The 2nd TIA Accelerate Symposium

AsahiKASEI

# Lithium Ion Battery (LIB)
# - Current, Past and Future -


**Dr. Akira Yoshino**

**Advisor, ASAHI KASEI Corp.**
**President of the Consortium for LIBTEC**
**Visiting Professor Kyusyu University**


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# Outline

1. **Course of development of the LIB**
   **"From initial research to commercialization"**
2. **Current situation of LIBs market for EV and four key words.**
3. **Innovations in LIBs technologies based on a new concept**
   3.1 Abnormally high concentration electrolyte
   3.2 Solid electrolyte technology

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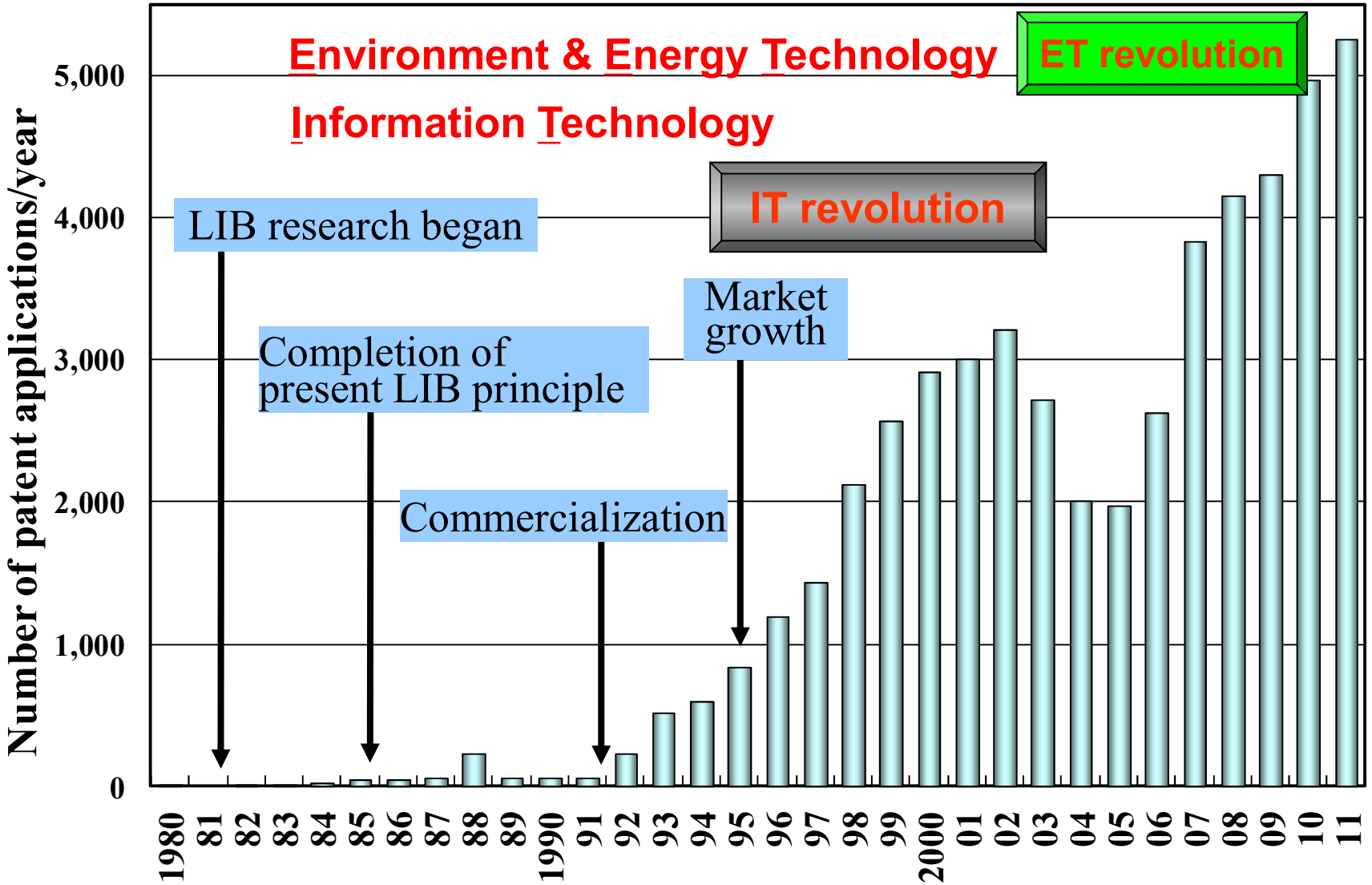
# LIB patent applications in Japan and the technology revolutions



