Silicon composite oxide(DMSO) anode material for LIB

DAEJOO

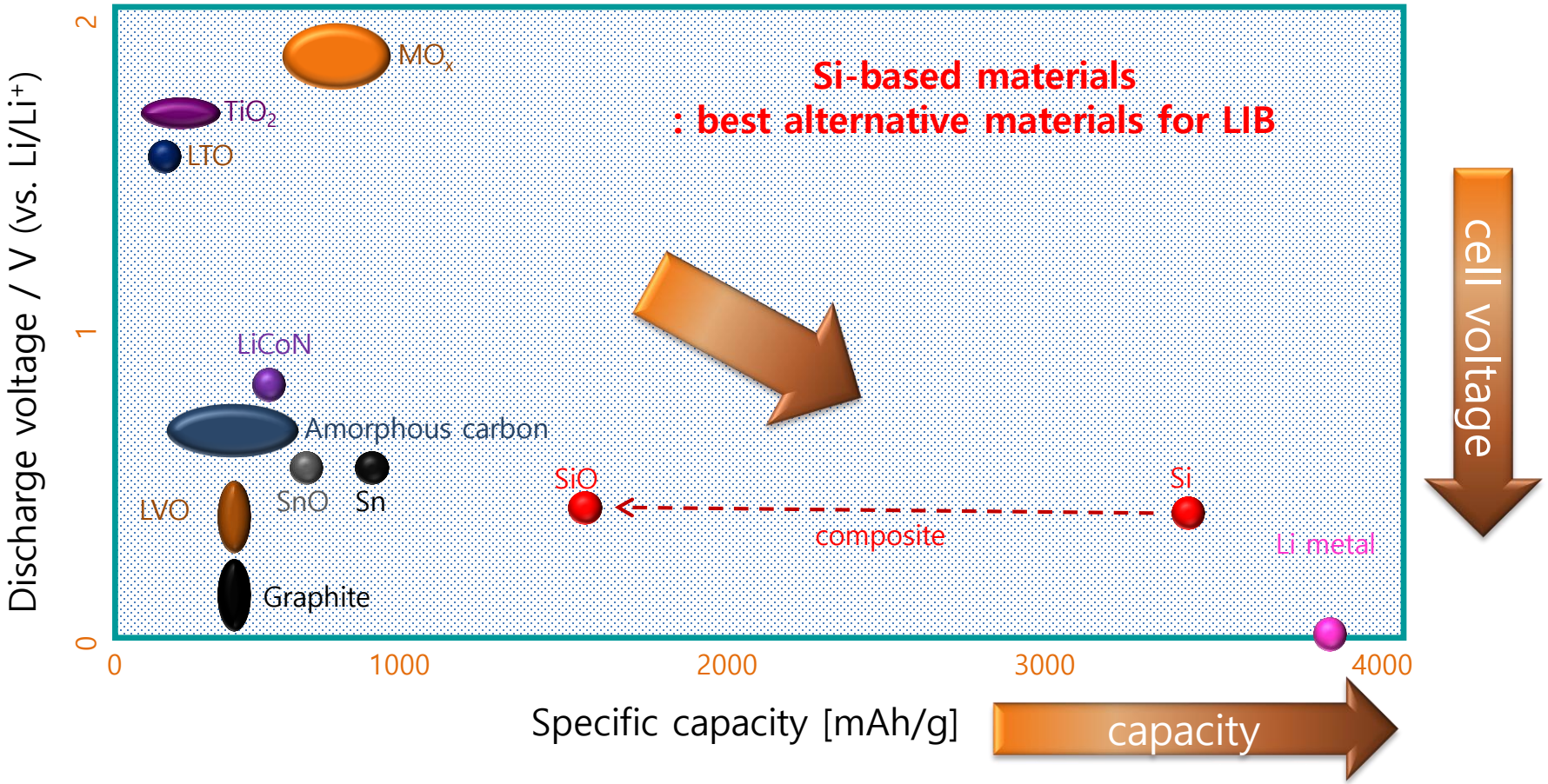
Daejoo Electronic Materials

Table of contents

Background

- Need for increasing Energy density

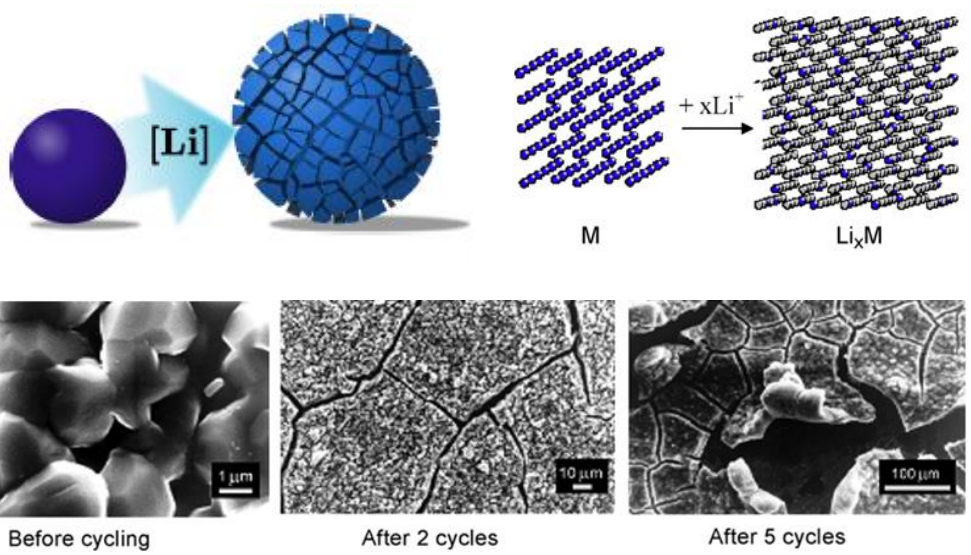
Si shows considerably high capacity and cell voltage similar to graphite.
Accordingly, *Si could be the best promising material for increasing energy density* as a candidate of anode material.



Background

- Problems of metal based anode materials

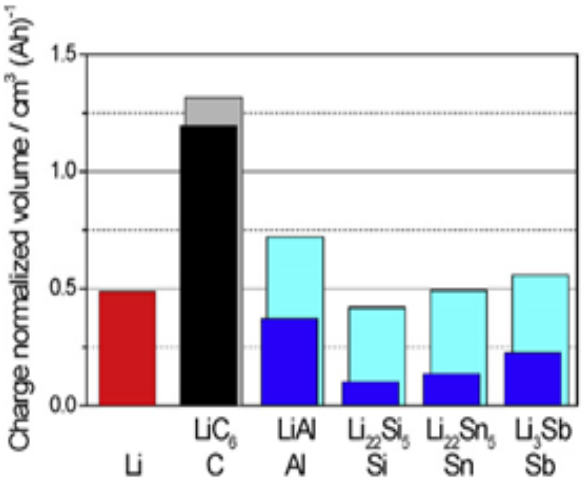
Metal is able to accommodate higher capacity. In the meantime, it brings bigger Volume expansion. Undergoing cyclic process of expansion & shrinkage, it is unavoidable to face degradation such as fracture or cracking. In result, it shortens life time and brings poor cycle stability.



