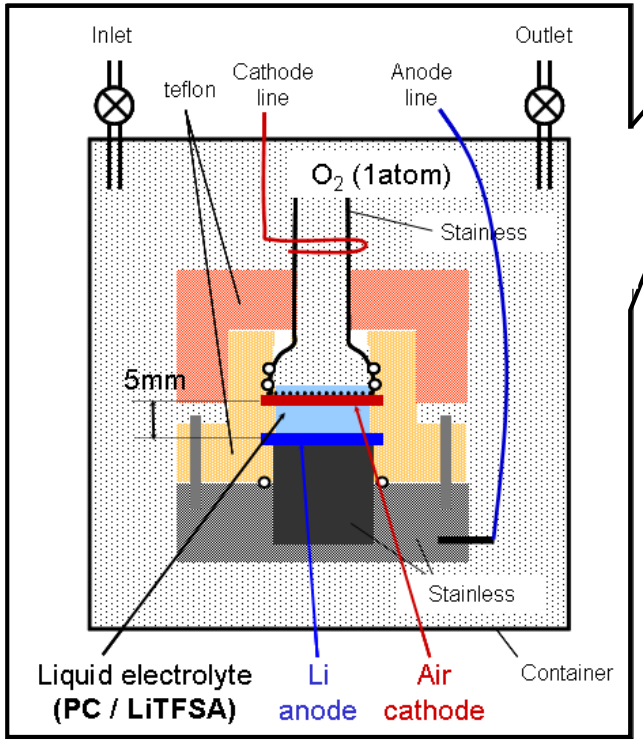
Experimental

Cross section of Li-Air batteries



Distance between anode and cathode
= 5mm
⇒ to prevent a damage of Li metal from O_2 gas and some contamination

Li-Air cell

Discharging @ O_2
Cut-off voltage: 2.0V
Temperature: 25℃
Current density: 0.02mA/cm^2

Charging @ Ar
Cut-off voltage: 4.3V
Temperature: 25℃
Current density: 0.02mA/cm^2

Cell disassembling

Collecting of gas

Rinsing of cathode
In an Ar glove box,
cathode was twice rinsed by a solvent.