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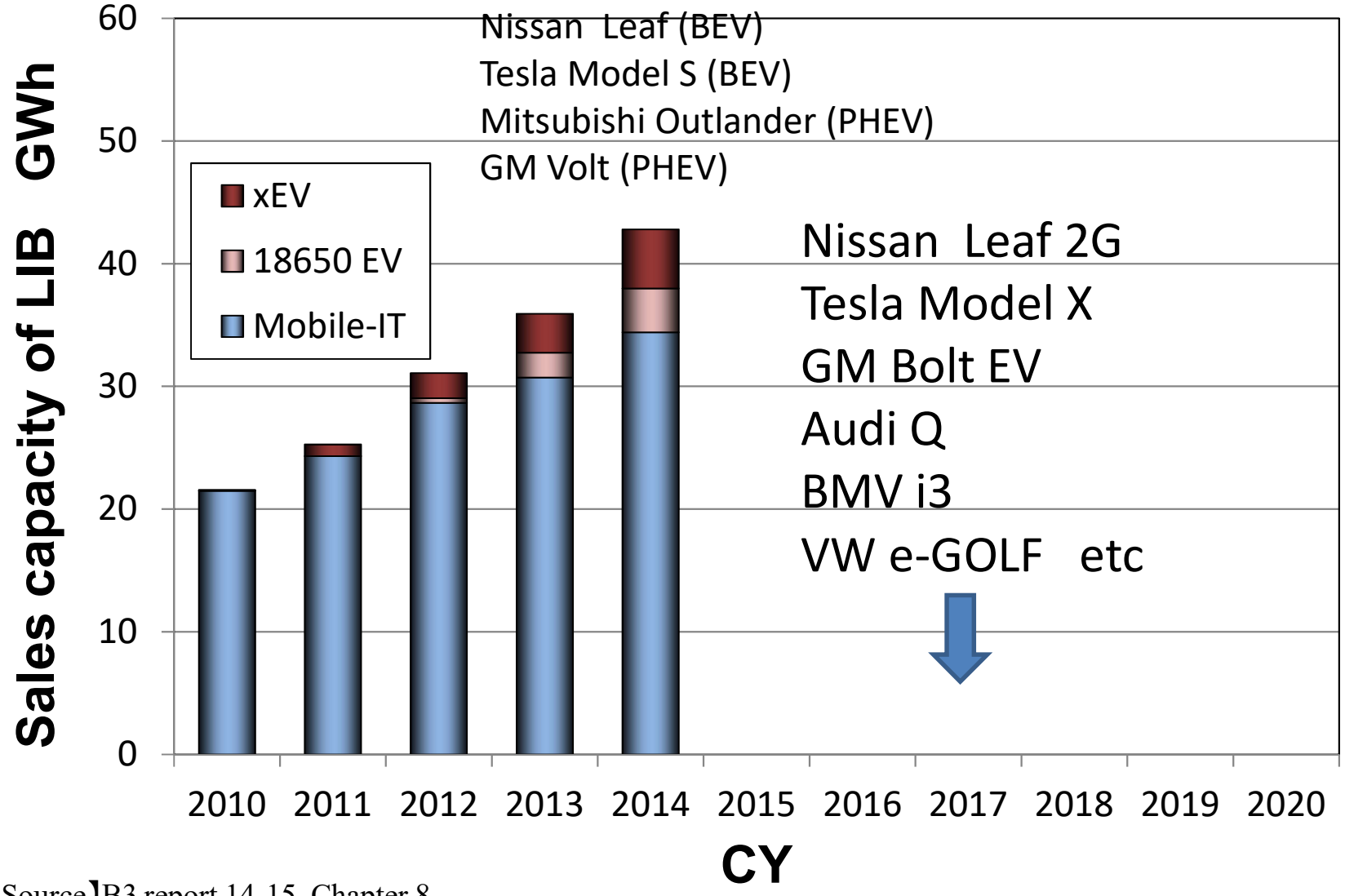
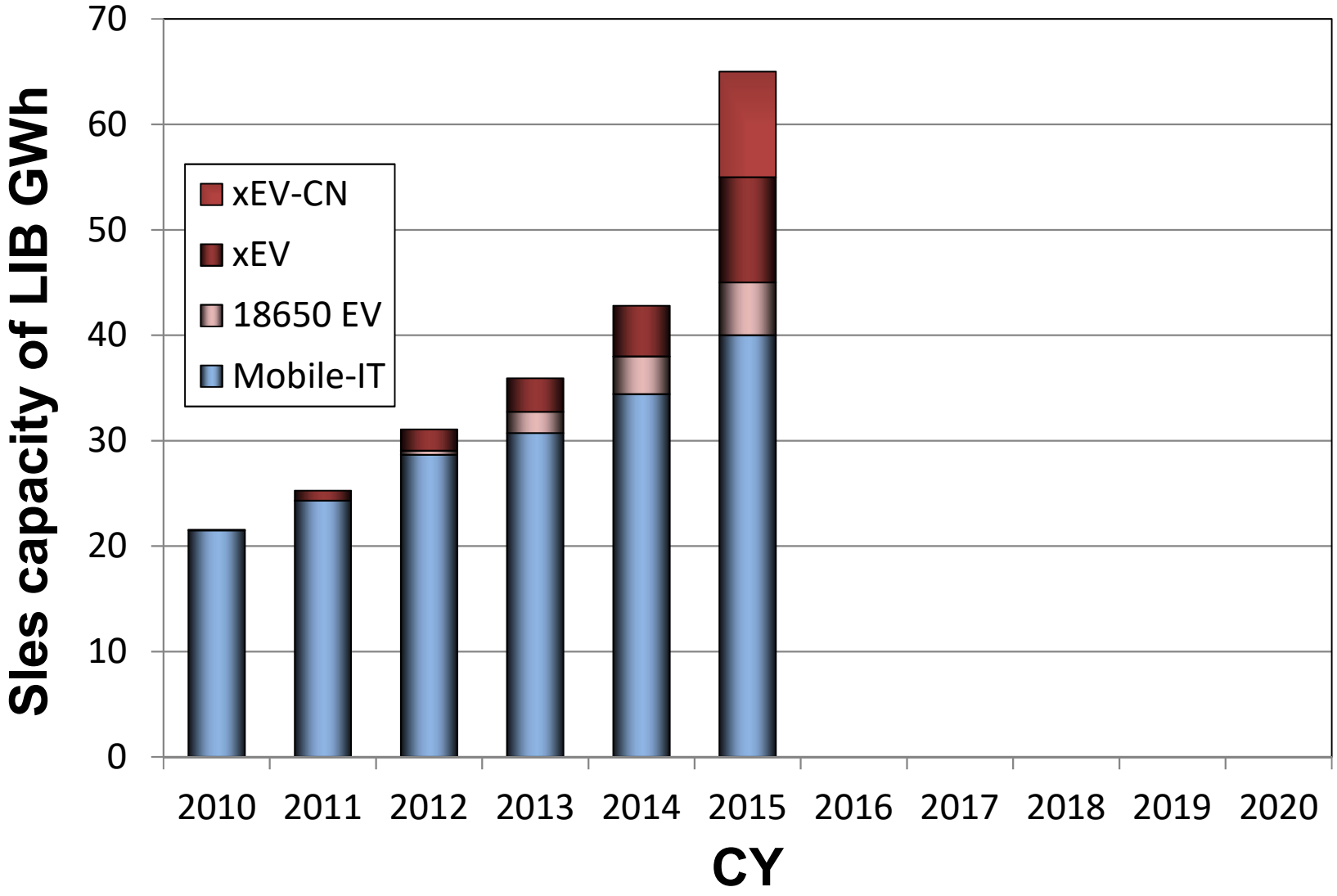
# Capacity-based Market Scale in Each LIB Market Category (CY2010-2014)

