evs 27
The 27th INTERNATIONAL ELECTRIC VEHICLE SYMPOSIUM & EXHIBITION.
Barcelona, Spain
17th-20th November 2013

Analysis of Degradation Mechanism of Lithium Iron Phosphate Battery

[1]**Genki Kaneko**, [1]Soichiro Inoue, [1]Koichiro Taniguchi
[1]Toshio Hirota, [1]Yushi Kamiya, [1]Yasuhiro Daisho, [2]Shoichi Inami

[1]Faculty of Science and Engineering
Graduate School of Environment and Energy Engineering, Waseda University
[2]Mitsui Engineering & Shipbuilding Co.,Ltd

Contents

1. **Introduction**
2. **Evaluation tests**
   - Calendar capacity loss tests (150 days)
   - Cycle capacity loss tests (3000 cycles)
   - AC impedance tests
3. **Discussions**
   - Calendar capacity loss
   - Cycle capacity loss
   - Optimization of the BEV's operation method
4. **Conclusions**

evs 27

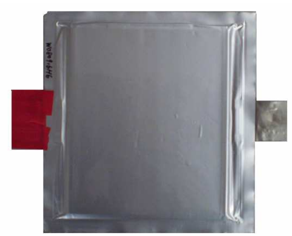
Introduction

Concept : Short range driving and very frequent charging

▸*Reduced costs and weight* ▸*Wireless / Rapid charging*

Fig. Developed “short-range, frequent-charging” electric vehicles

Developed $LiFePO_4$ battery



- Micronizing $LiFePO_4$
- Carbon film coating

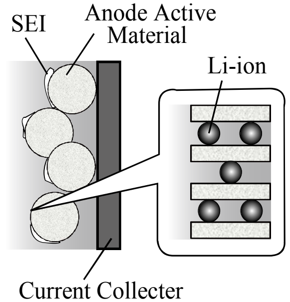
→ *Superior rapid charging and cycle performance.*

Unknown degradation characteristics have to made clear to use our battery wisely.

Introduction

Reported degradation factors

Formation of SEI



$$Li^+ + \text{electrolyte} \rightarrow \underline{SEI}$$

- $ROCO_2R + Li^+ + e^- \rightarrow \underline{ROCO_2Li} + R^+$
- $ROCO_2Li + Li^+ + e^- \rightarrow \underline{Li_2CO_3} + R^+$
- $LiPF_6 + 3ROCO_2Li + H_2O \rightarrow 2HF + R_3PO_4 + 3CO_2 + \underline{4LiF}$

Fig. SEI reaction model

Structural disorder

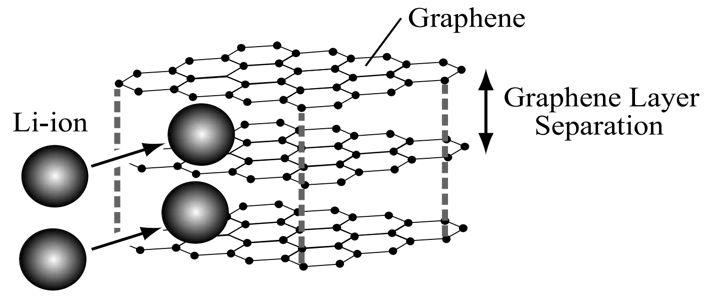


Fig. Structural disorder model

Aim of this research

- Analyzing the degradation characteristics
  Picking up the dominant factors
- Quantifying the degradation
  Modeling of calendar/cycle capacity loss

Realizing the long life of battery.

EVS 27

Calendar capacity loss progressed under high temperature, SOC conditions.

Fig. Test Cell

Tab. Test Cell Specification

Cathode Material	$LiFePO_4$
Anode Material	C_6 (Graphite)
Rated Voltage	3.25 V
Rated Capacity	6.2 Ah
Dimensions (mm)	L120 × W3 × H140

Tab. Test Conditions

Temperature	5°C, 25°C, 45°C
SOC	90%, 50%, 10%

9 conditions, 150 days *of calendar tests have carried out.*

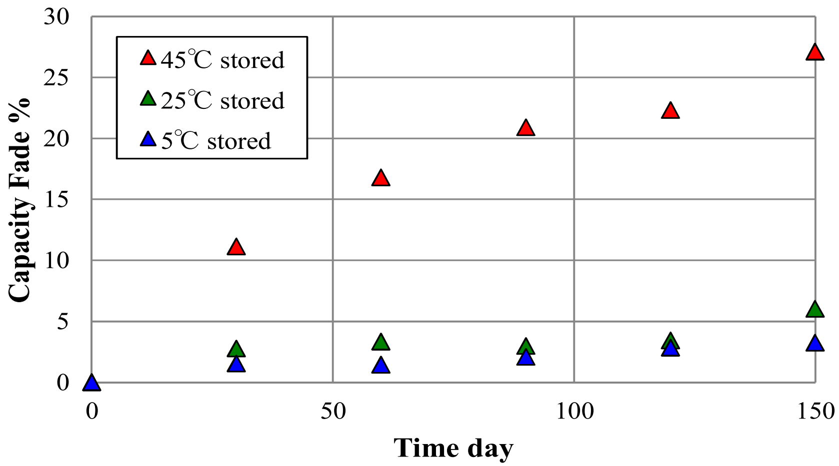


Fig. Temperature Dependency(90%SOC)