Charged gas

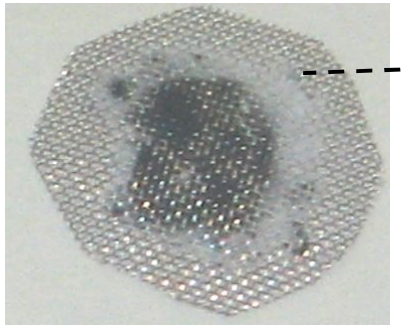
Drying
with no heating

Discharged cathode
with products

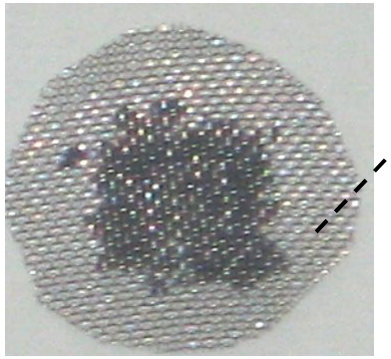
Surface of cathode

Li / PC, $LiClO_4$(1M) / MnO_2-loaded cathode / O_2

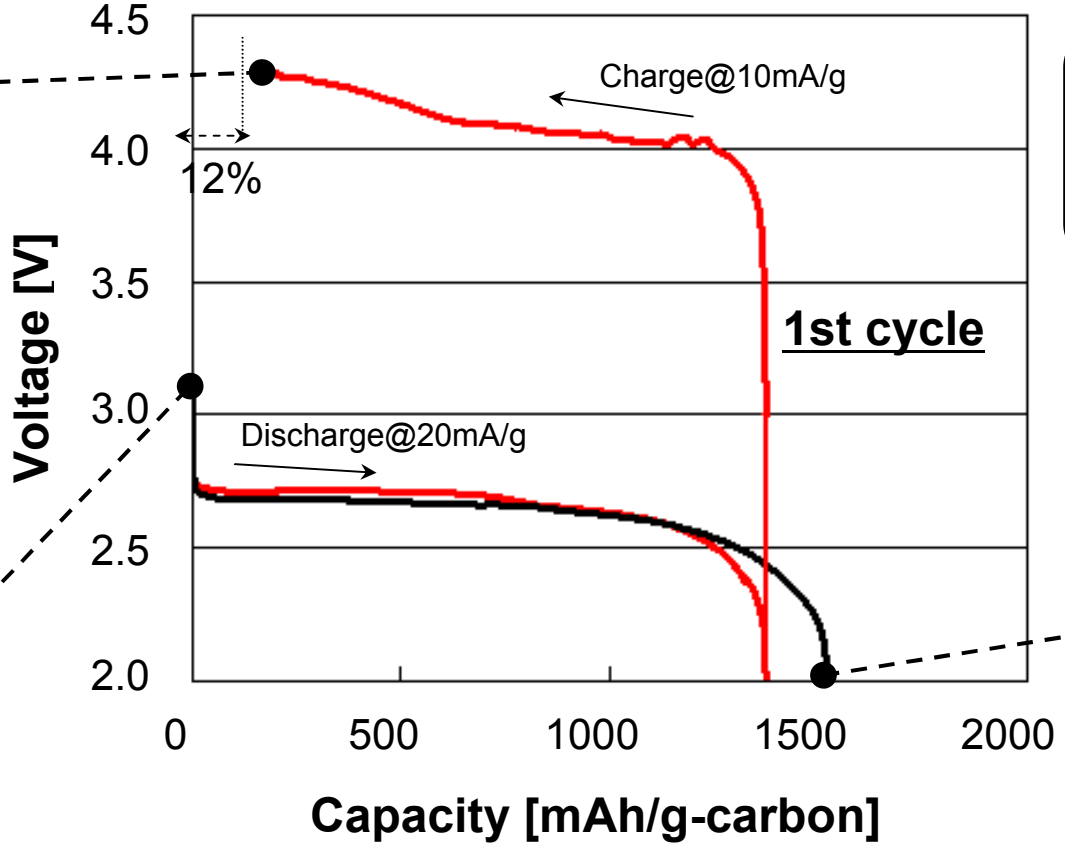
(c) After charging



(a) Before discharging



KB/MnO_2/PTFE pellet



Rinsing process

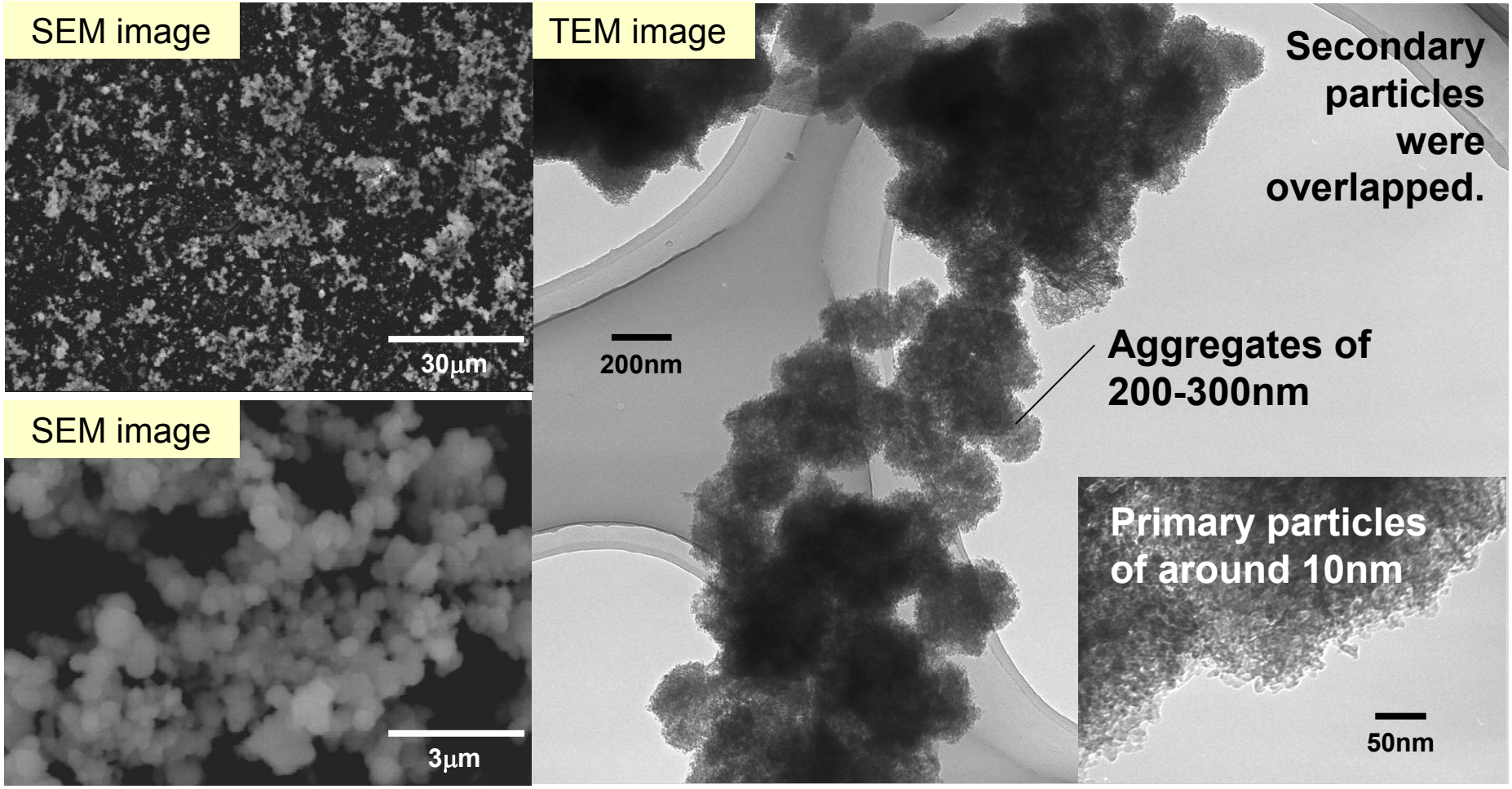
After disassembling the cell, wet air cathodes are rinsed and dried in Ar glove box.

(b) After discharging

White-colored discharged deposit

White-colored deposits were formed after discharging and then disappeared after recharging.

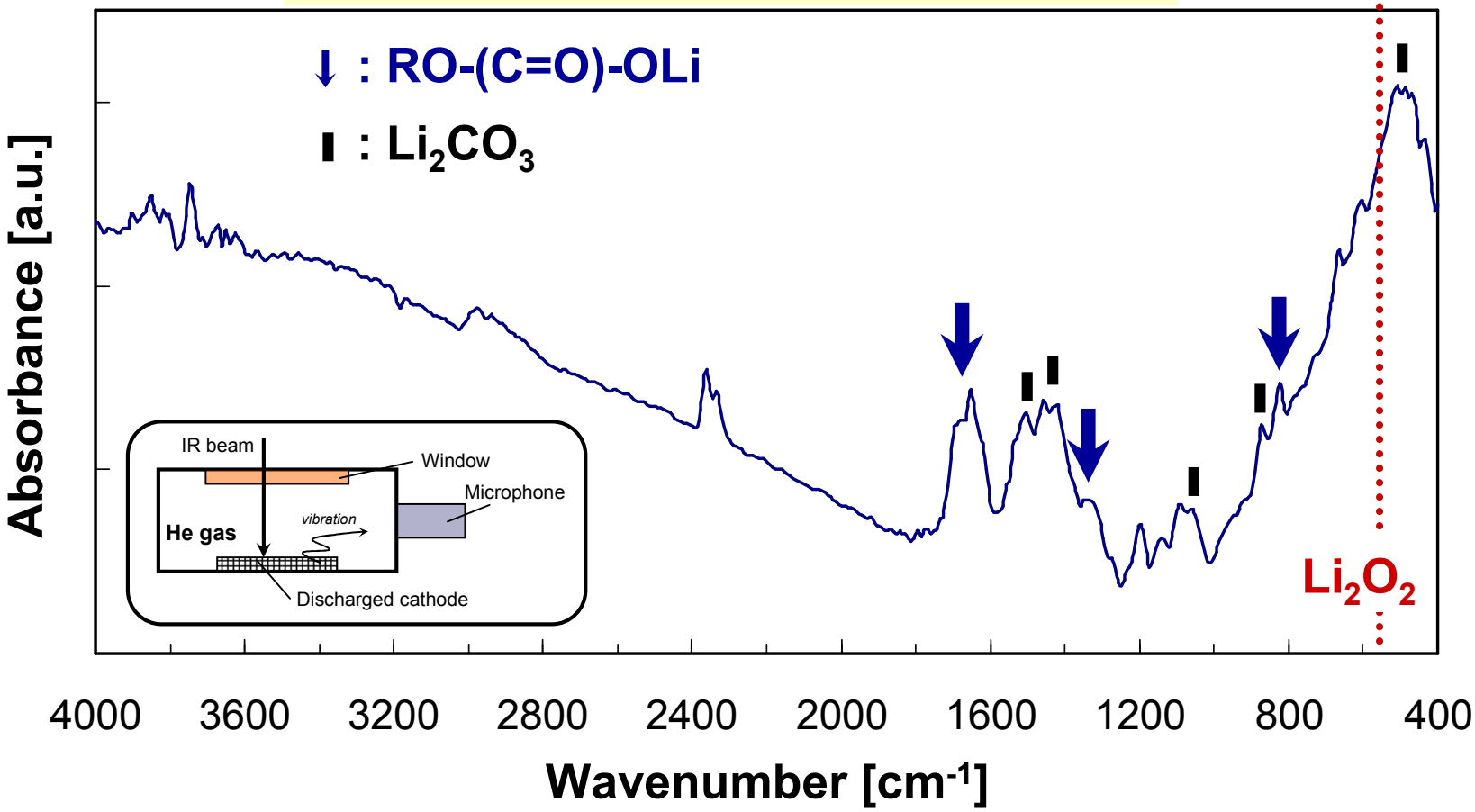
Surface of discharged products



Discharged deposits on a cathode were composed of aggregates of 200-300nm in size with 10 nm primary particles.