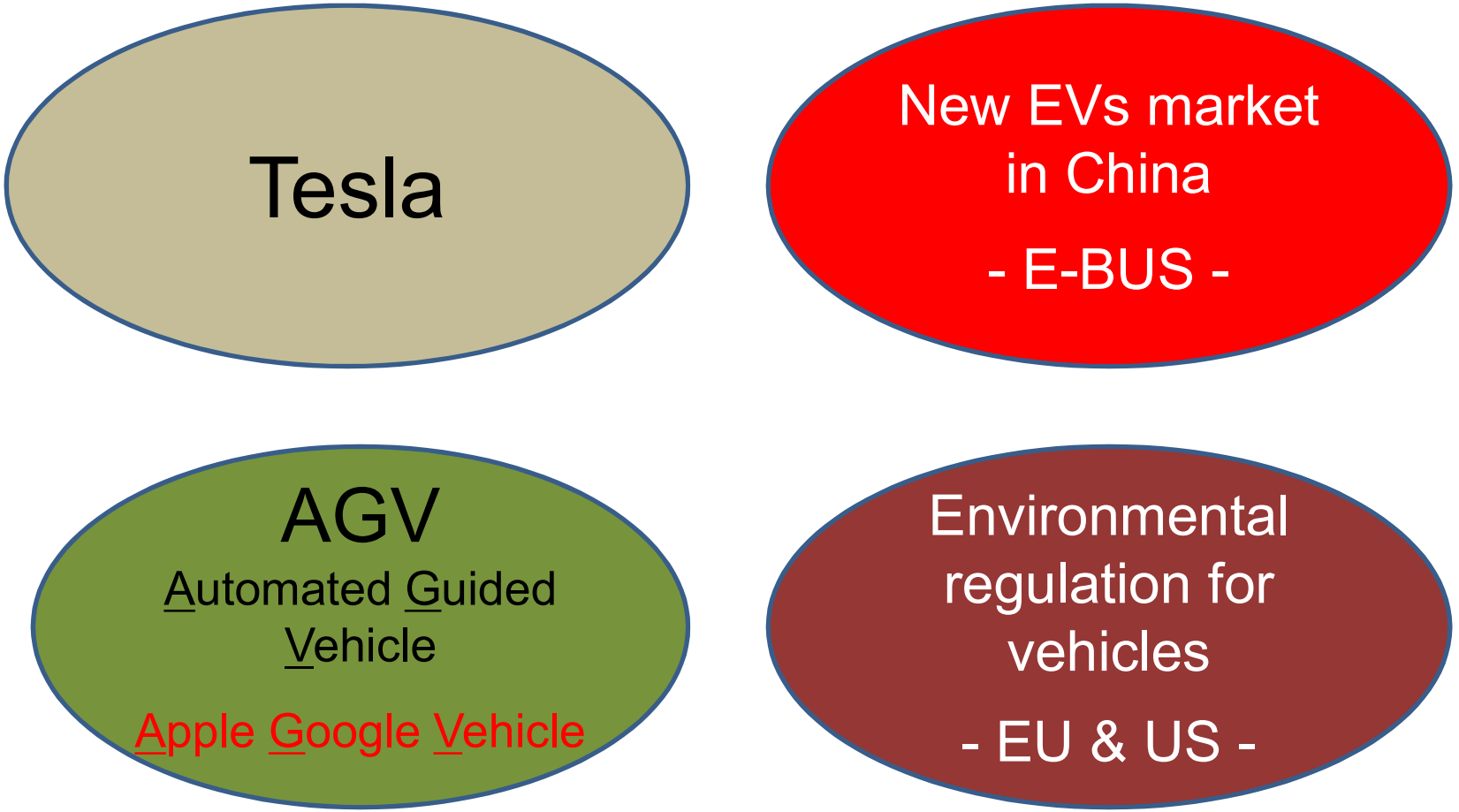



【Source】B3 report 14-15, Chapter 8,

# Capacity-based Market Scale in Each LIB Market Category (CY2015)

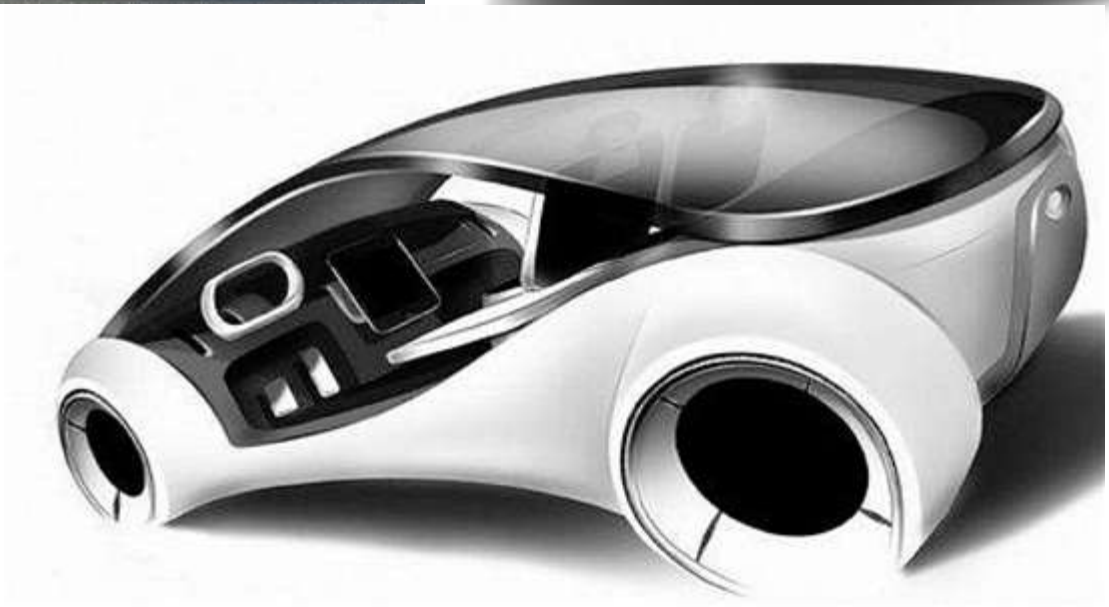


# Four keywords in current EVs market



# AGV=Automatic Guided Vehicle

## =Apple Google Vehicle



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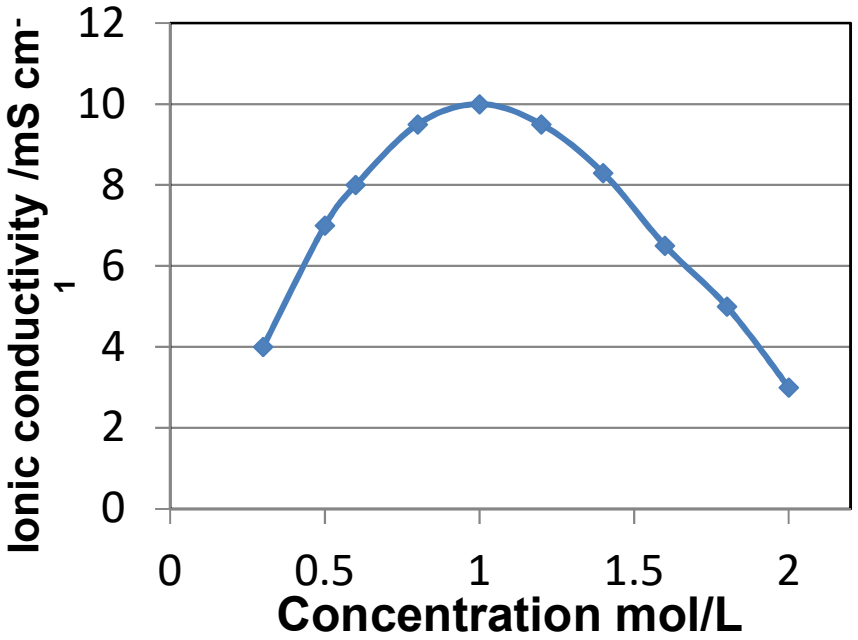
# Conventional concept of Liq-electrolyte

$Li^+$ dissociates by solvation and ionic conductivity is created.

Increasing of concentration reduces ionic conductivity by ion association and by increasing of viscosity.

Optimal concentration is around 1mol/L. (Fig. below)



# Simple question for the classic common sense of the electrolytic solution

- What would be the characteristics of LIBs using electrolyte solution without solvation of Li cation?
- What would be the characteristics of LIBs using electrolyte solution having a transport number of 1?
- What would be the characteristics of LIBs using electrolyte solution having no counter anion?

# Research trend of abnormally high concentration electrolyte

## Advent of Ionic liquid (IL)

There is no concept of ion solvation in the IL.
Because of cations and anions aggregate in the IL, there is no concept of ion dissociation and association.