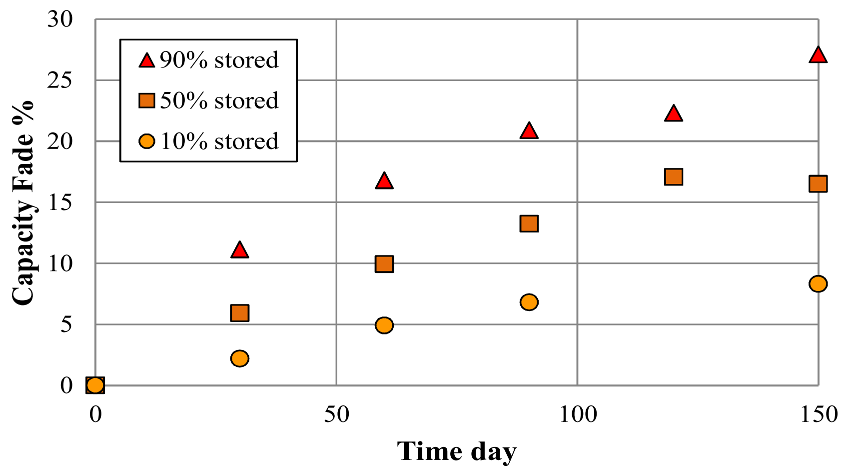


Fig. SOC Dependency(45℃)

Cycle capacity loss progressed under high temperature, SOC conditions.

Fig. Test Cell
(Same spec.)

Tab. Test Conditions

Temperature	5℃, 25℃, 45℃
SOC Range (ΔSOC=20%)	90-70% 70-50% 40-20%
Charge/Discharge Rate	14.88A/7.44A
Charge/Discharge Amount	1.24Ah/1.24Ah

9 conditions*, *3000 cycles *of cycle tests have carried out.*

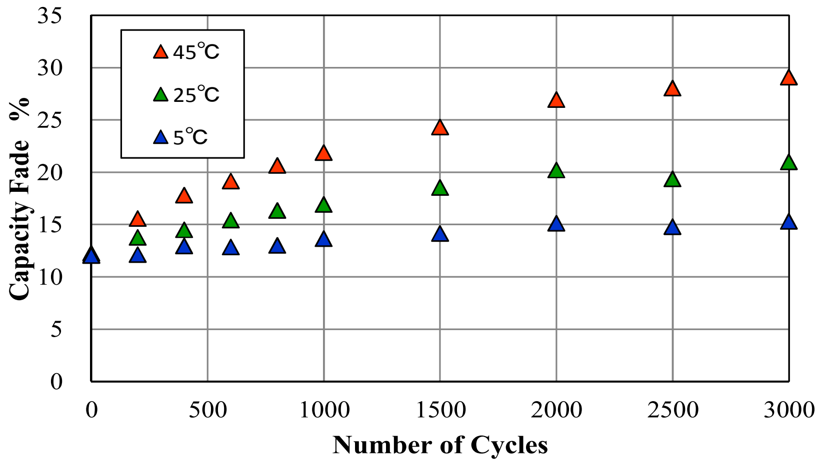


Fig. Temperature Dependency (90% SOC)

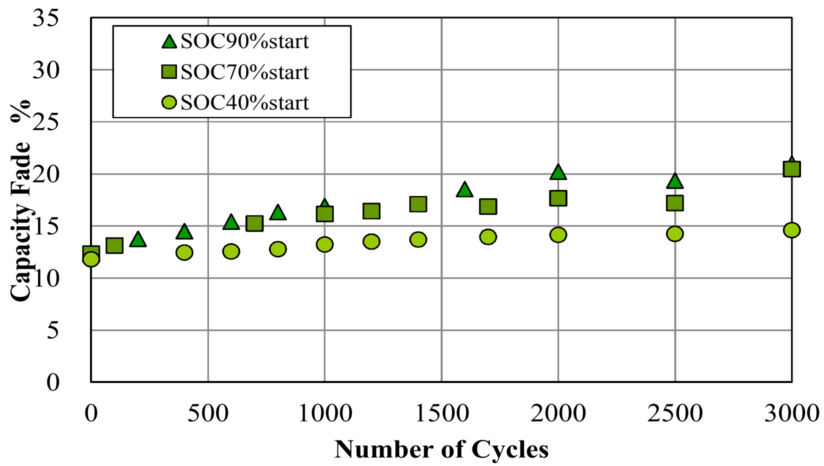
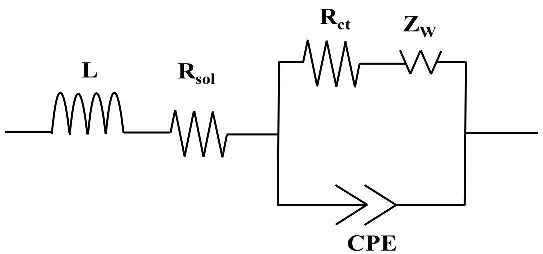