Ref) Bruno Scrosati and Jurgen Garche, Journal of Power Sources, 195 (2010) 2419.

$Li + 6C \Rightarrow LiC_6$ (372mAh/g)

$4.4Li + Si \Rightarrow Li_{4.4}Si$ (4200mAh/g)



Background

- Comparison of candidate anode materials

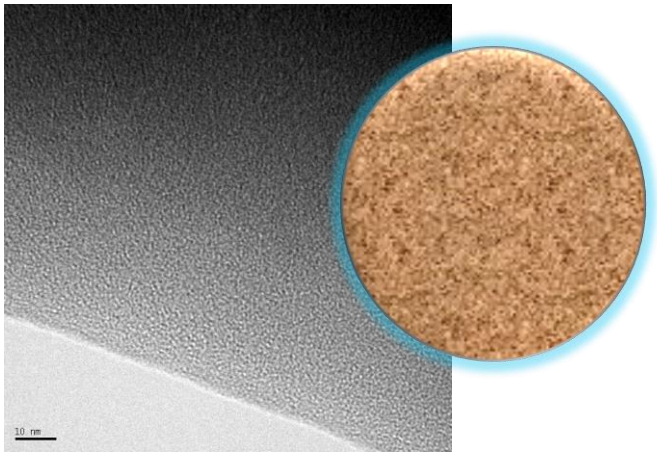
Cell manufacturers are facing the need to increase energy density of anode, and have tried to find new metal-based anode materials. From the viewpoint of capacity, Si shows ten times higher than graphite, and SiO shows five times higher than graphite while still showing normal-level stability.

Item	Carbon	Si	SiO	Si/C	Si alloy
Discharge capacity	372 [mAh/g]	~4200 [mAh/g]	**~1650 [mAh/g]**	~1300 [mAh/g]	~1000 [mAh/g]
Stability	Good	Poor	**Normal**	Poor	Poor
Eco-friendly	Normal	Good	**Good**	Normal	Normal
Status of development	commercial	Under development	**Market validation**	Market validation	Under development

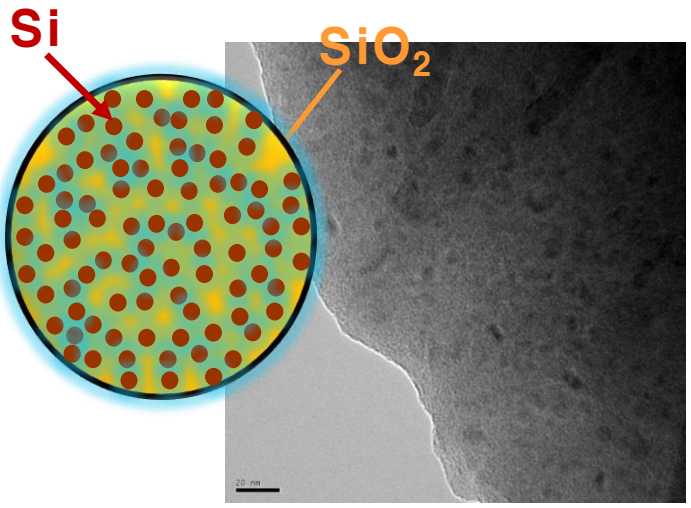
Background

- Structural feature of silicon oxide

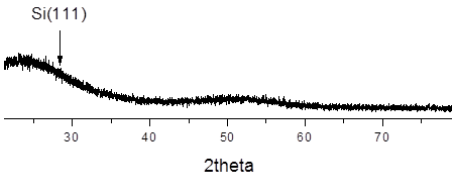
Si nano particles are uniformly dispersed in Si oxide matrix. It helps to suppress volume expansion and to extend life-time. The structure is stable better than any other silicon-based materials such as Si-alloy, Si-C composite, or Pure Si.

