Understanding thermal processes in many nanoparticle-related applications

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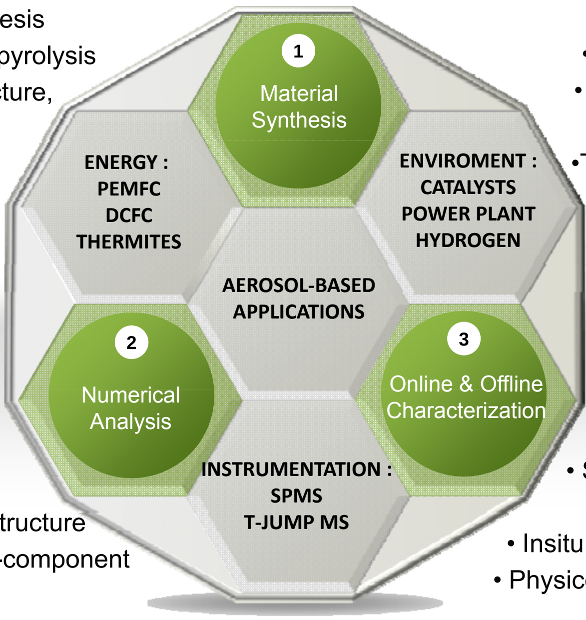
Summary of on-going researches: what & how

- One-step continuous synthesis
- Flame, Aerosol-gel, Spray pyrolysis
- Under control of microstructure, size & composition
- Pt/C & PtRu/C Inks
- Wet-surface electrode
- Energetic combustion

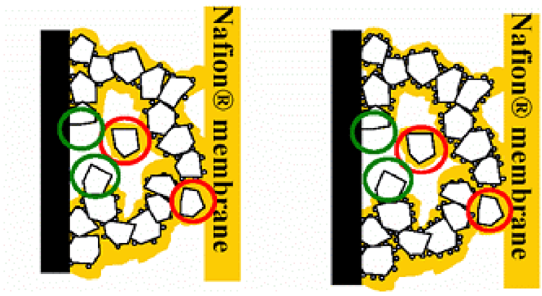
- de-NOx & de-SOx catalysts
- Catalytic regneration of DPF
- Sulfur effect on slagging
- Thermochemical cycle for H2

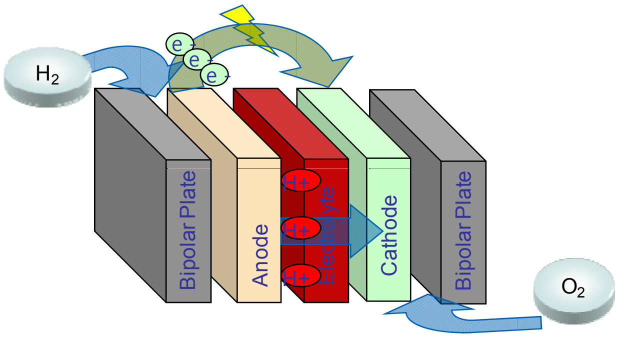


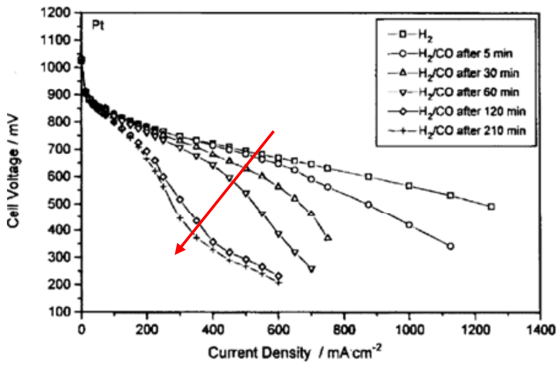
- CFD : Particle-laden flow
- CFD : Atomization
- MC : aggregation & microstructure
- LB : heterogenueous multi-component structure

- Single particle mass spectro.
- T-jump mass spectrometry
- Insitu thermal analyser (hot stage)
- Physicochemical & electrochemical

- Key factors for commercialization
  - long-term reliability
  - a minimal use of Pt
- Potential Solutions
  - make smaller Pt particles
  - enhance Pt surface dispersion
  - develop more cost-effective method
  - find less-expensive catalysts (Ru, Co, Y)