Fig. SOC Dependency (25℃)

Internal resistance increases under high temperature, high SOC conditions.

Tab. Test Conditions

SOC	50%
Temperature	25°C
Frequency Range	0.1-10k Hz
Applied Voltage	15mV



L : inductor factor of measurement systems
R_{sol} : resistance of electrolyte
R_{ct} : resistance of moving electric charge
Z_w : Warburg impedance of diffusion
CPE : Constant phase element

Fig. Equivalent Circuit

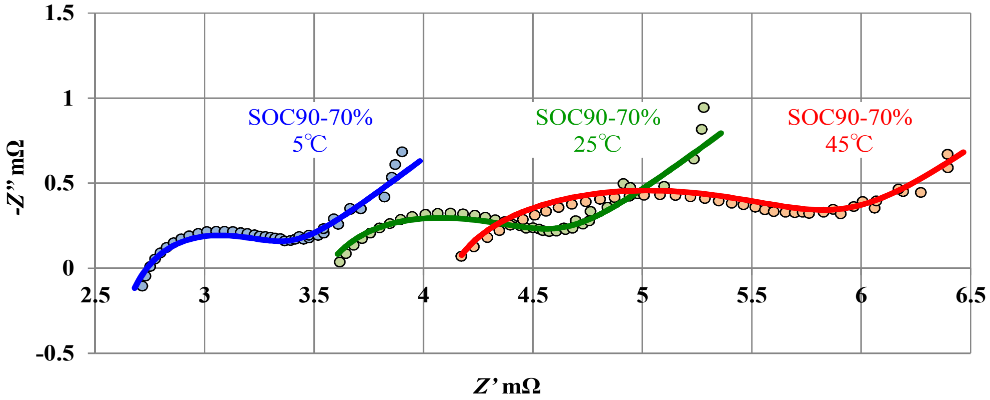


Fig. Temperature Dependency (@3000cycle)

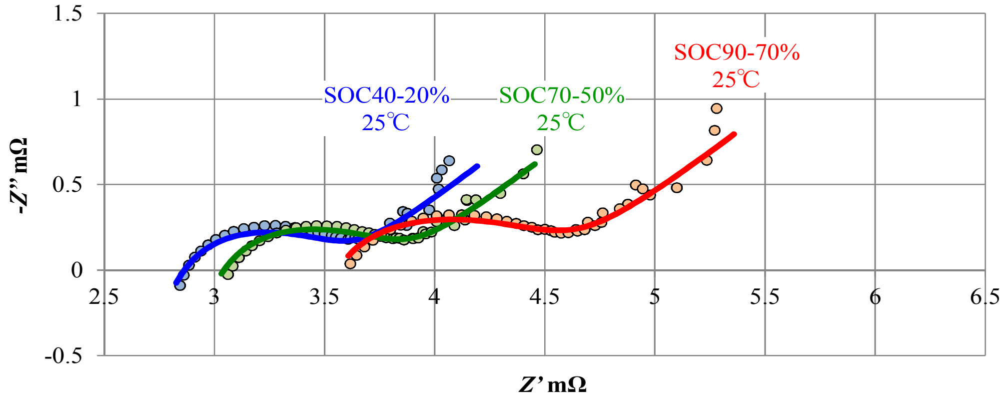


Fig. SOC Dependency(@3000cycle)

Degradation prediction of calendar capacity loss.