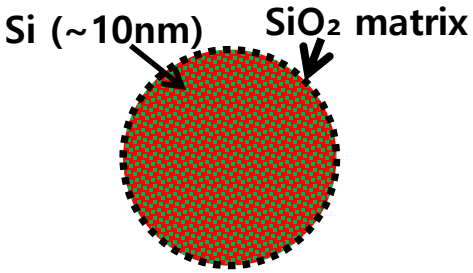


Amorphous SiO

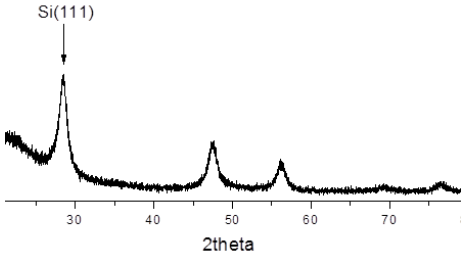


Crystalline SiO





C-coated Si oxide

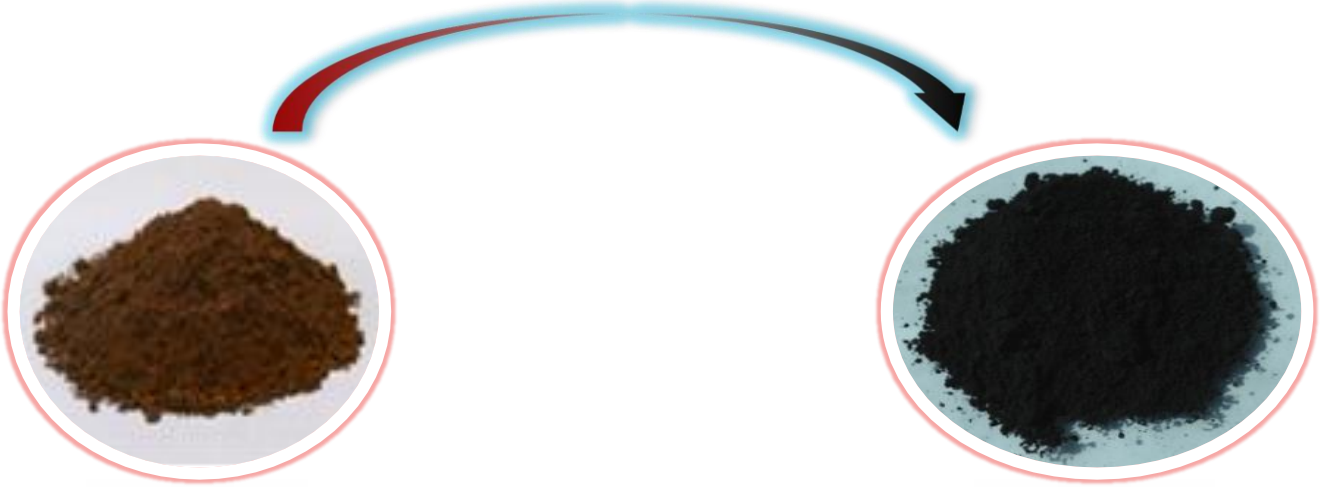


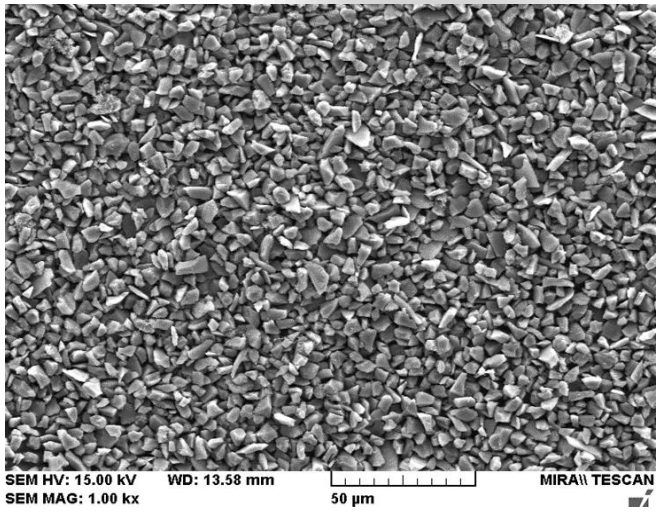
Background

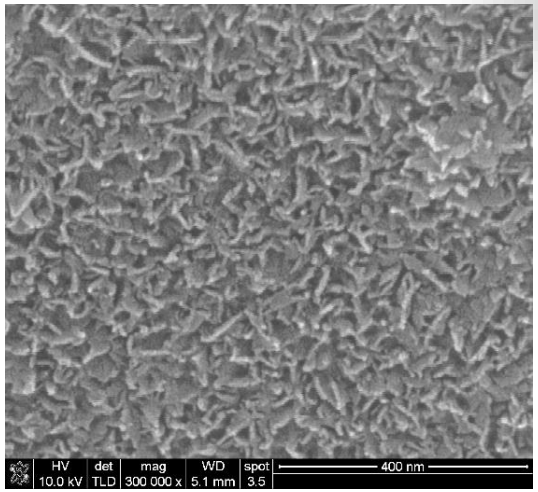
- Structural feature of silicon oxide

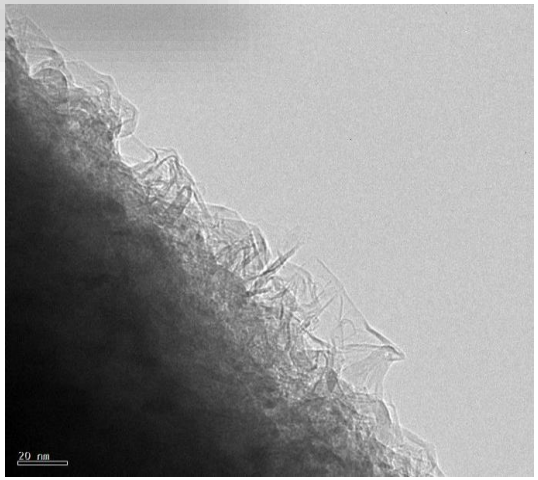
CONFIDENTIAL

Carbon coating for better electrical conductivity







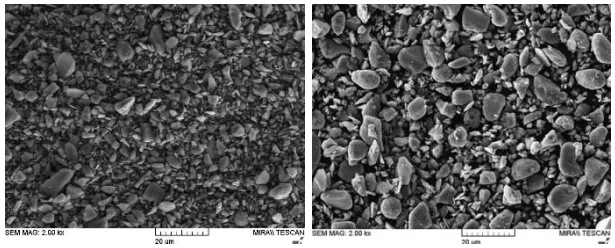


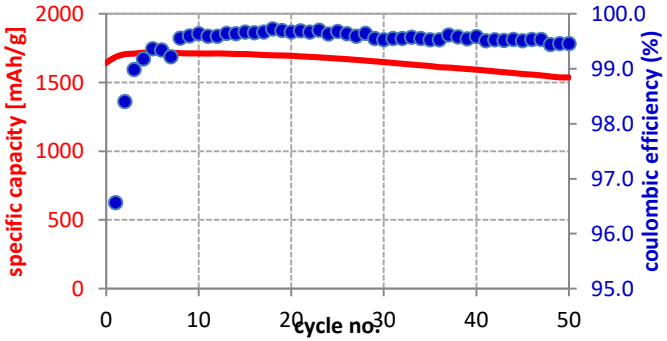
Background

- Properties of Silicon oxide

Basic properties

- Silicon crystal size ---- <10 nm
- Particle size[D_{50}] ------ 4~7 ㎛
- BET surface area ------ 4~12 m^2/g
- Oxygen content ------- 34~35 wt%
- Carbon content ------- 3~7 wt%



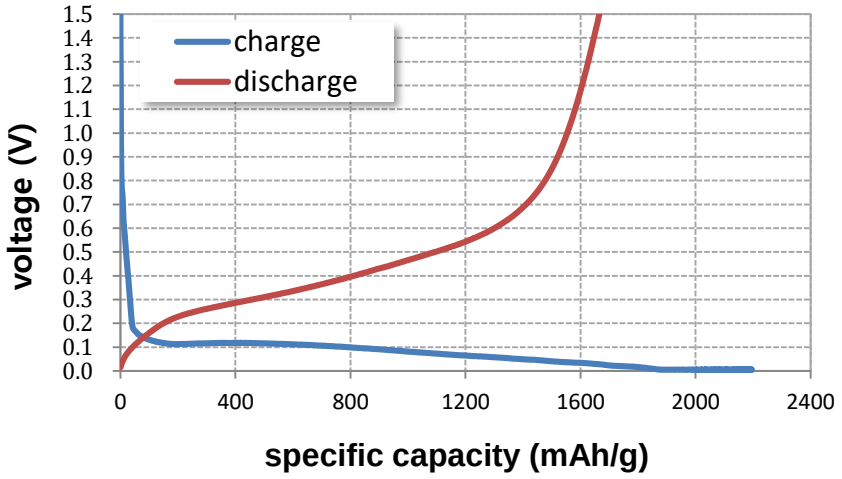


Electrochemical performances

- Initial Efficiency (ICE) : 74~75%
  (Charge 2050~2200mAh/g, Discharge 1550~1650mAh/g)
- Lifetime (retention rate of capacity) > 90%@50cycle

Coin half cell test condition

- Formulation: AM/SP/PAA = 8/1/1
- Formation:
  - charge : 0.1C/0.005V, CC/CV to 0.005C
  - discharge : 0.1C CC to 1.5V
- Cycling
  - charge : 0.2C/0.005V, CC/CV to 0.005C
  - discharge : 0.2C CC to 1.5V