Surface of discharged cathode

FT-IR spectrum by Photo Acoustic Spectroscopy

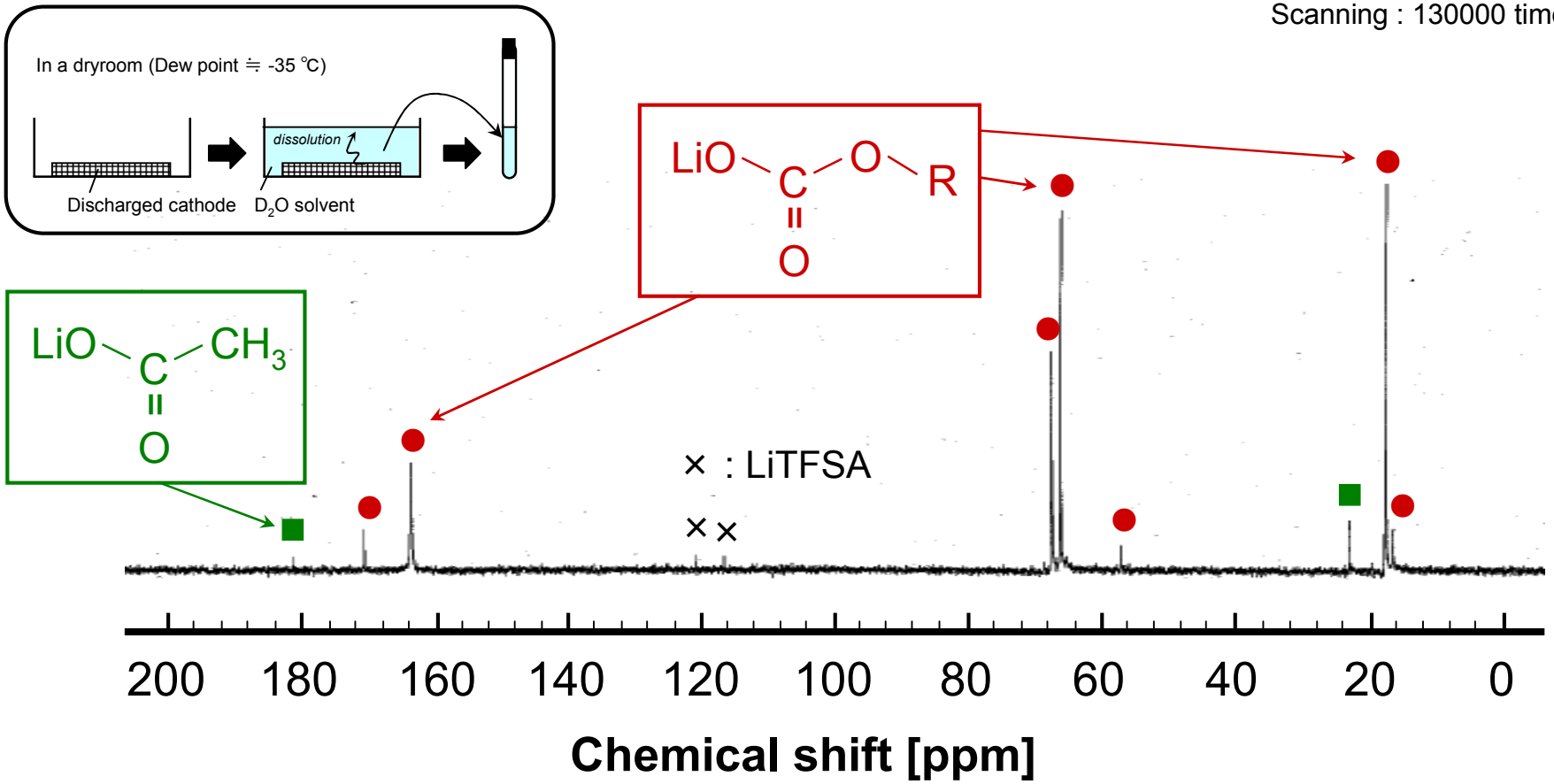


Lithium alkylcarbonate (RO-(C=O)-OLi) and lithium carbonate (Li_2CO_3) were formed. Li_2O_2 might be hidden.

Bulk of discharged cathode

^{13}C CP-MAS NMR spectrum

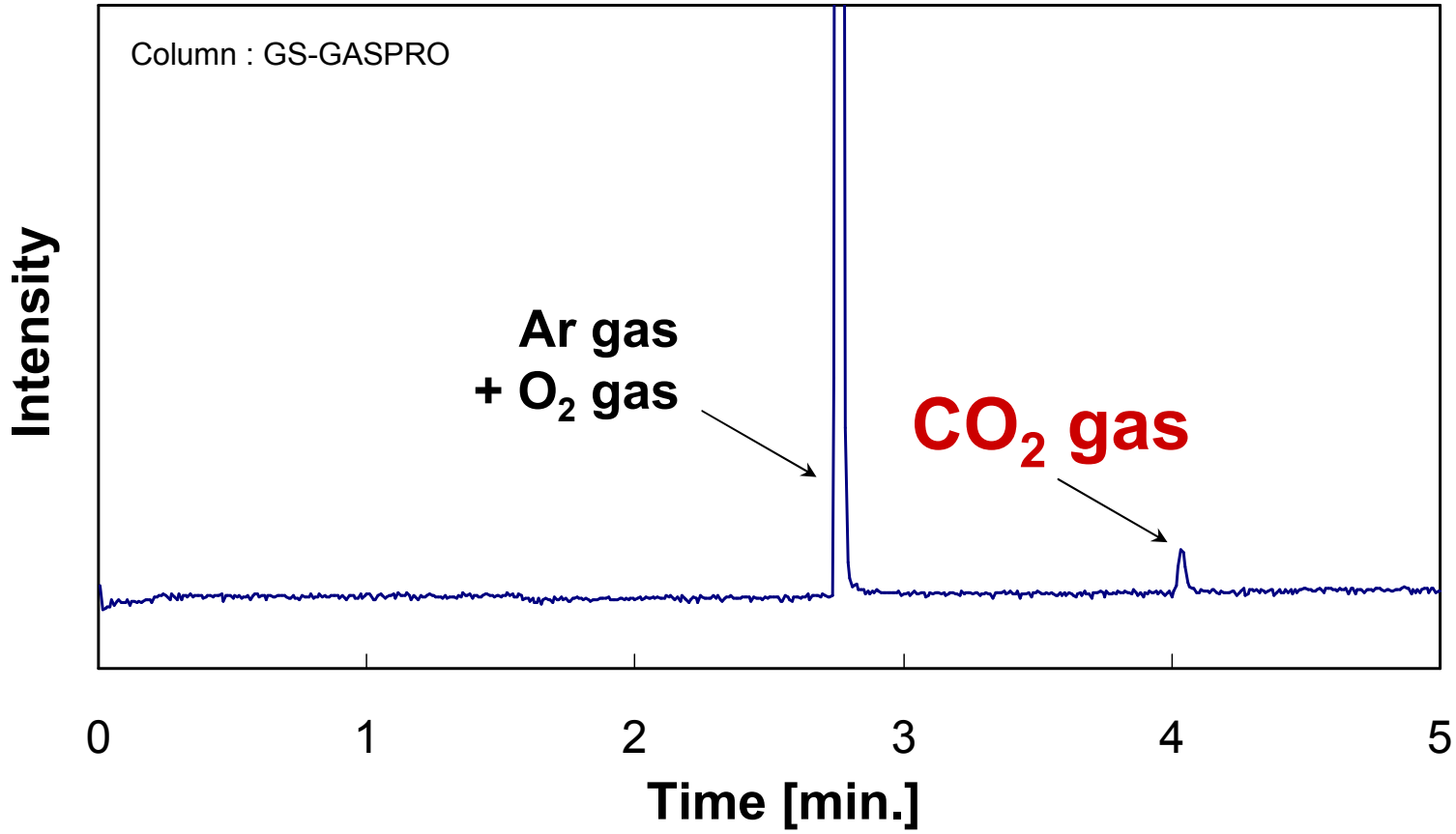
Scanning : 130000 times



Lithium alkylcarbonate (RO-(C=O)-OLi) and lithium acetate (CH_3COOLi) were dissolved in the D_2O solvent.