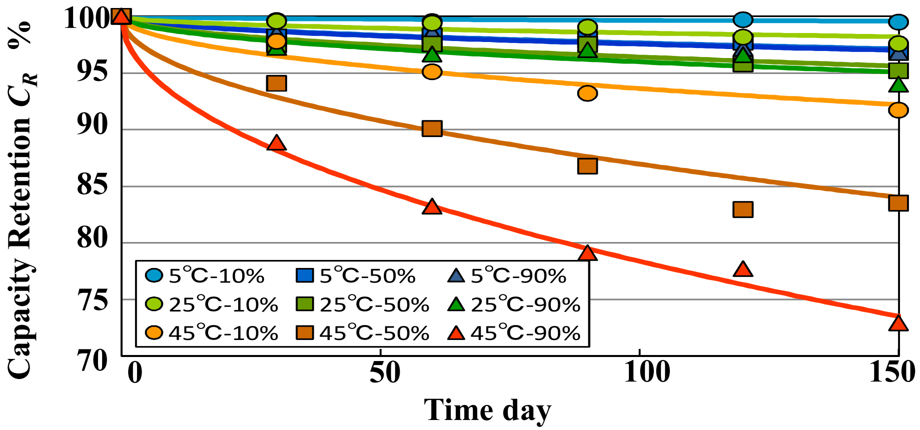


Fig. Results of Calendar Tests

Progressed linearly with the square root of time.

Caused by the chemical reactions.

A simple model for generation of SEI films

$$Li^{+}+Electrolyte+e^{-}\rightarrow SEI \quad ...(1)$$

The reaction rate are defined with
Concentration of Li^{+}, potential energy, temperature

$$v = A'\left[Li^{+}\right]\exp\left(-\frac{E_a-(1-\beta)F\Delta E}{RT}\right) \quad ...(2)$$

(***A'*** *:Frequency factor,* ***[Li+]*** *:Concentration of Li^{+}*
E_a *:Activation energy,* ***β*** *:Symmetry factor,* ***F*** *:Faraday constant*
ΔE *:Potential energy,* ***R*** *:Gas constant,* ***T*** *:Temperature*)

Calendar capacity loss = $K_S \times time^{0.5}$

$$k_s = 4475(SOC)\exp\left(-\frac{49767-811V}{RT}\right) \quad ...(3)$$

Organized by Fira Barcelona avele

Hosted by AVERE NEA Ajuntament de Barcelona

In collaboration with EVAAP EDTA

Supported by European Commission

Degradation prediction of "real" cycle capacity loss.

***Real cycle capacity loss* = (Cycle capacity loss) – (Calendar capacity loss)**

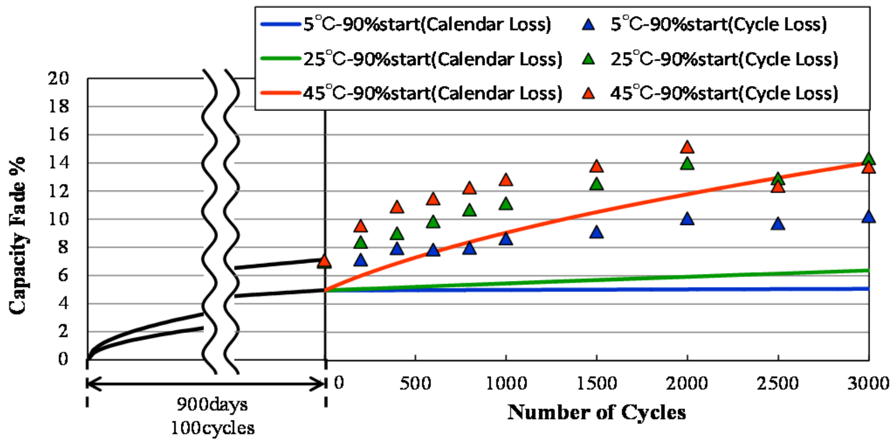


Fig. Real cycle loss and calendar loss

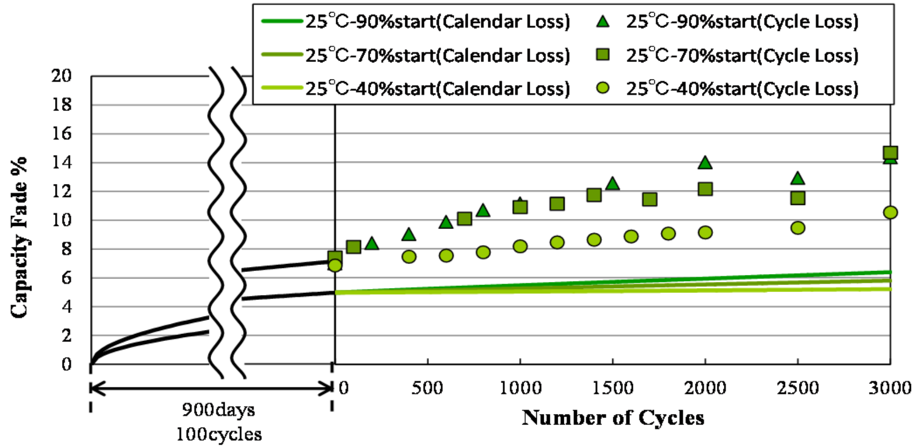


Fig. Real cycle loss and calendar loss

Real cycle capacity loss even contains chemical reactions.