Background

- Battery Industry Trends

CONFIDENTIAL

Silicon oxide + Graphite

Si / C + Graphite

Longer lifespan & less swelling ⟵ ⟶ *Higher ICE*

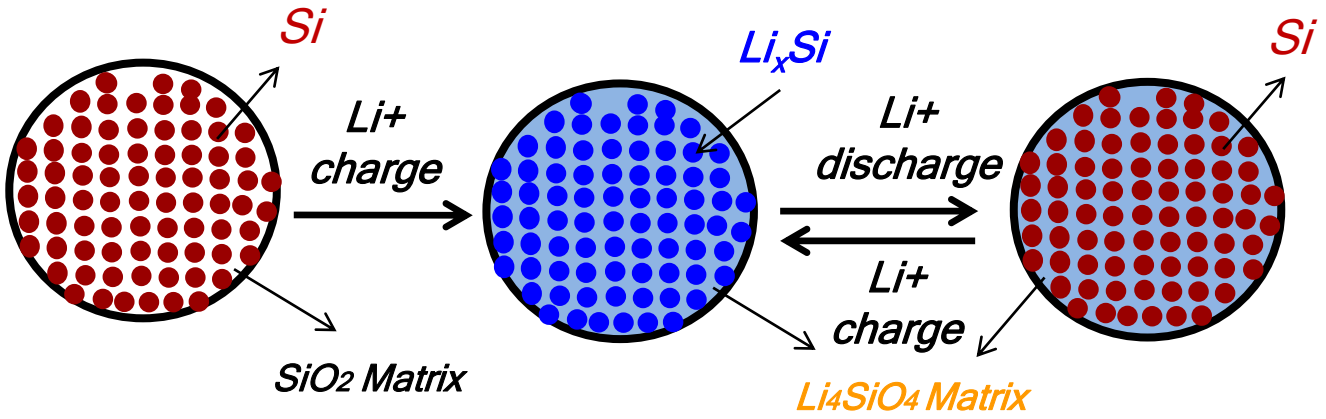
LGC, SKI	*ATL, BAK,*	*SamsungSDI*
JEVE, EVE, CATL, BYD,	*Farasis, Wanxiang,*	*Zhuoneng*
Lishen, MGL, Guoxian,	*Kokam, Coslight*	
CALB, CETC,	*Northvolt*	
Panasonic, Maxell,		
Murata,		
	Apple, Huawei,	
Tesla, Porsche, GWM,	*BMW*	
Hyundai, Toyota,		
Toshiba, Honda		

Background

- Problems of conventional silicon oxide

Chemical reaction [SiO + Li] causes irreversible product, which lowers initial efficiency

$$4SiO+(3x+4)Li \longrightarrow 3Li_xSi + Li_4SiO_4 \rightleftarrows 3Si +(3x)Li + Li_4SiO_4$$



Initial charging causes irreversible product Li_4SiO_4

⟶ Initial Coulombic Efficiency [ICE] < 75%

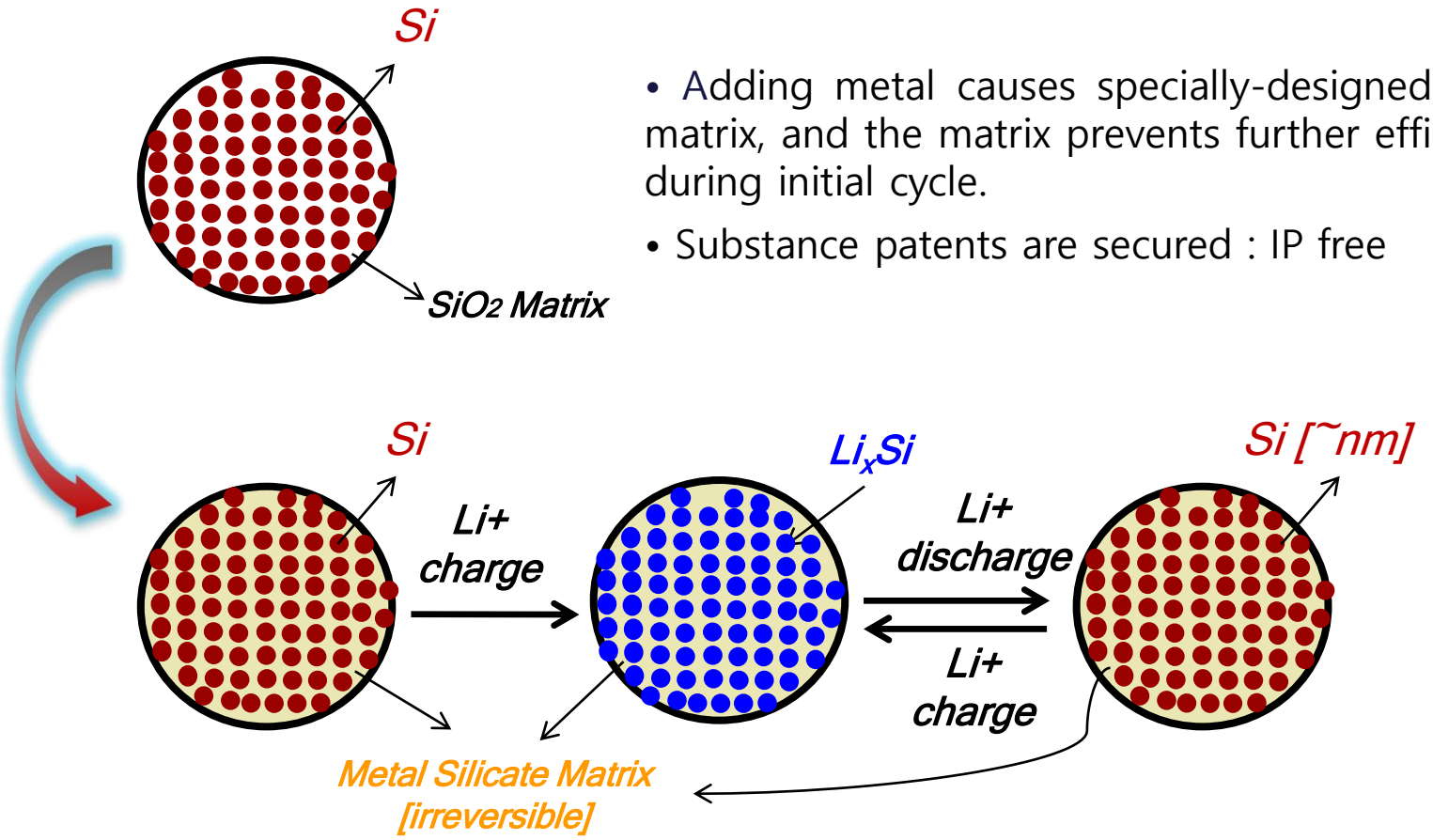
The low initial columbic efficiency is the limit against wide application of Si

New silicon composite oxide

- Structure & concept of DMSO

CONFIDENTIAL

DMSO shows ideal Si-silicate matrix, and prevents the formation of irreversible product intrinsically during charging & discharging process.