## Advent of Pseudo-IL

M. Watanabe et. al., J. Am. Chem. Soc. 133 (2011) 13121

Equimolar mixture of $Li^+$ and Triglyme shows similar behavior to the IL.
Oxidative resistance of Triglyme increases above 4V.

## Advent of abnormally high concentration electrolyte

A. Yamada et. al., The 79th Annual meeting of electrochemical society of Japan (2012) 13121

High concentration electrolyte shows specific electrochemical behavior.

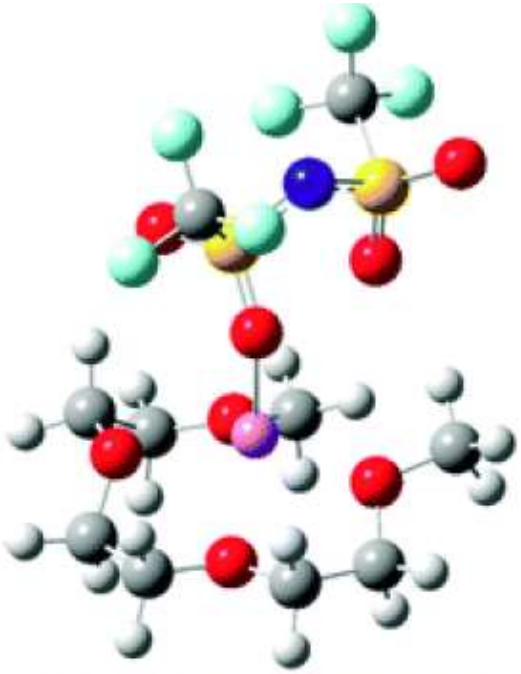
## Advent of LiFSA

S. Ishikawa et. al., The 54th Battery Symposium of Japan (2013)

New electrolyte salt LiFSA dissociates ions without solvation and shows specific electrochemical behavior at anode.

# Pseudo-Ionic liquid of Triglyme/TFSA


Triglyme

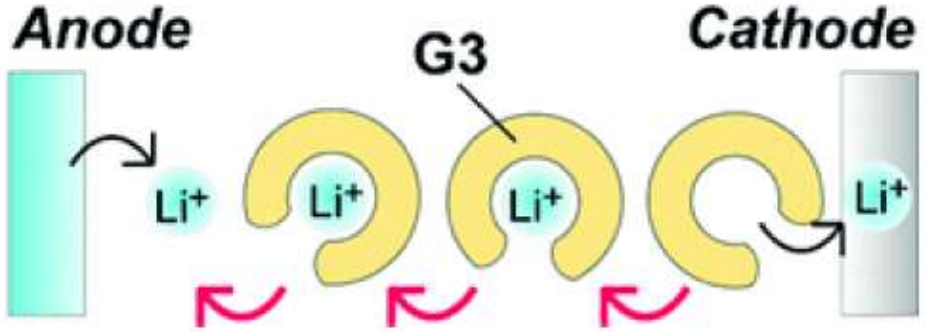


[Li(G3)1][TFSA]