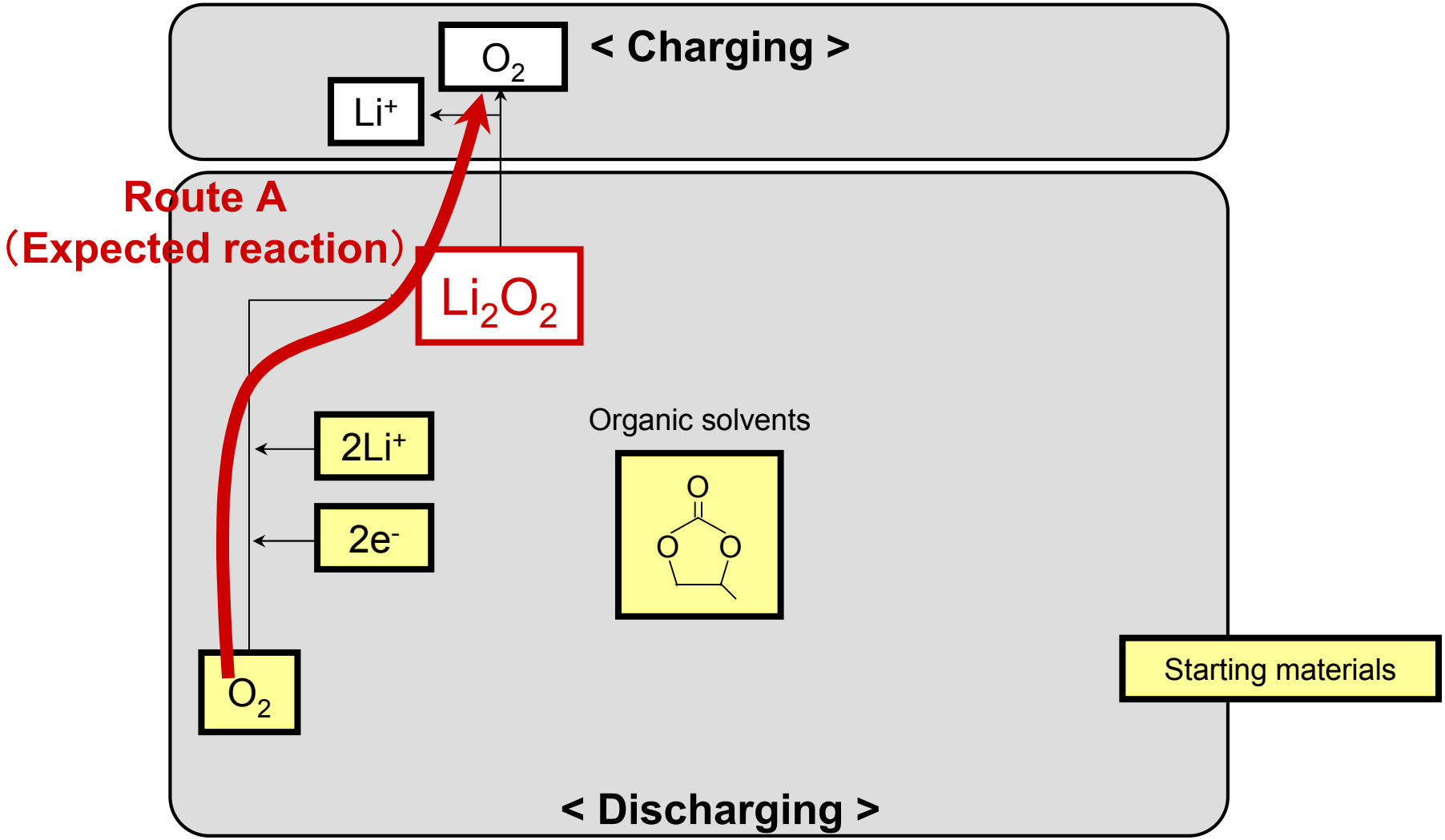
Component of charged gas

Gas chromatograph by MS



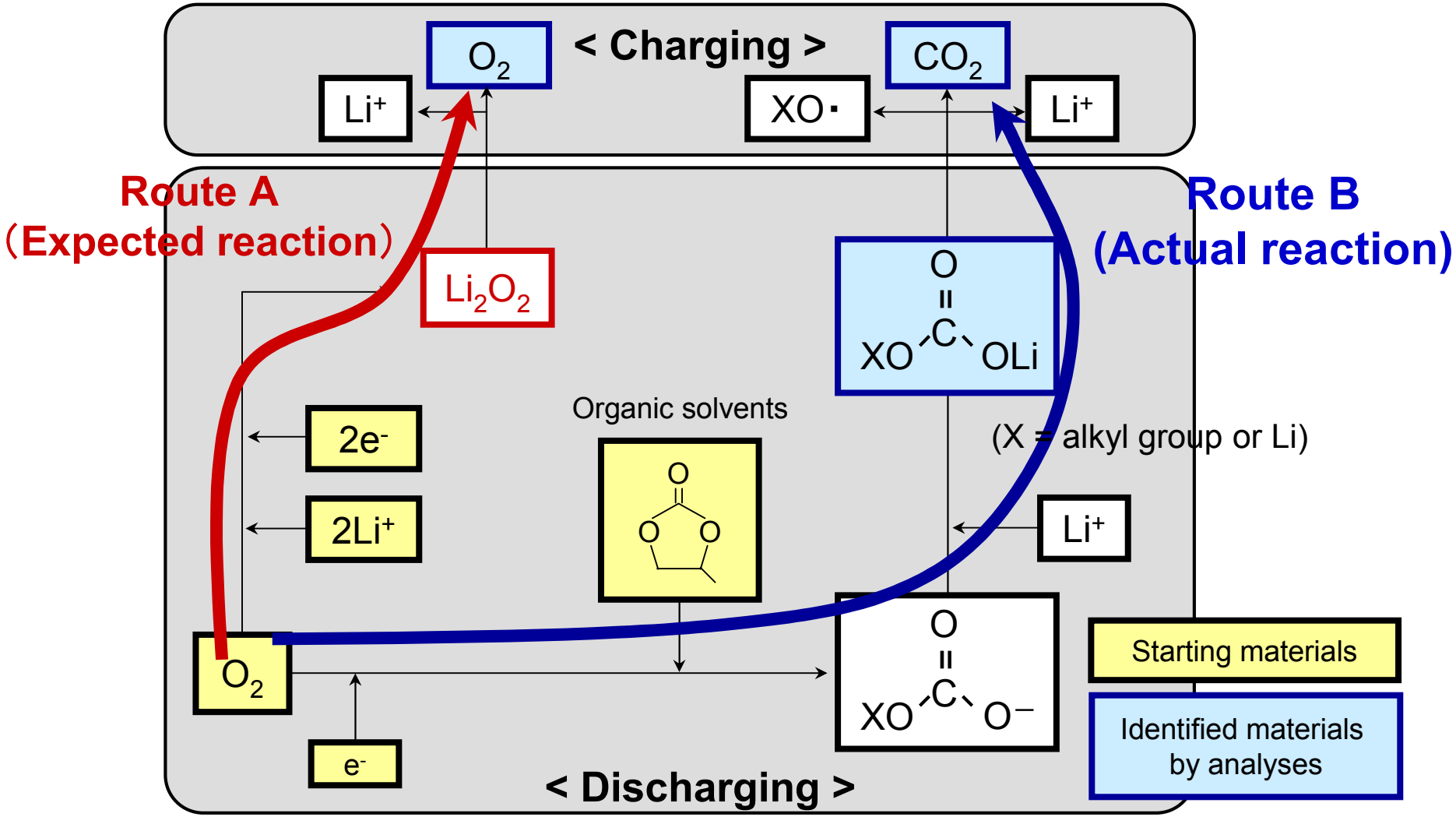
CO_2 gas also evolved with O_2 gas after charging.