Cycle capacity loss

$$= K_C \times cycle^{0.5} + K_{C,\ mechanical}$$

$$\begin{cases} k_c = 394.1 * (SOC) * \exp\left(-\dfrac{31013 - 0.01734 * V}{RT}\right) + k_{c,mechanical} \\ k_{c,mechanical} = \begin{cases} 1.540 * 10^{-1} (5°C) \\ 8.539 * 10^{-2} (25, 45°C) \end{cases} \end{cases} \quad \ldots(4)$$

Optimization of BEV's operation method.

Long life of battery

Minimizing the degradation

▸*Low SOC operation*
is required.

Battery degradation progresses rapidly in the warm seasons.

Safety driving

Ensuring the power, cruising range

▸*High SOC operation*
is required.

The risk of achieving the lower limit voltage increases in the cold seasons.

Honjo mode

・Round trip from CH-DY to IPS station on the campus.
・Rapid charge every trip in the CH-DY

Fig. WEV-1

Tab. Mode spec.

Cruising Distance	2095 m
Cruising Time	10 min.
Energy Consumption	160 Wh (20%SOC)
Max. Slope Degree	6.5 °

Fig. Honjo mode

Batteries can last 4 times longer under optimized conditions.

▸Minimum start SOC are calculated with a driving simulator.

Warm/Normal Seasons	24%	With a margin	30%
Cold Season	38%		45%

Fig. Calculated Minimum Start SOC

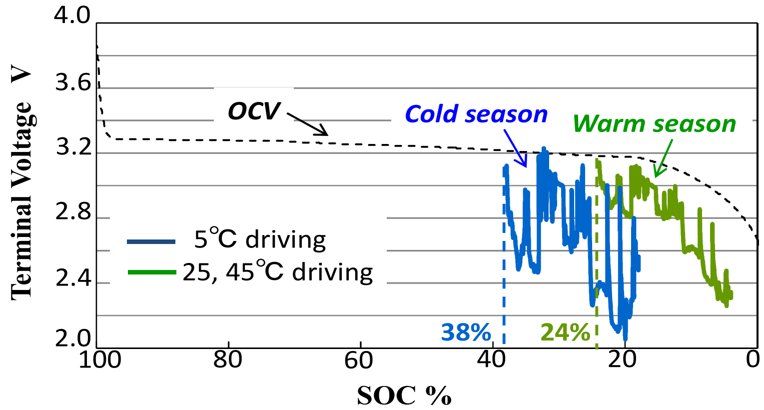


Fig. Cell Voltage Behavior while driving

Tab. Start SOC
(Present state and optimized state)

Normal season (25℃)	87%→30%
Warm season (45℃)	87%→30%
Cold season (5℃)	87%→45%

70% of initial capacity is defined as the end of life.

Can last about 4 times longer.

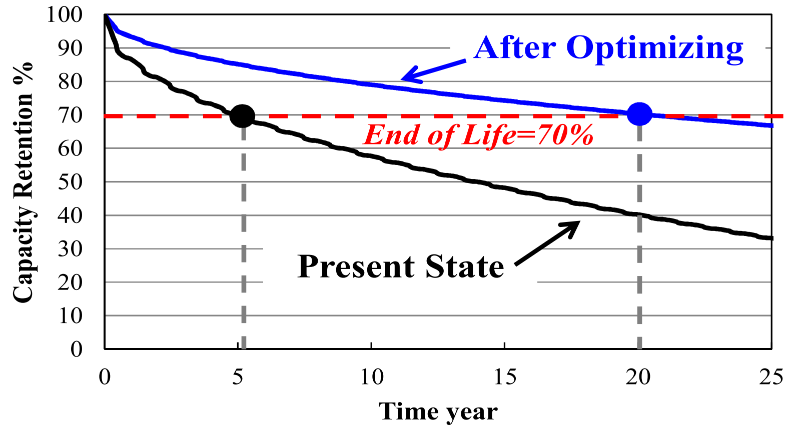


Fig. Life Time Prediction

Conclusions

●Calendar capacity loss

Calendar capacity loss increased under the higher temperature and SOC conditions, and progresses linearly with the square root of time. Capacity loss is caused by chemical reactions.

●Real cycle capacity loss

Real cycle capacity loss includes both degradation factors; chemical reactions and structural disorder.

●Optimization of BEV's operation

With extremely optimizing the SOC range used in the operation, there is a possibility that batteries can last about 4 times longer.

Acknowledgements

A part of this work was supported by
New Energy and Industrial Technology Development Organization (NEDO) of Japan.

The authors would like to express their gratitude to parties concerned.

New Energy and Industrial Technology Development Organization

Thank you for listening !