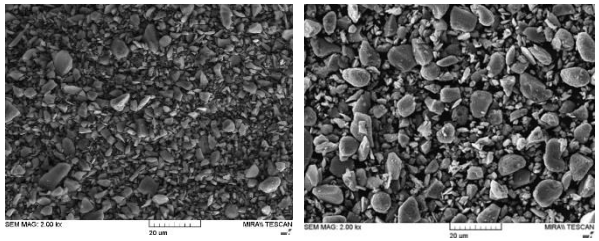
- Adding metal causes specially-designed Si/Silicate matrix, and the matrix prevents further efficiency loss during initial cycle.
- Substance patents are secured : IP free

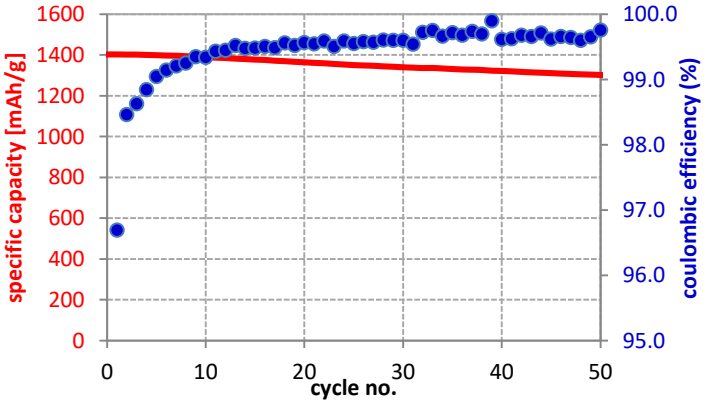
New silicon composite oxide

– Properties of DMSO

Basic properties

- Silicon crystal size ---- < 10 nm
- Particle size[D_{50}] ------ 4~7 ㎛
- BET surface area ------ 4~12 m^2/g
- Oxygen content ------- 28~33 wt%
- Carbon content ------- 3~7 wt%



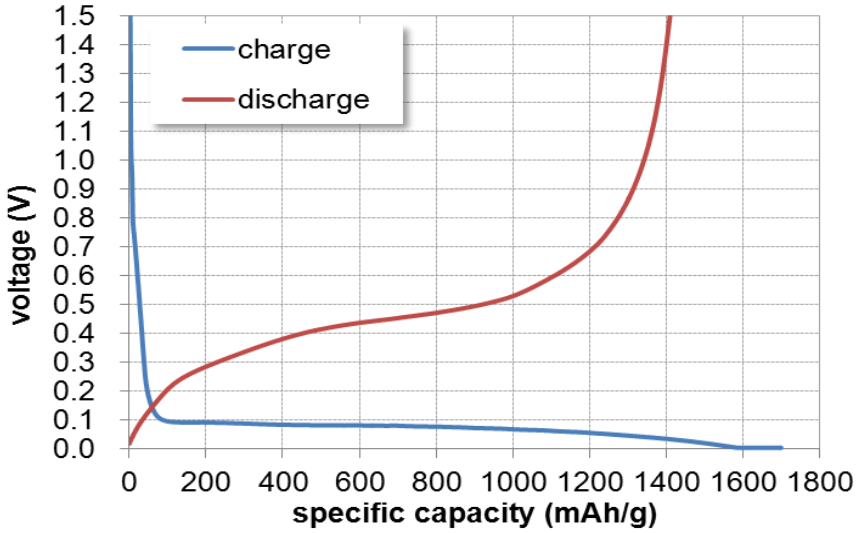


Electrochemical performances

- Initial Coulombic Efficiency (ICE) : 80~82%
  (Charge 1700~1850mAh/g, Discharge 1300~1450mAh/g)
- Life time (retention rate of capacity) > 90%@50cycle

Coin half cell test condition

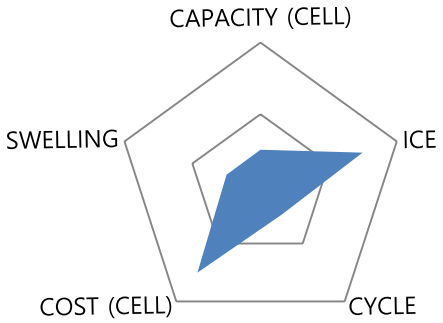
- Formulation: AM/SP/PAA = 8/1/1
- Formation:
  - charge : 0.1C/0.005V, CC/CV to 0.005C
  - discharge : 0.1C CC to 1.5V
- Cycling
  - charge : 0.2C/0.005V, CC/CV to 0.005C
  - discharge : 0.2C CC to 1.5V



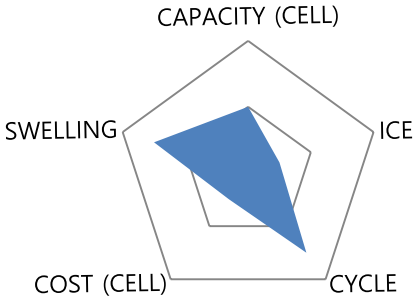
New silicon composite oxide

– SiC Vs. Silicon oxide Vs. DMSO

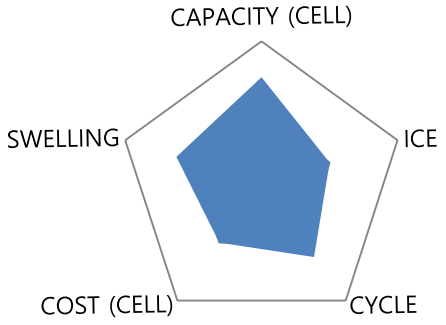
SiC



SiO



DMSO



		Si/C	SiO	DMSO
CAPACITY	ANODE	POOR	GOOD	FAIR
	FULL CELL	POOR note1	FAIR note2	GOOD
ICE		GOOD	POOR	FAIR
LIFE CYCLE		POOR	GOOD	GOOD or FAIR
COST	ANODE	GOOD	GOOD	FAIR
	FULL CELL	GOOD	POOR note3	FAIR
SWELLING		POOR	GOOD	GOOD or FAIR

NOTE:
1. Because of swelling problem the added amount of Si materials is limited.
2. Low efficiency causes big amount of capacitance loss in cathode.
3. Waste of cathode material which is higher price.

Performances of DMSO

– Electrochemical performances of DMSO

DMSO is applied to anode mixed with graphite in the range of 5wt% to 25wt%.

The capacity of the anode increases with the addition of DMSO, but the initial efficiency drops.