Expected reaction route



Li_2O_2 and O_2 are obtained after discharging and charging.

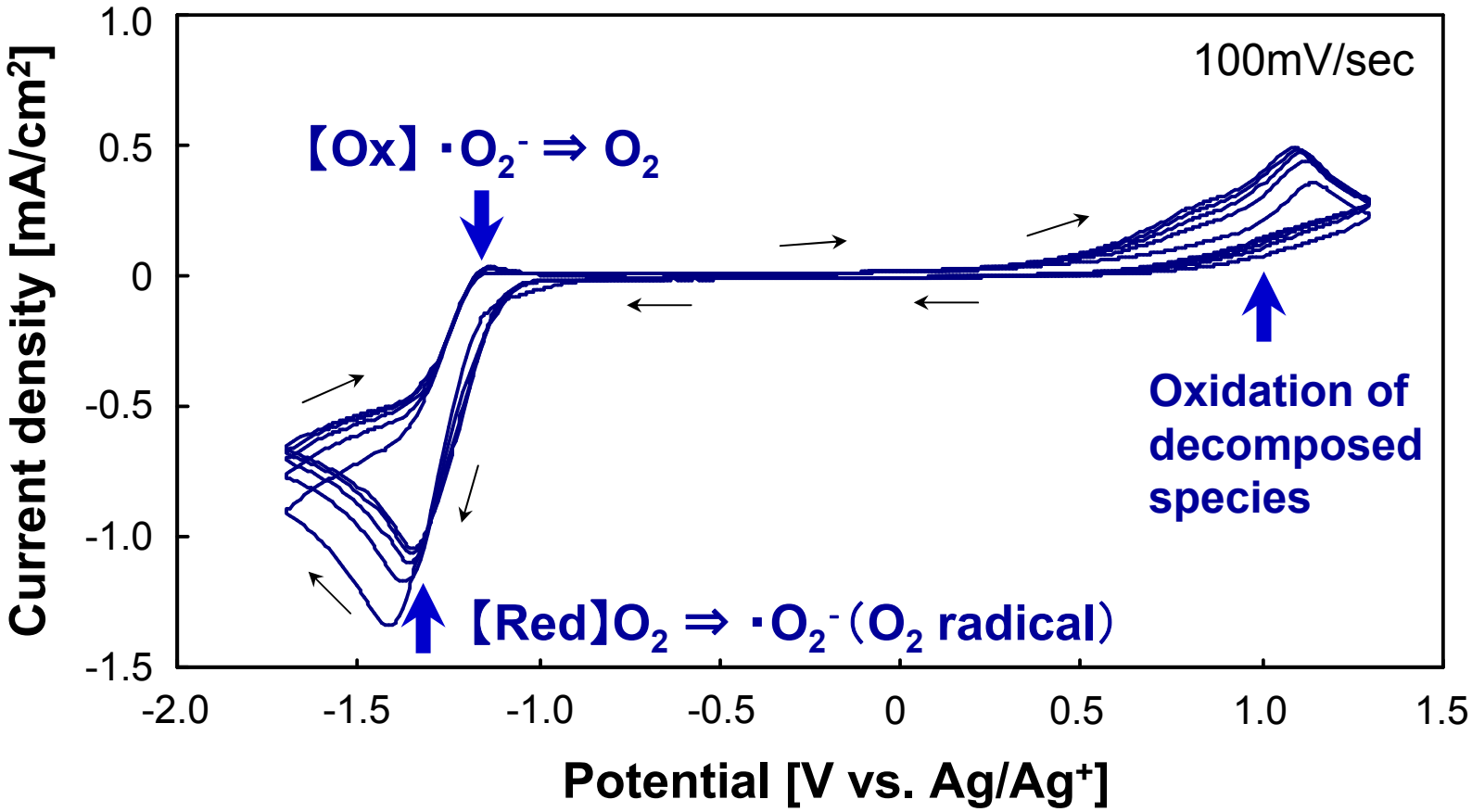
Actual reaction route



Carbonate solvents would strongly influence on actual reaction.