Contact me

Name : Genki Kaneko

E-mail : genkikaneko@suou.waseda.jp

Appendix.

Test data of calendar tests

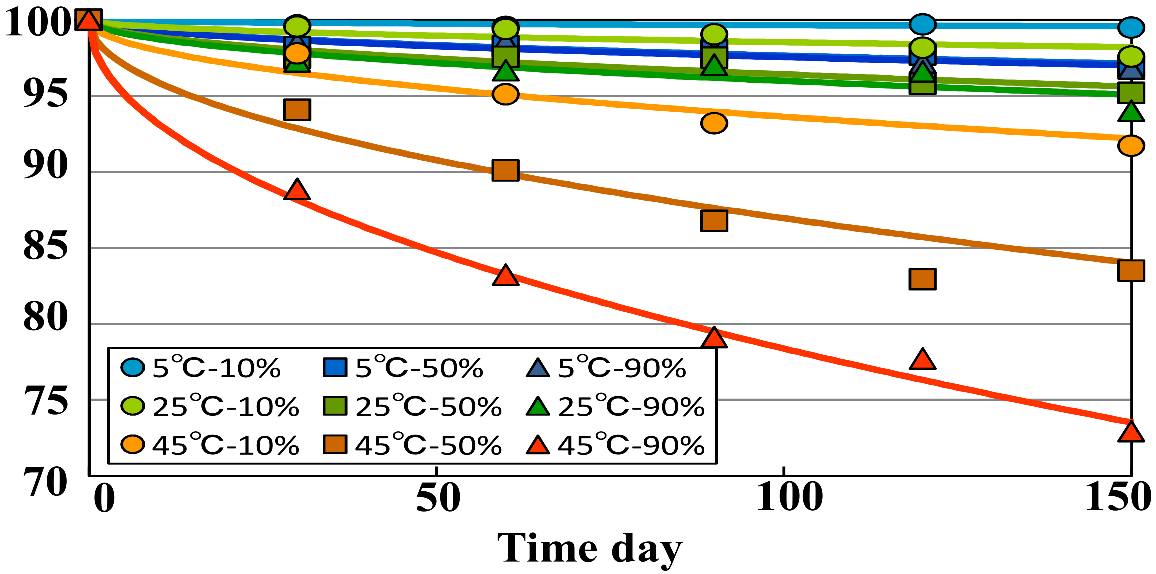
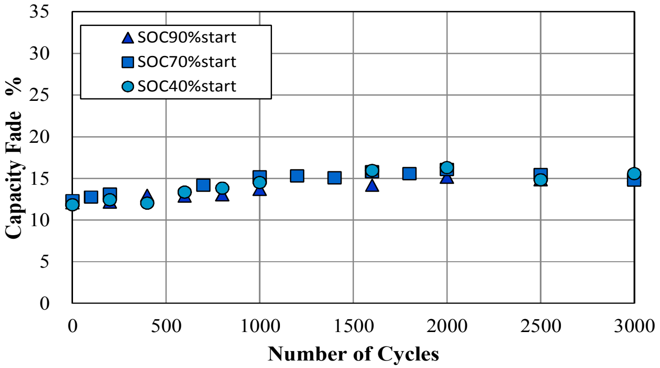