	DMSO Single formulation	Formulation [Graphite + DMSO]			
		DMSO 5wt%	DMSO 10wt%	DMSO 15wt%	DMSO 25wt%
Initial charge cap. [mAh/g]	1715	435	500	570	700
Initial discharge cap. [mAh/g]	1410	400	450	500	610
Initial coulombic efficiency [%]	82	92	90	88	87
Cycle life (capacity retention, %)	90@50cycle	97@100cycle	95@50cycle	95@50cycle	90@50cycle

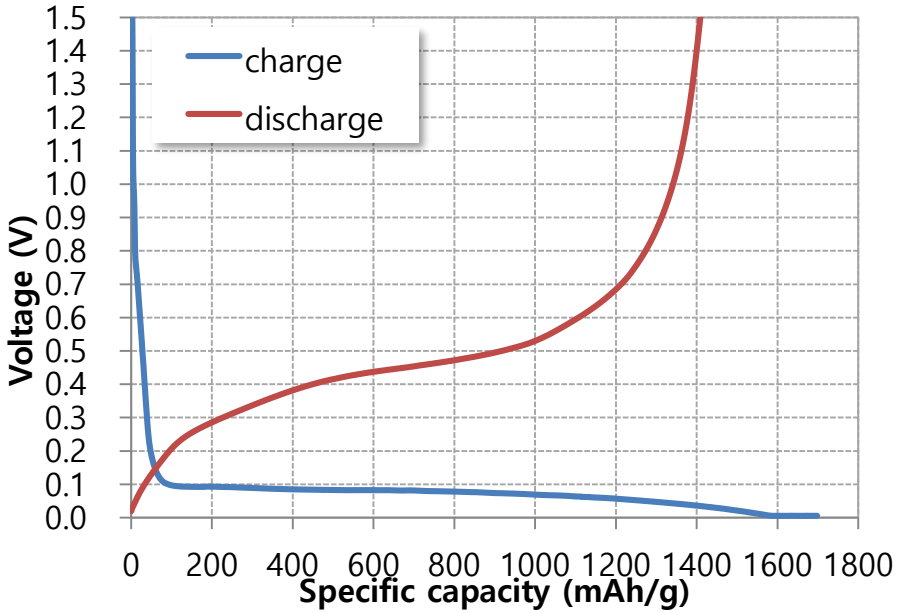
- Si composite oxide (DMSO Single formulation) : composition AM/SP/PAA = 8/1/1
- Formulation (Graphite + DMSO) : composition AM/CMC/SBR = 97/1.5/1.5

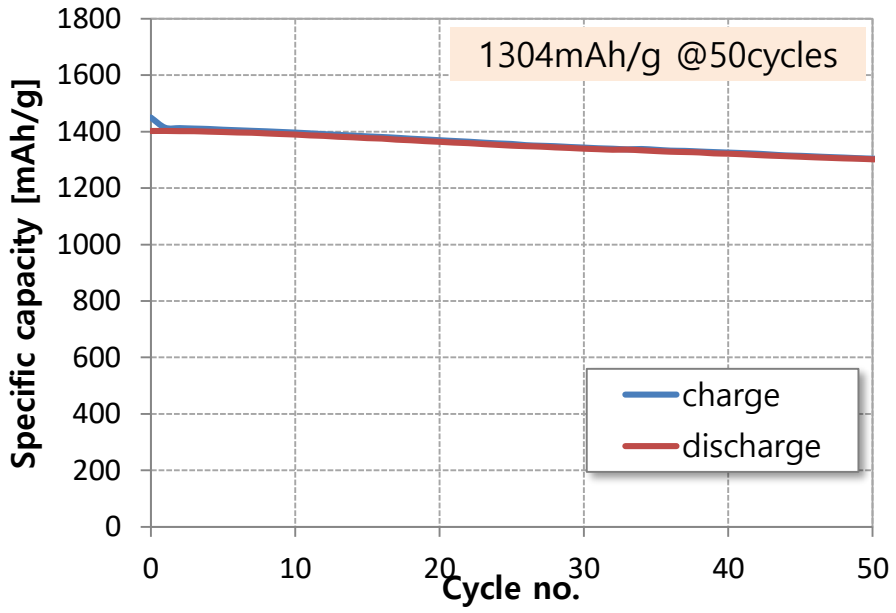
Performances of DMSO

– DMSO single

Formulation (DMSO 100%)

Formulation	specific capacity(mAh/g)		ICE(%)
	charge	discharge	
DMSO 100%	1715	1410	82





Formation condition

- charge : 0.1C/0.005V, CC/CV to 0.005C
- discharge : 0.1C CC to 1.5V

Test condition

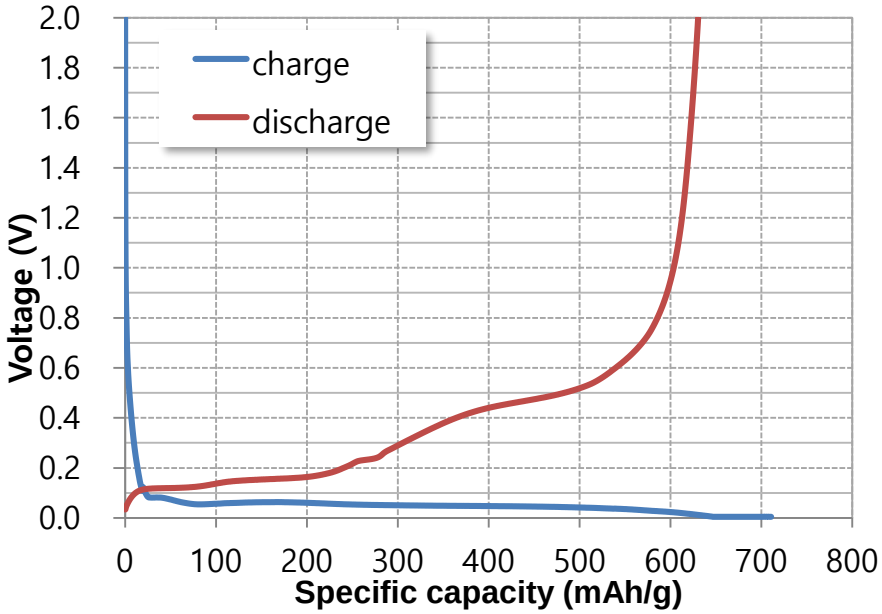
- charge : 0.2C/0.005V, CC/CV to 0.005C
- discharge : 0.2C CC to 1.5V