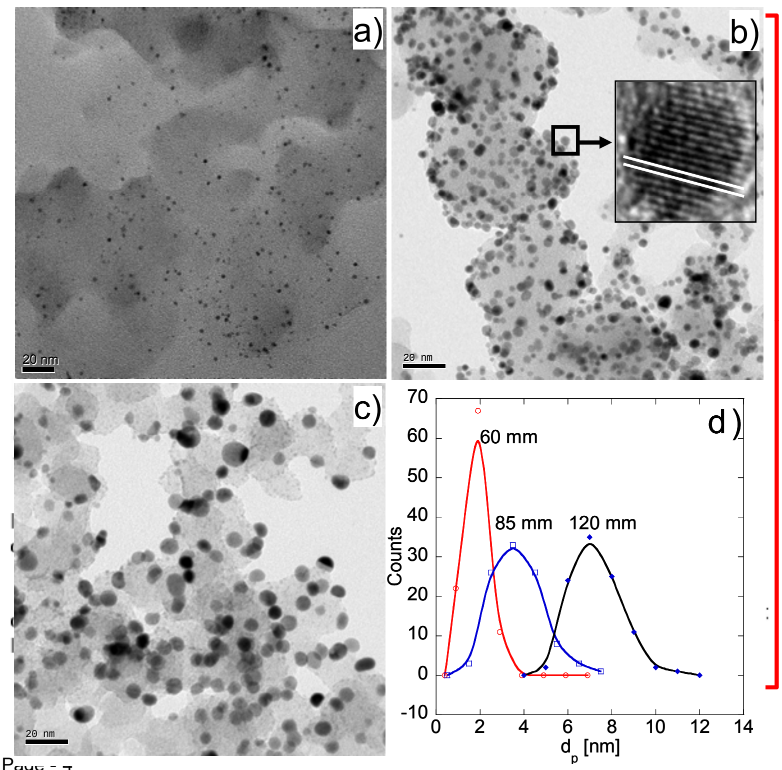


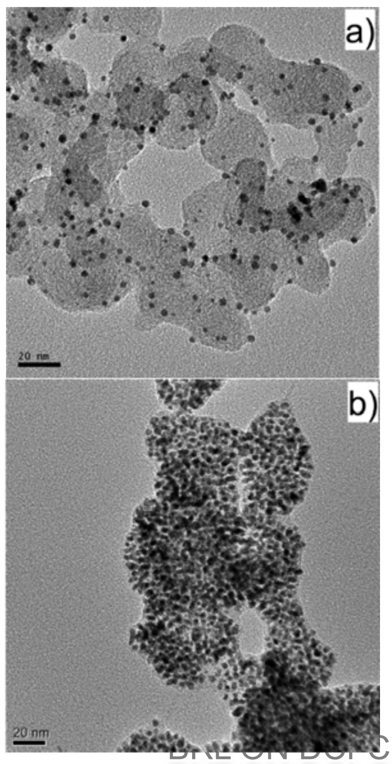




BRL ON DCFC

1. Energy
1) Pt catalyzed fuel electrode of PEMFC





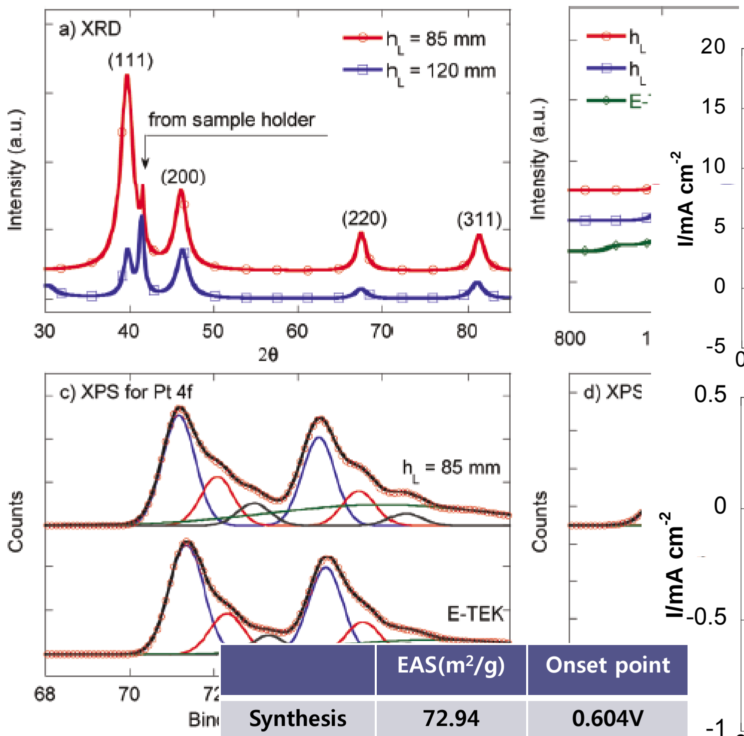
BRL ON DCFC

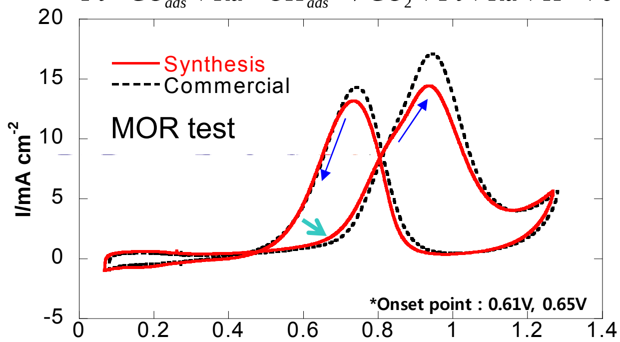
1. Energy

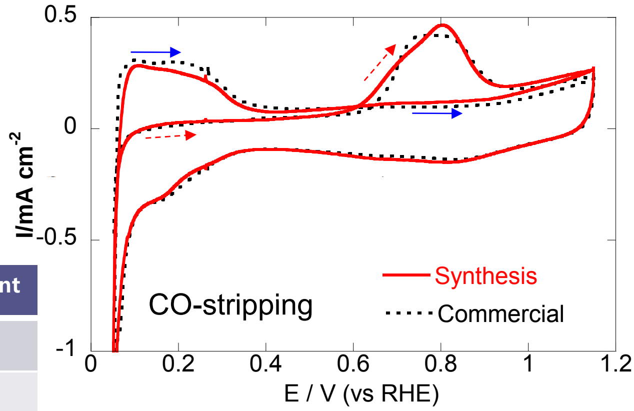
1) Pt catalyzed fuel electrode of PEMFC

$$Ru + H_2O \rightarrow Ru - OH_{ads} + H^+ + e^-$$