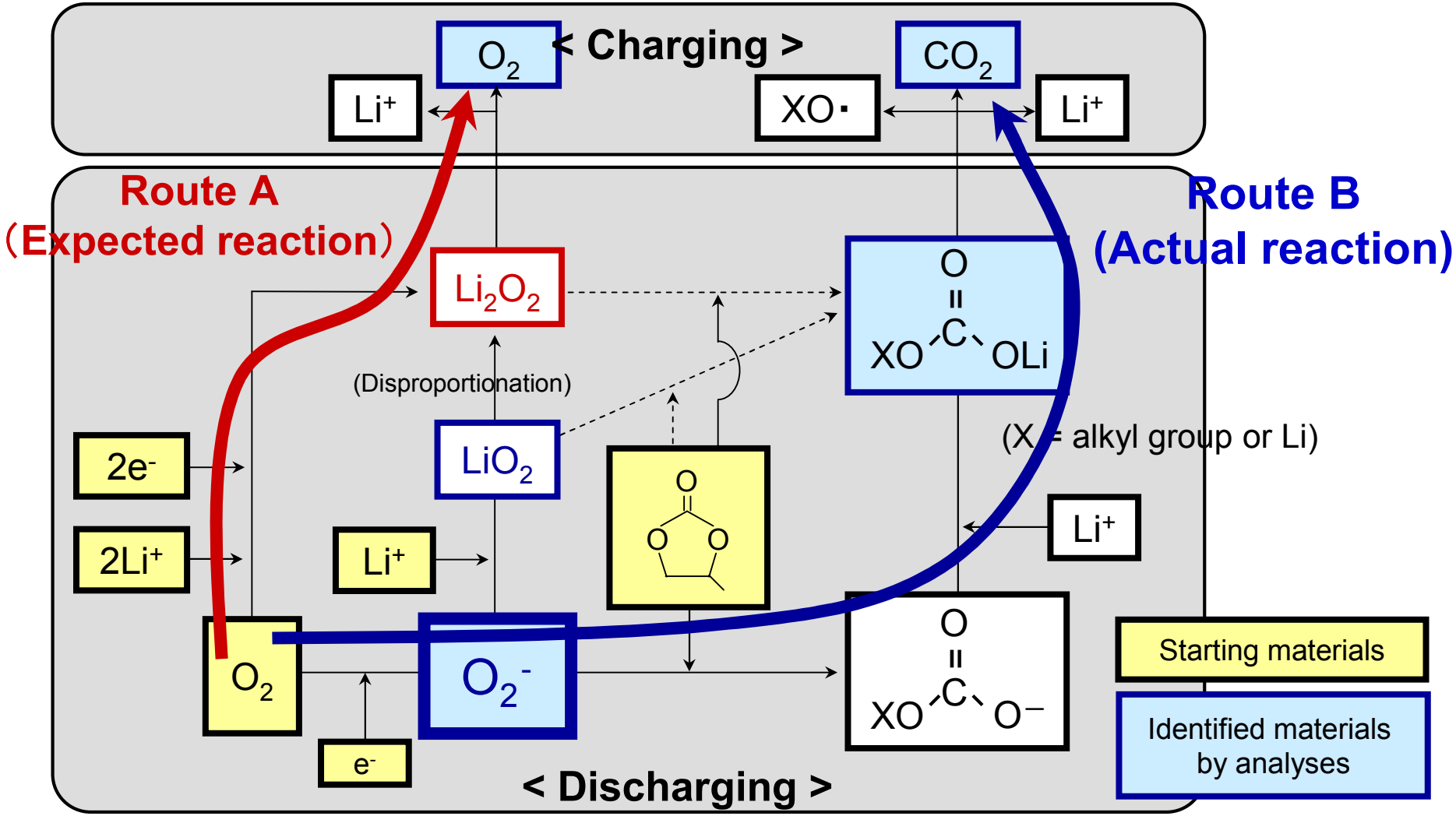
Electrochemical stability

Ni / PC, TEATFSA(0.1M) / GC / O_2



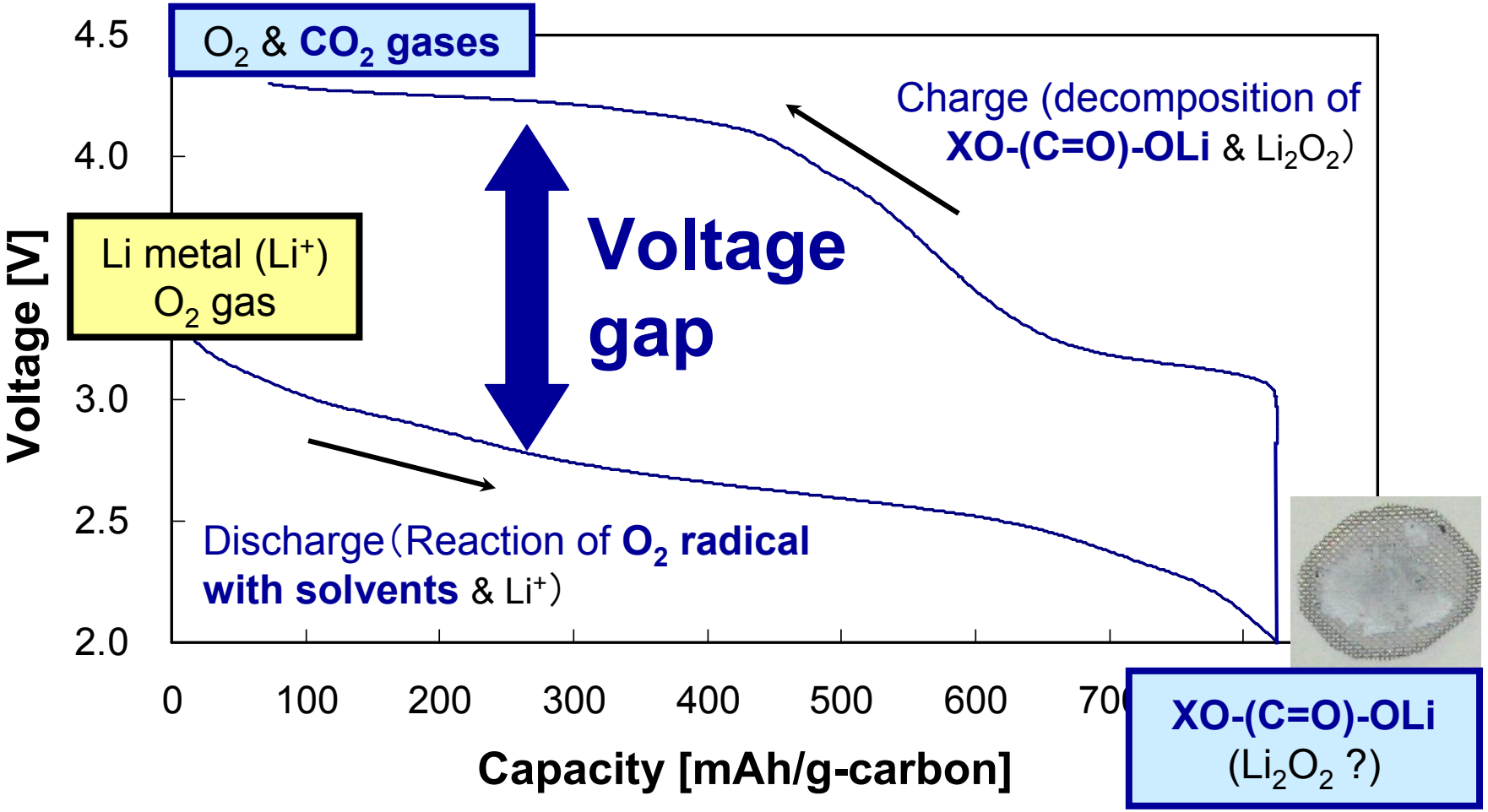
Oxidation peak for O_2 radical was not observed. Electrochemical stability of O_2 radical was very low in the PC media.

Actual reaction route



Complicated cathode reactions related with O_2 radical occurred.

Reason for large voltage gap



Large voltage gap was caused by the formation of XO-(C=O)-OLi due to a side reaction of O_2 radical with solvents.

Outline

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Problems to be solved

Large voltage gap of 1.4V

⇒ Reaction of electrolyte solvents with O_2 radical and formation of XO-(C=O)-OLi

Our research items

1) Catalyst for direct 2-electron reduction of O_2 gas via no formation of 1-electron reductant, O_2 radical

2) Li salt with high reactivity against O_2 radical

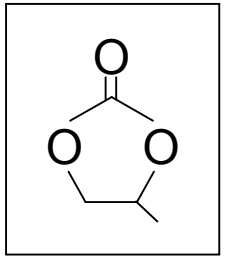
3) Electrochemically stable electrolyte solvent against O_2 radical

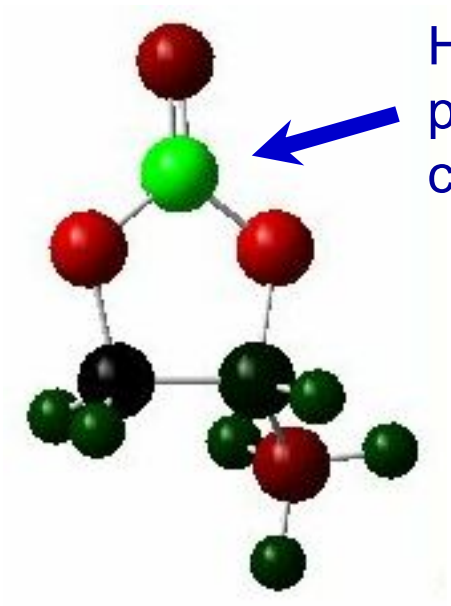
Electronic distribution

Prof. Katayama et al., *J. Electrochemical Soc.*, 141 (2004) A59.