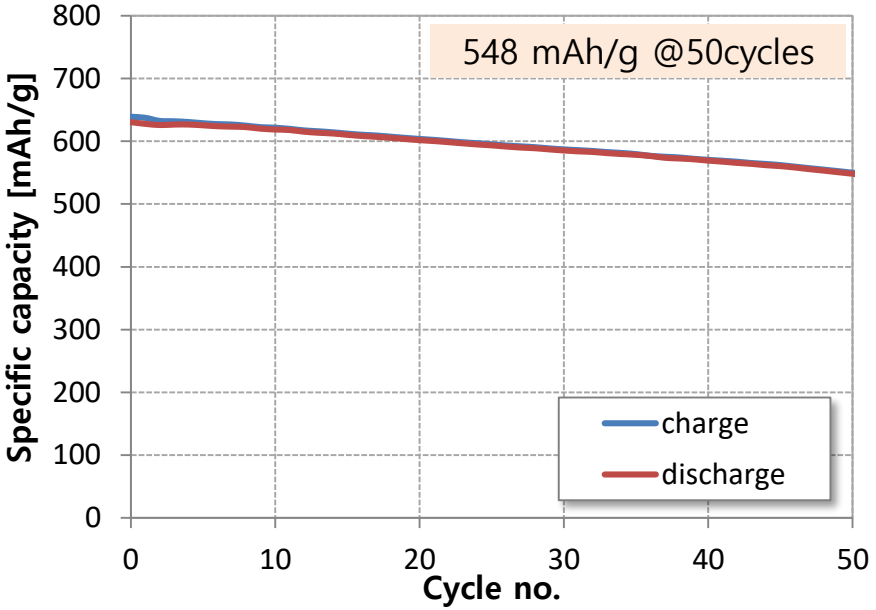
Performances of DMSO

– DMSO 27 wt%

Formulation (NG + DMSO 27 wt%)

Formulation	specific capacity(mAh/g)		ICE(%)
	charge	discharge	
DMSO 27 wt%	720	630	87





Formation condition

- ❖ charge : 0.1C/0.005V, CC/CV to 0.05C
- ❖ discharge : 0.1C CC to 2.0V

Test condition

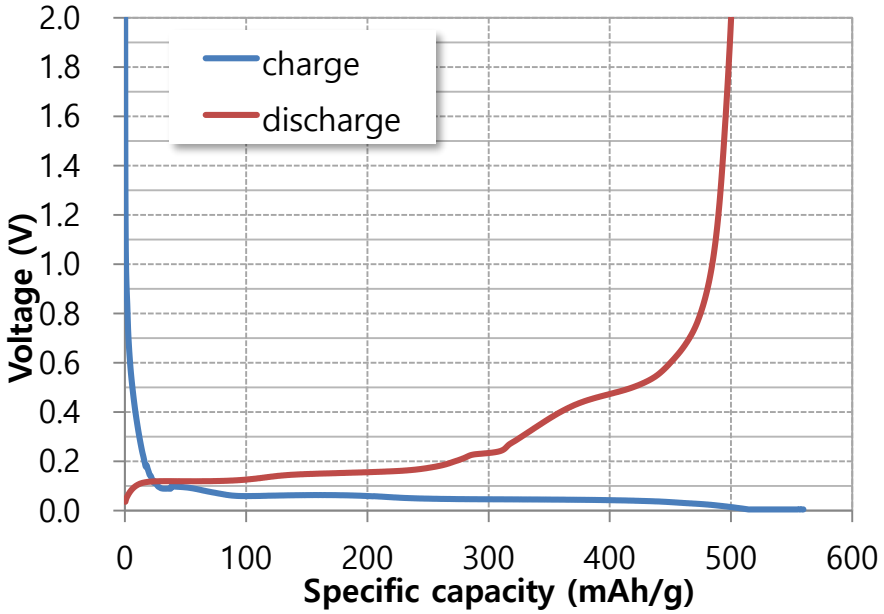
- ❖ charge : 0.5C/0.005V, CC/CV to 0.05C
- ❖ discharge : 0.5C CC to 2.0V

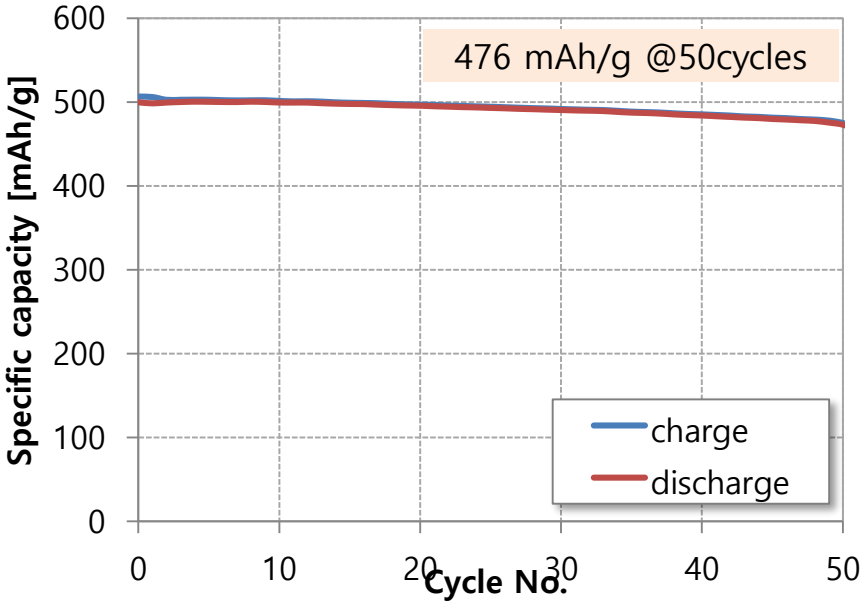
Performances of DMSO

– DMSO 13 wt%

Formulation (NG + DMSO 13 wt%)

Formulation	specific capacity(mAh/g)		ICE(%)
	charge	discharge	
DMSO 13 wt%	560	500	89





Formation condition

- charge : 0.1C/0.005V, CC/CV to 0.05C
- discharge : 0.1C CC to 2.0V

Test condition

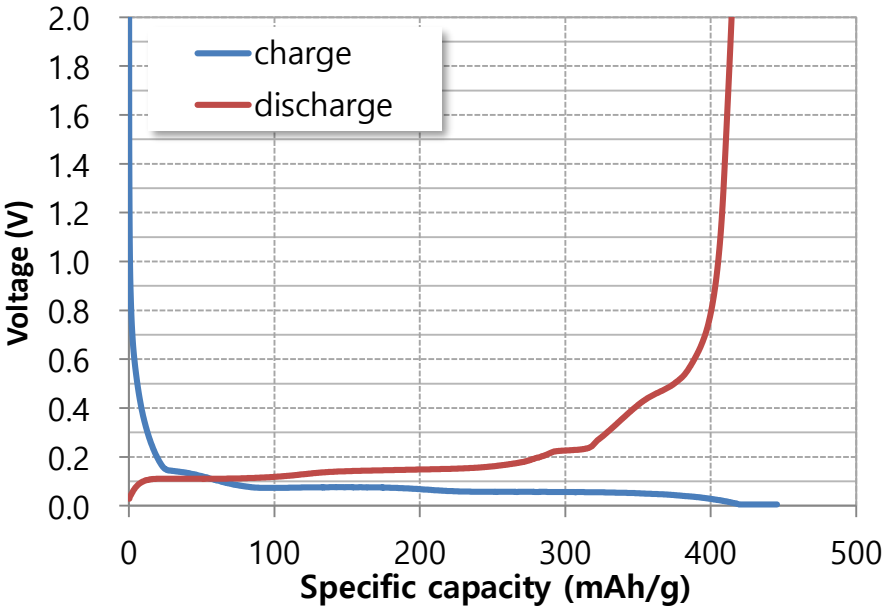
- charge : 0.5C/0.005V, CC/CV to 0.05C
- discharge : 0.5C CC to 2.0V