Fig. Results of Calendar Tests

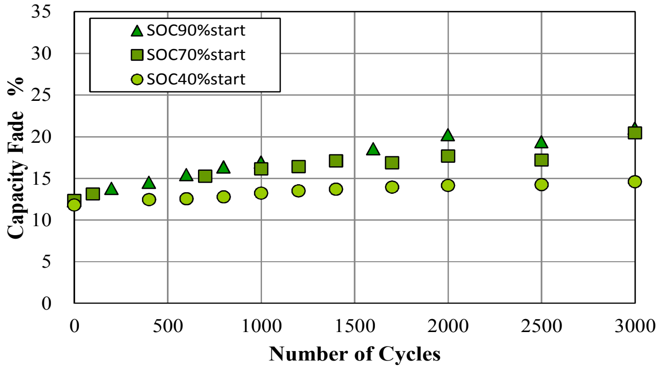
EVS 27

Test data of cycle capacity loss tests

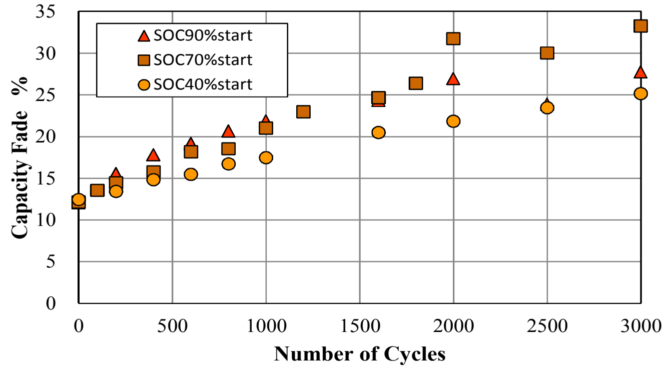
SOC dependency



(a) 5℃

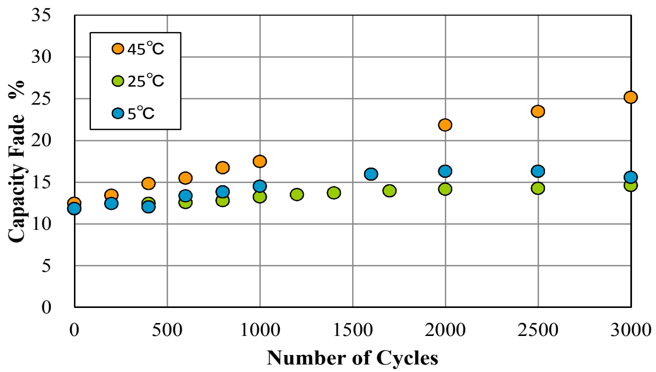


(b) 25℃

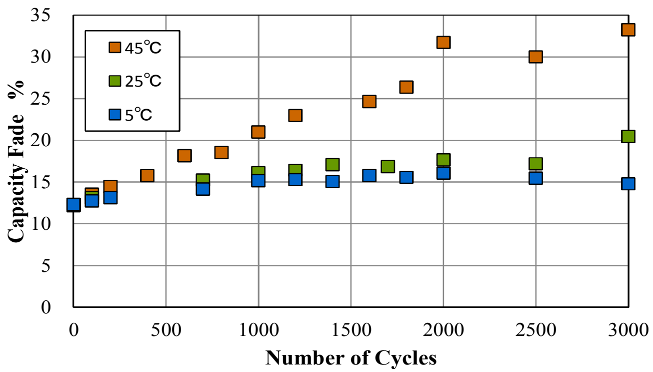


(c) 45℃

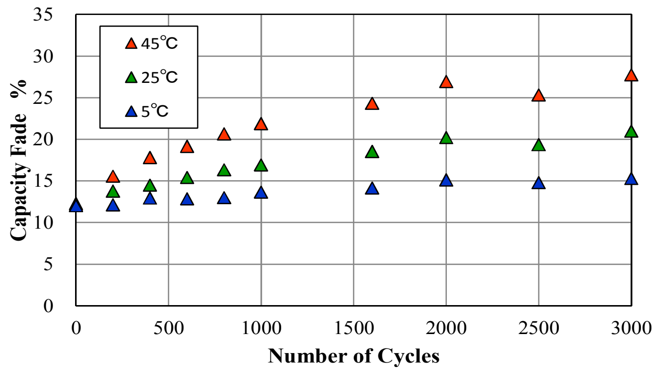
Temperature dependency



(a) SOC 40-20%

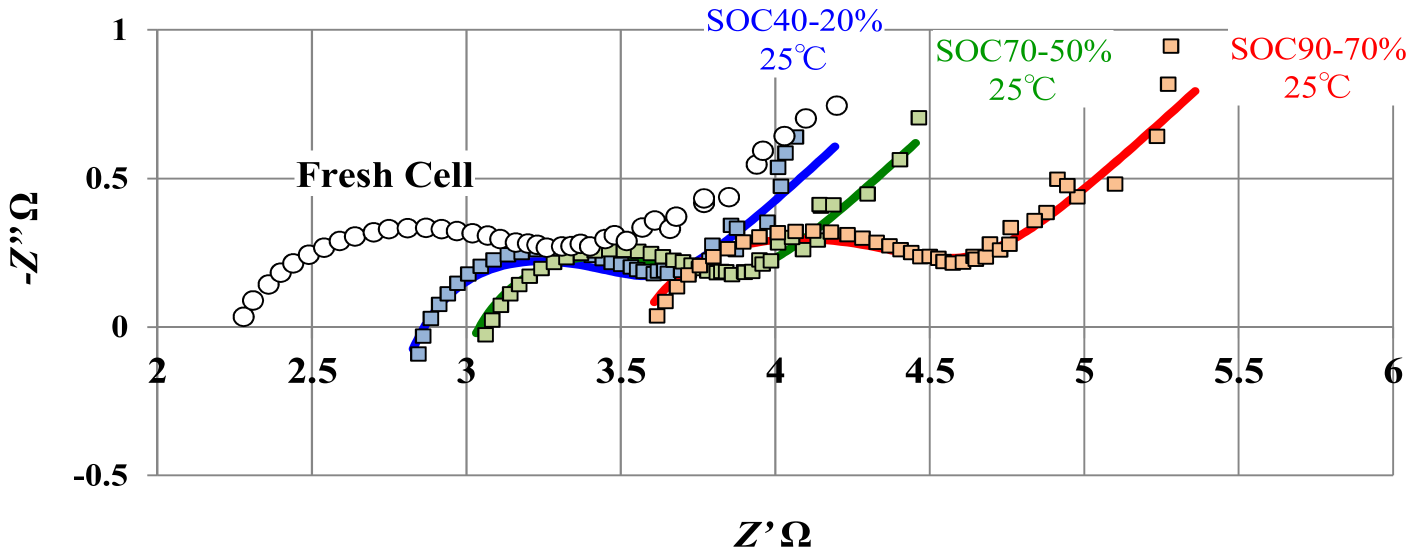


(b) SOC 70-50%



(c) SOC 90-70%

Impedance spectrum of cycled cells and fresh cell



- Large shifting along the axis Z' is observed.
- Length of radius is not increased.

evs 27

Capacity measurement

All capacity measurement tests are carried out on the condition of 25℃.

①CC charge (0.5C=3.1A) to higher limit (4.0V)