Relationship between Mulliken charge of cations of ILs and reversibility of O_2/O_2^- redox couple

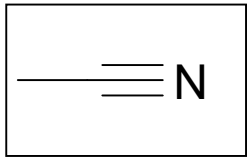
(a) Propylene carbonate (PC)

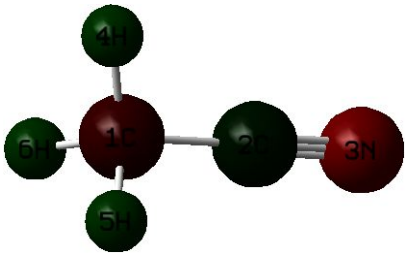




Highly positive charge

(b) Acetonitrile (AcN)



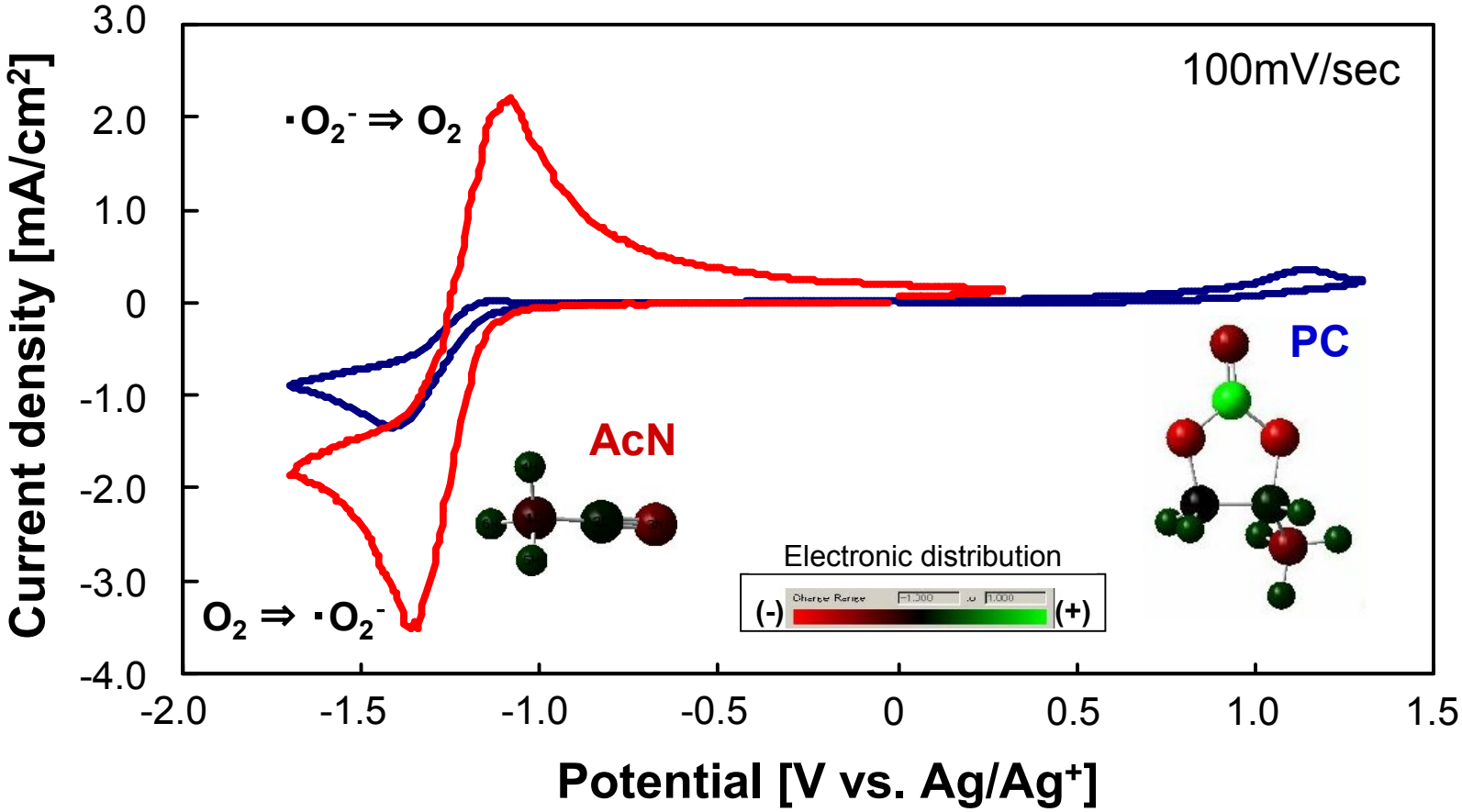


Electronic distribution

PC molecule had a highly positive charge at C atom ,while AcN molecule had negative charges at all atoms.

Electrochemical stability

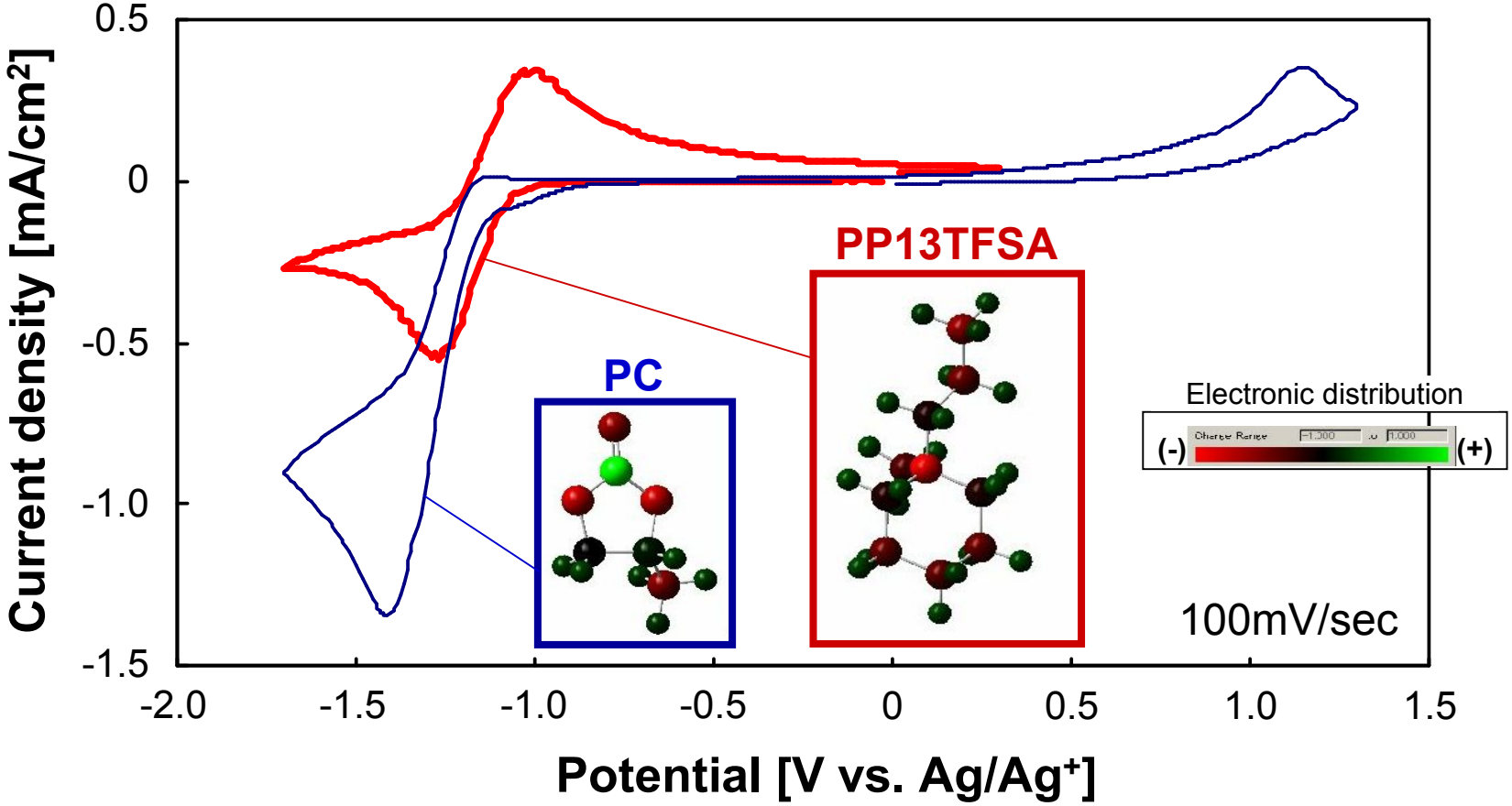
Ni / organic solvent, TEATFSA(0.1M) / GC / O_2