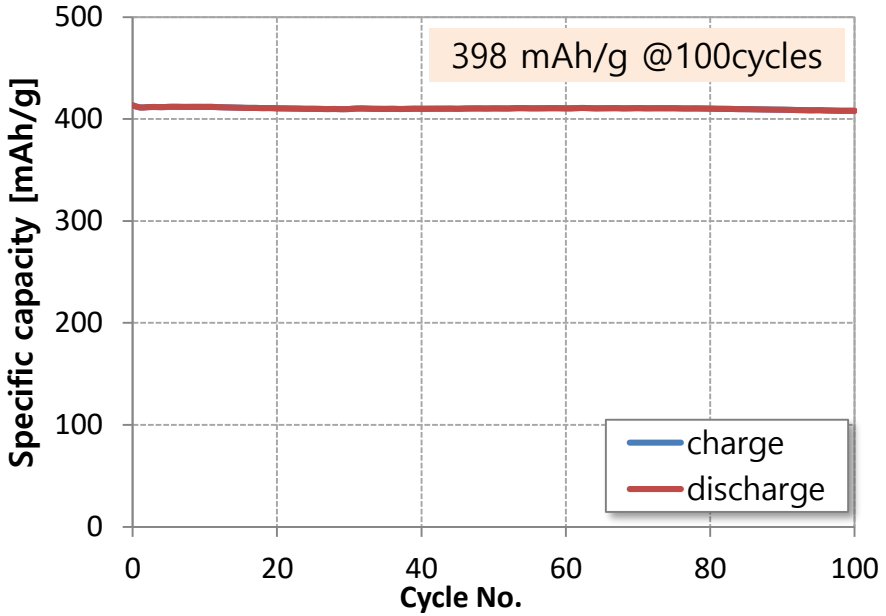
Performances of DMSO

– DMSO 6.5 wt%

Formulation (NG + DMSO 6.5 wt%)

Formulation	specific capacity(mAh/g)		ICE(%)
	charge	discharge	
DMSO 6.5 wt%	442	408	92





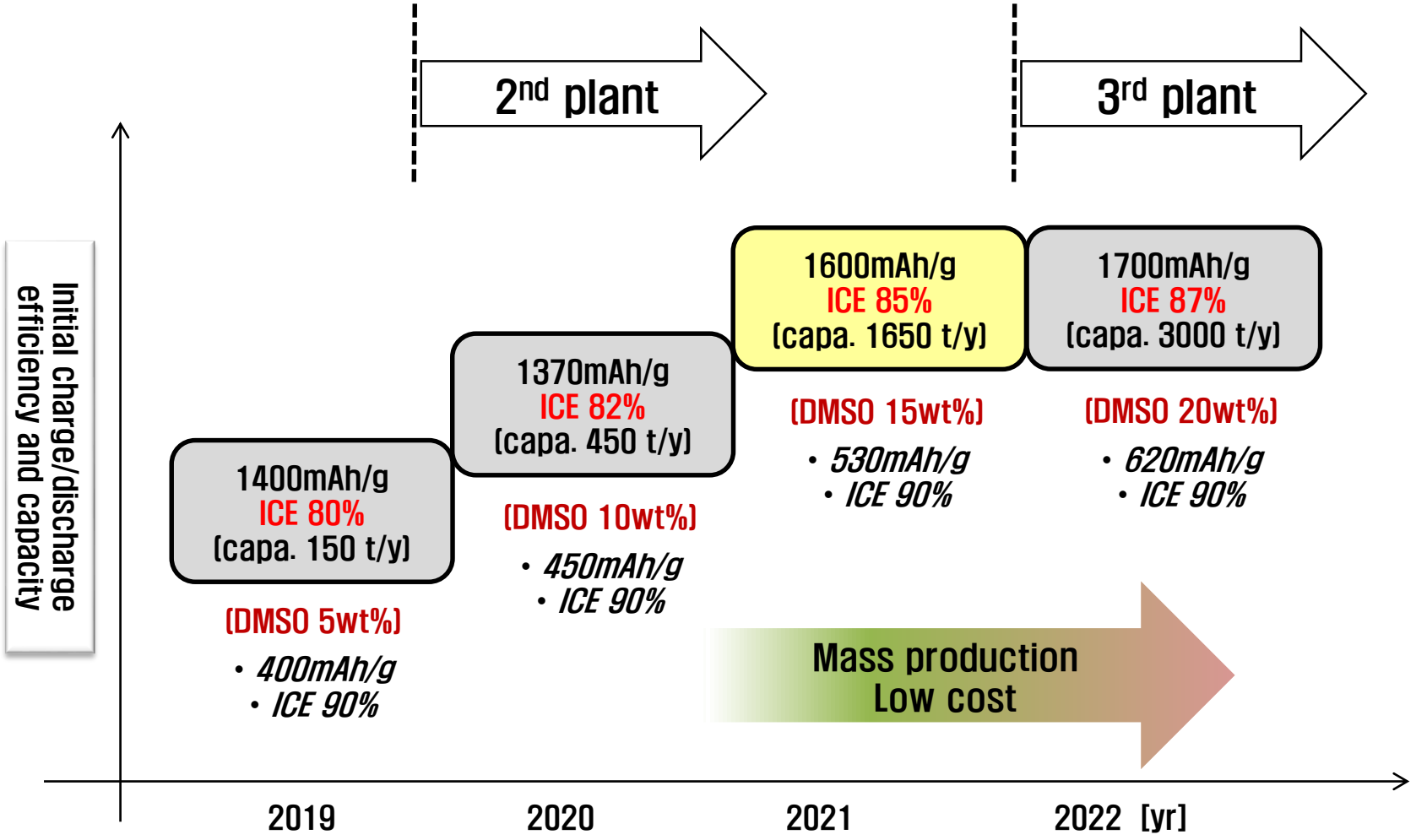
Formation condition

- charge : 0.1C/0.005V, CC/CV to 0.05C
- discharge : 0.1C CC to 2.0V

Test condition

- charge : 0.5C/0.005V, CC/CV to 0.05C
- discharge : 0.5C CC to 2.0V

Roadmap of DMSO



DAEJOO

Daejoo Electronic Materials Co., Ltd.