$$Pt - CO_{ads} + Ru - OH_{ads} \rightarrow CO_2 + Pt + Ru + H^+ + e^-$$







	EAS(m^2/g)	Onset point
Synthesis	72.94	0.604V
Commercial	65.67	0.641V

1. Energy

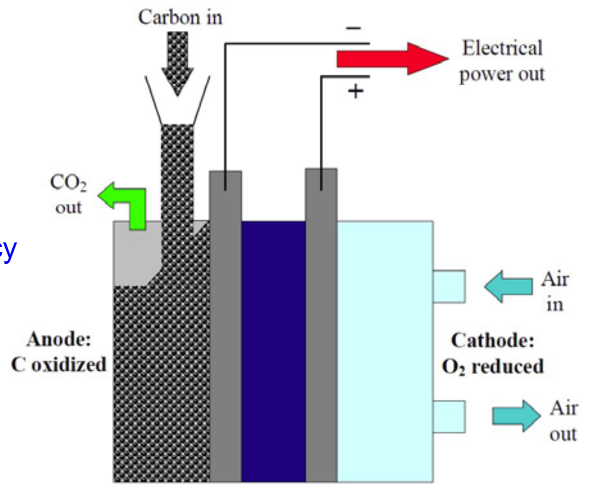
2) Basic Research Lab on DCFC

Anode : $C + 2CO_3^{2-} \rightarrow 3CO_2 + 4e^-$

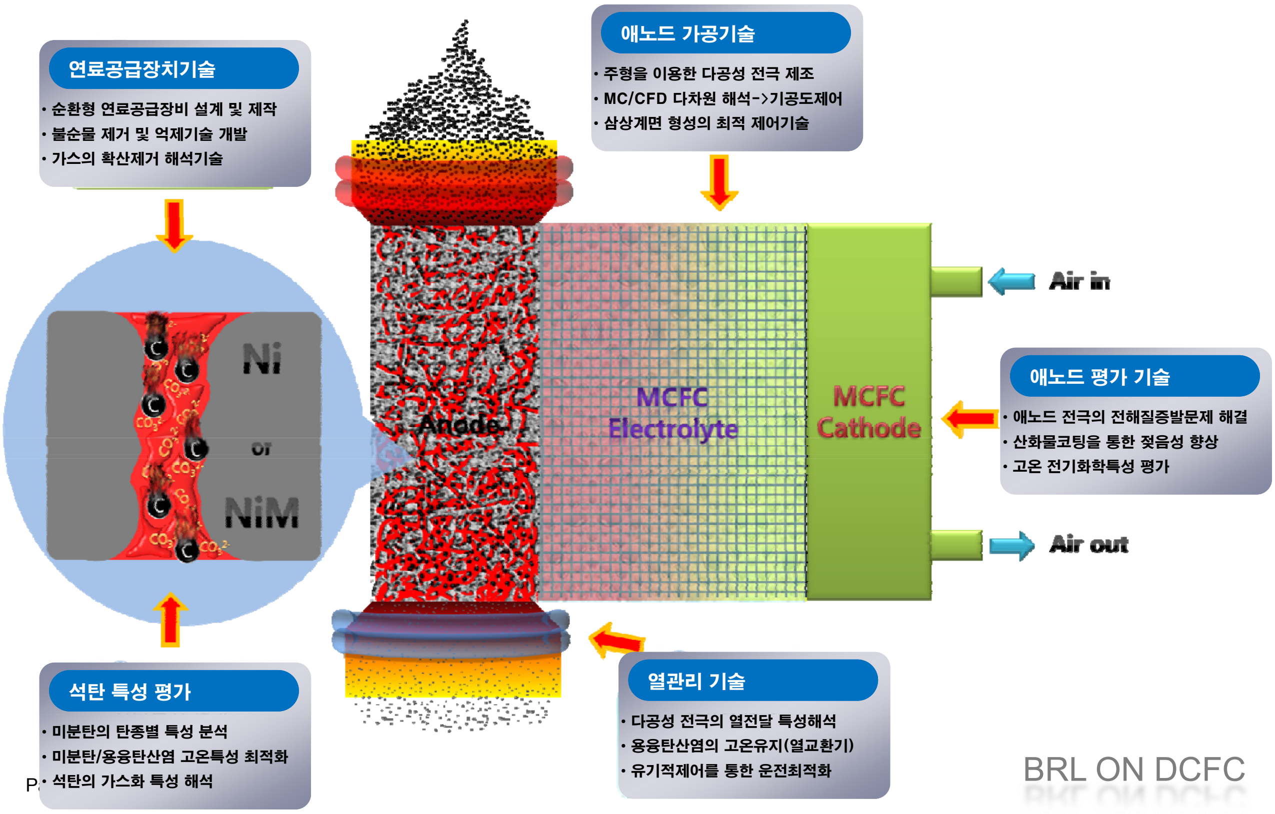
Cathode : $O_2 + 2CO_2 + 4e^- \rightarrow 2CO_3^{2-}$