G3 = triglyme HOMO Level

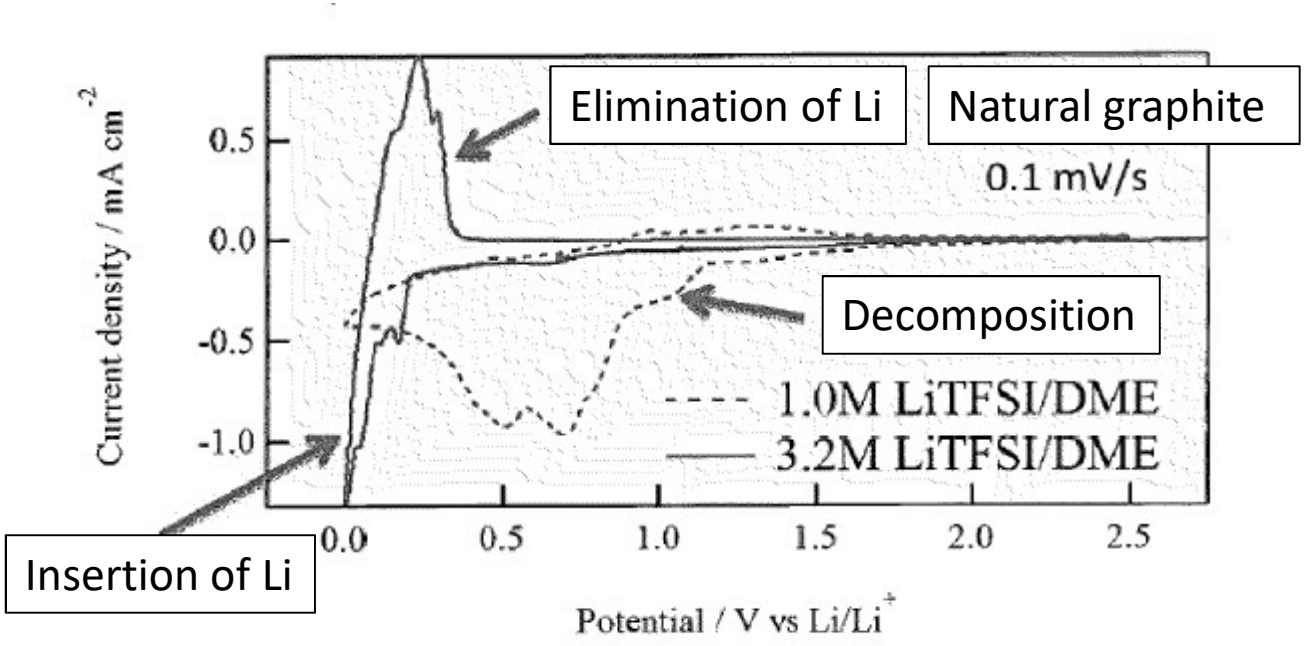
G3 -11.45 eV

[Li(G3)1][TFSA] -12.10 eV




M. Watanabe et. al. *J. Am. Chem. Soc.* 133 (2011) 13121

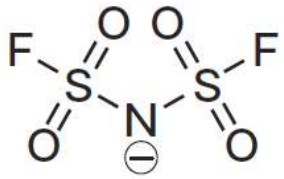
# 3.2M LiTFSA/DME shows specific behavior

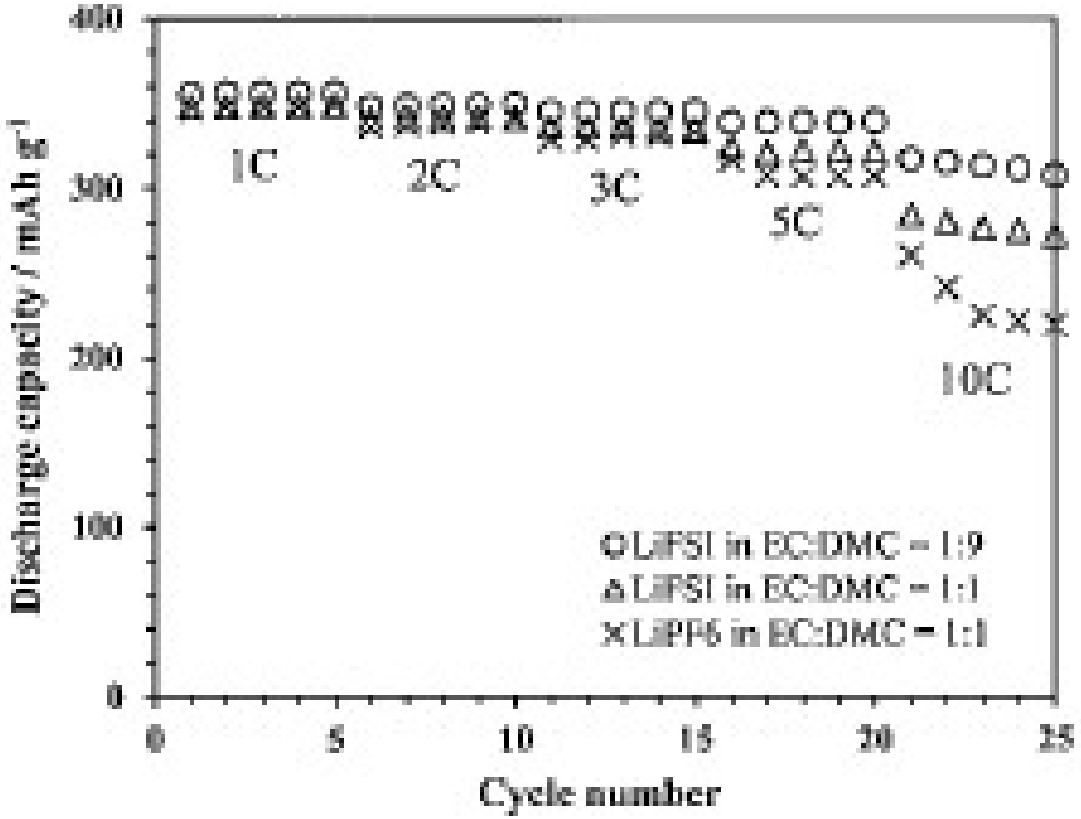



A. Yamada et. al., The 79th Annual meeting of electrochemical society of Japan (2012) 13121

# Specific electrochemical behavior of LiFSA

LiFSA




S. Ishikawa et. al., The 54th Battery Symposium of Japan (2013)

# Significant advance in solid electrolyte technology

## New Solid Electrolyte $Li_{10}GeP_2S_{12}$

Liquid electrolyte

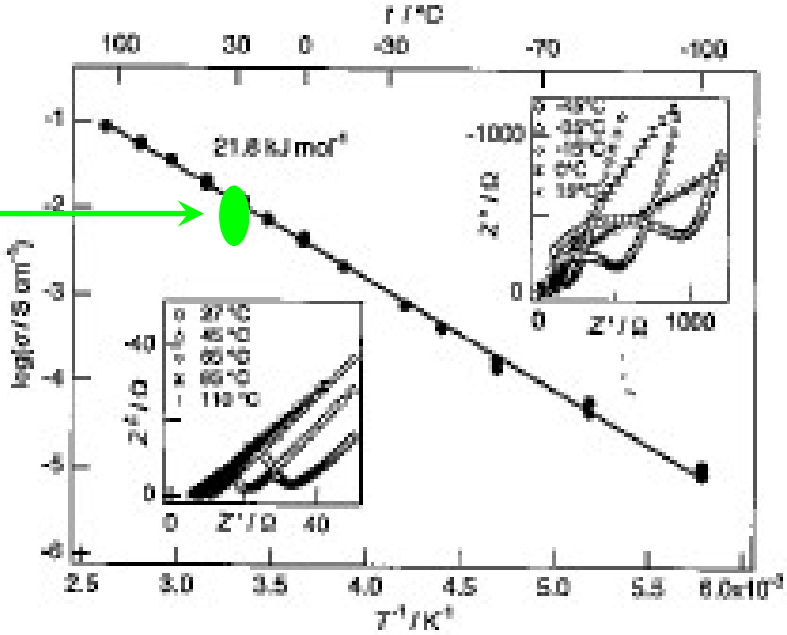



Fig. 1 Impedance plots and Arrhenius plots of ionic conductivity for $Li_{10}GeP_2S_{12}$