Bad reversibility of O_2/O_2^- redox couple was obtained in the PC solvent with highly positive atomic charge.

Electrochemical stability

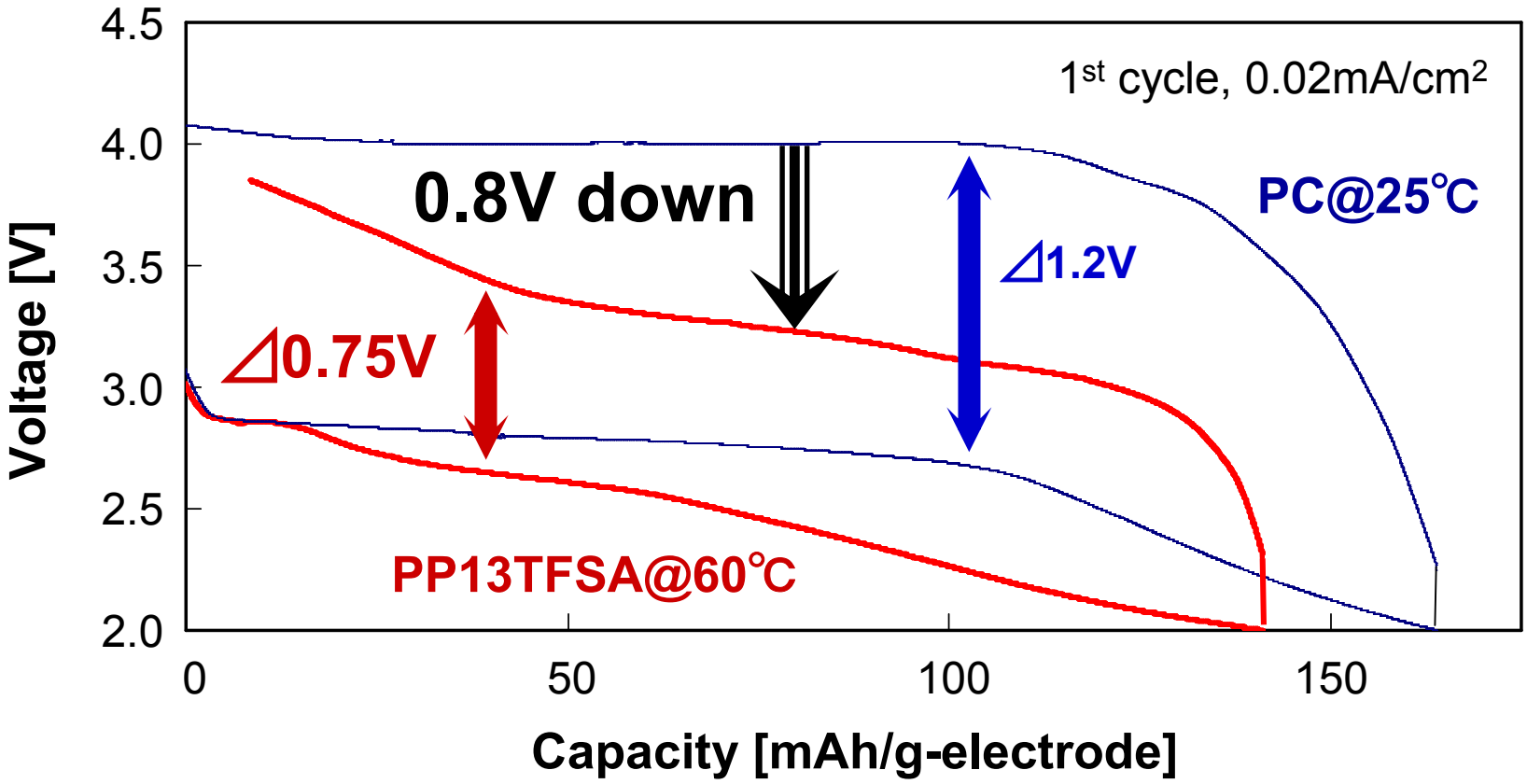
Ni / PP13TFSA or PC-TEATFSA(0.1M) / GC / O_2



PP13TFSA ionic liquid was highly stable against O_2 radical and Li metal, which is a promising electrolyte solvent for Li-air batteries.

Discharge-charge curves

Li / PP13TFSA, LiTFSA(0.32mol/kg) / MnO_2-loaded cathode / O_2



Using electrochemically stable electrolyte solvents against O_2 radical, both charging voltage and voltage gap were lowered.

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Summary

- In the Li-air cells with carbonate-based liquid electrolytes, the rechargeability of over 100 cycles was confirmed. However, a large voltage gap of 1.4 V during discharging and charging was observed.

- From analytical results, Li_2O_2 was not detected as a discharged product. XO-(C=O)-OLi such as lithium alkylcarbonate and lithium carbonate was mainly formed, and then CO_2 gas evolved after recharging.

- From electrochemical stability of organic solvents, O_2 radical formed in a PC media was not stable by itself and attacked the PC solvent to decompose.

- In conclusion, the large voltage gap was caused by the side reaction due to O_2 radical and formation of XO-(C=O)-OLi.

- Electrolyte solvents with high electrochemical stability against O_2 radical were found by cyclic voltammetry and molecular orbital calculation.

- The Li-O_2 cells with PP13TFSA ionic liquid exhibited lower charging voltage of 3.2 V and lower voltage gap of 0.75 V than the cells with carbonate-based electrolytes.

- The direction to decrease the large voltage gap was obtained.

TODAY for TOMORROW

Thank you for your kind attention.