②CV charge with 4.0V for 5 min.

③Rest for 30min.

④CC discharge (1.0C=6.2A) to lower limit (2.0V).

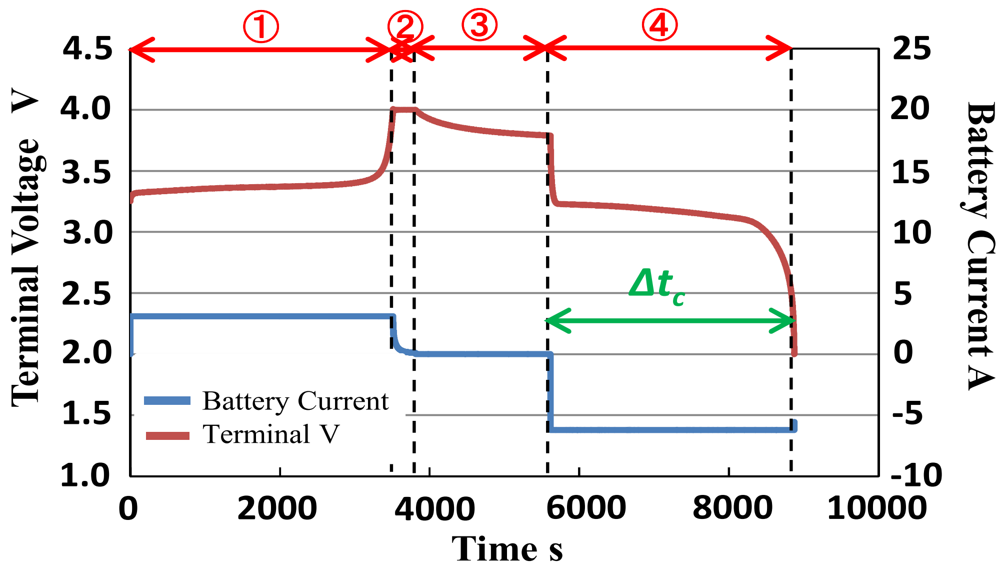


Fig. Capacity measurement

Capacity are calculated with the discharge time t_c

$$\text{Capacity} = 6.2 \times \frac{\Delta t_c}{3600} (Ah)$$

Organized by Fira Barcelona avele

Hosted by AVERE rreA Ajuntament de Barcelona

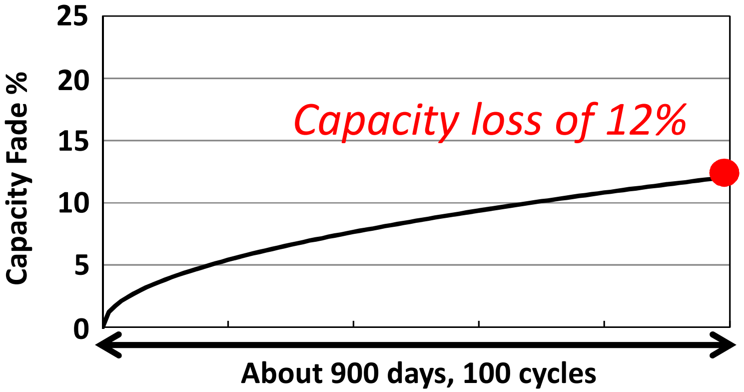
In collaboration with EVAAP EDTA

Supported by European Commission

Test cells for cycle tests.

16 series - 5 parallel

WEV-0 (2010–2012)



16 series – 4 parallel

WEV-1 (2013-)

16 test cells for cycle tests

Vehicle Specifications

Organized by Hosted by In collaboration with Supported by