Source: R. Kanno et. al., Extended Abstract, The 52th Battery Symposium in Japan (2011) Nov.17-20, Tokyo, Japan p255

# Number of $Li^+$ and Mobility in Solid Electrolyte

Ionic conductivity = Number of $Li^+$ X Mobility X α

α = Dissociation constant, Transport No.

| | Number of $Li^+$ | Mobility | Ionic conductivity |
|---|---|---|---|
| **Liquid electrolyte** | 1 | 1 | 1 |
| **LGPS $Li_{10}GeP_2S_{12}$** | **(30)** | **1/30** | **1** |
| **$Li_{9.54}Si_{1.74}P_{1.44}S_{11.7}Cl_{0.3}$ *** | (30) | (2.5/30) | 2.5 |
| **Oxide-based solid electrolyte** | **?** | **?** | **0.1** |

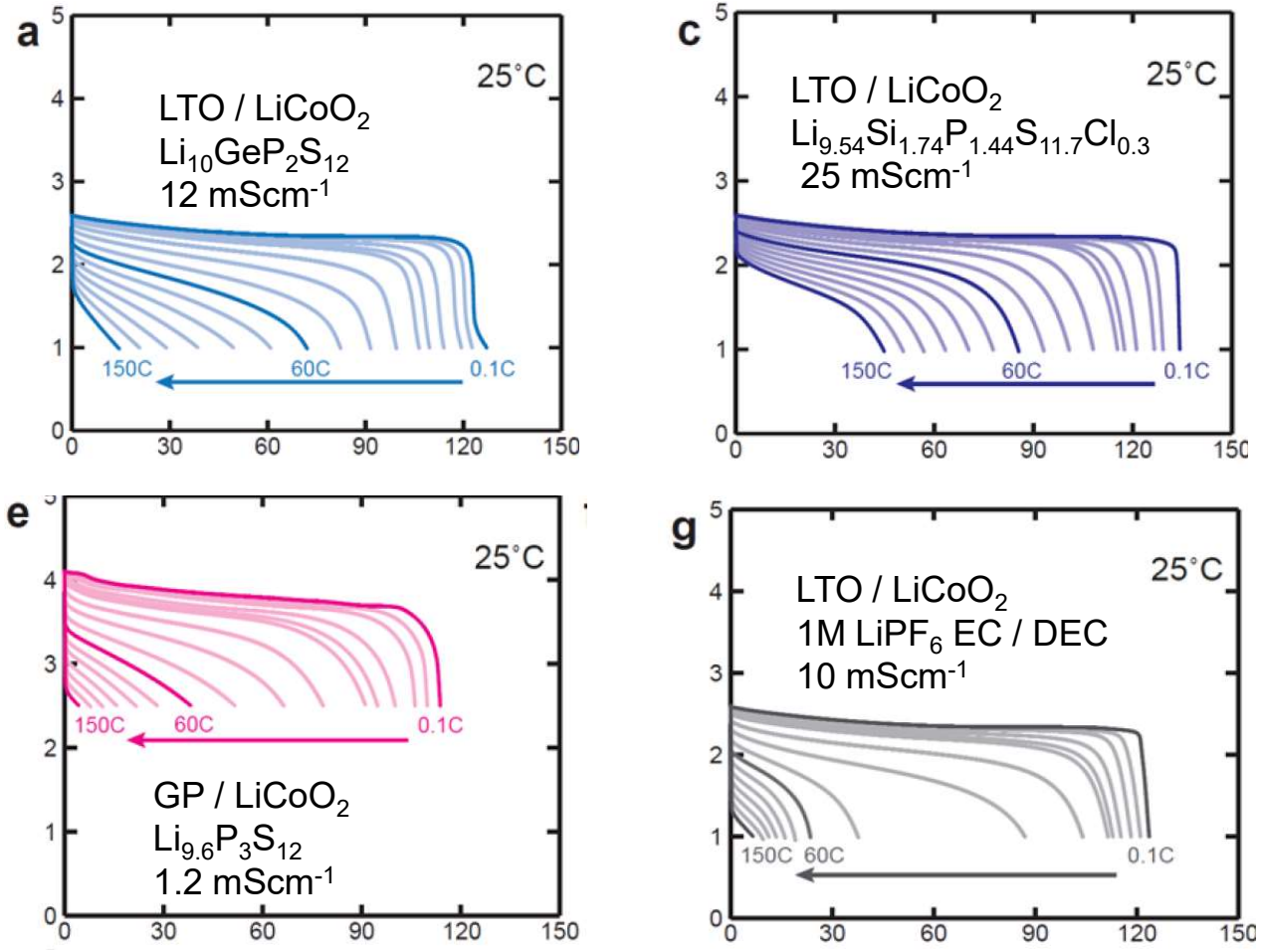
* R. Kanno et. al., http://www.titech.ac.jp/english/news/2016/033769.html

Reconsideration of number of $Li^+$ is the entrance of new concept

# (Dis-)Advantages of all solid state LIBs that has been said up to now

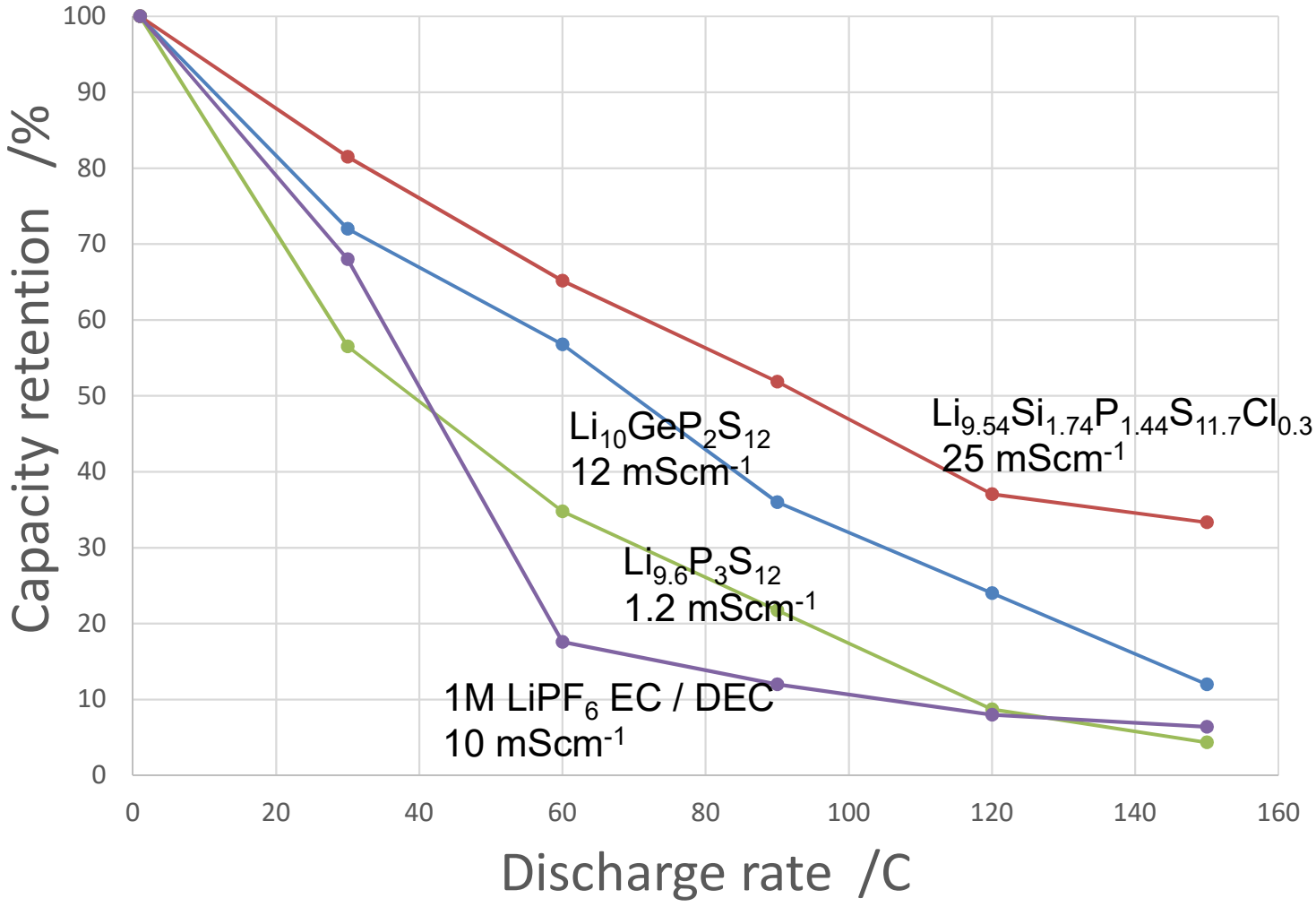
| Advantage | Disadvantage |
|---|---|
| Non inflammability | Rate capability |
| Suppressing dendrite of metallic Li | Low temp. characteristic |
| Metallic Li can be used | Mass production of solid electrolyte |
| Bipolar technology | Mass production of electrode |
| High temp. stability | Mass production of cell assembly |
| No leakage | |

# Unexpectedly high rate capability of all solid state LIBs




Source: R. Kanno et. al., http://www.titech.ac.jp/english/news/2016/033769.html

# Comparison of rate capability of all solid state LIBs and liq-electrolyte LIBs



# (Dis-)Advantages of all solid state LIBs that has been proven by experiments

| Advantage | | Disadvantage |
|---|---|---|
| ***Rate capability*** | Non inflammability | Mass production of solid electrolyte |
| ***Low temp. characteristic*** | Suppressing dendrite of metallic Li | Mass production of electrode |
| Bipolar technology | Metallic Li can be used | Mass production of cell assembly |
| High temp. stability | | |
| No leakage | | |

# The reason why all solid state LIBs have unexpectedly high rate capability

- What would be the characteristics of LIBs using electrolyte solution without solvation of Li cation?
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