Net reaction : $C + O_2 \rightarrow CO_2$

- no need of CO_2 separation
- Highest theoretical electrochemical efficiency
- easy retrofitting to MCFC or SOFC
- still in an idea-developing stage
- suffer from limitted triple-phase interfaces
- unknown thermal stabilities of various coals



BRL ON DCFC

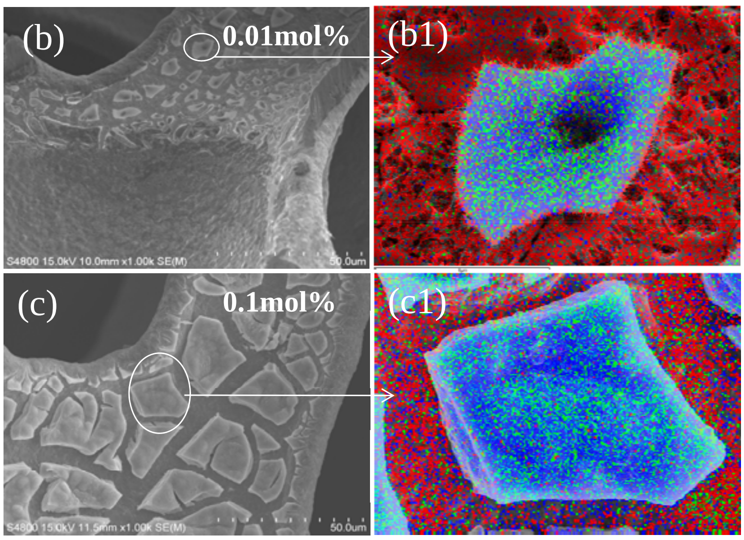


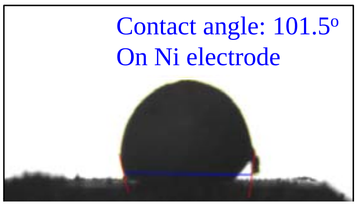
1. Energy
2) Basic Research Lab on DCFC

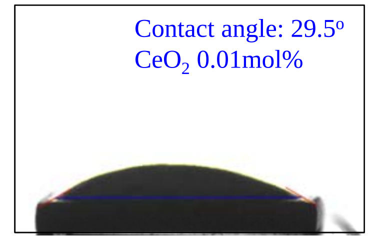
Sol-gel reaction for CeO2 coating

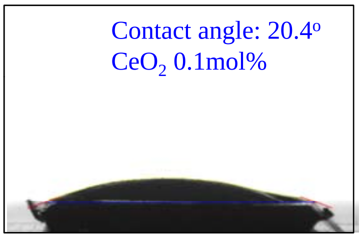
1. $CeCl_3$ + citric acid + ethanol (50ml)
2. Stirring_3000ppm (30min)
3. Ni foam dipped into sol solution for several time
4. Dried at 60℃ for 15min
5. Calcination at 500 ℃ for 30min In a Ar atomsphere

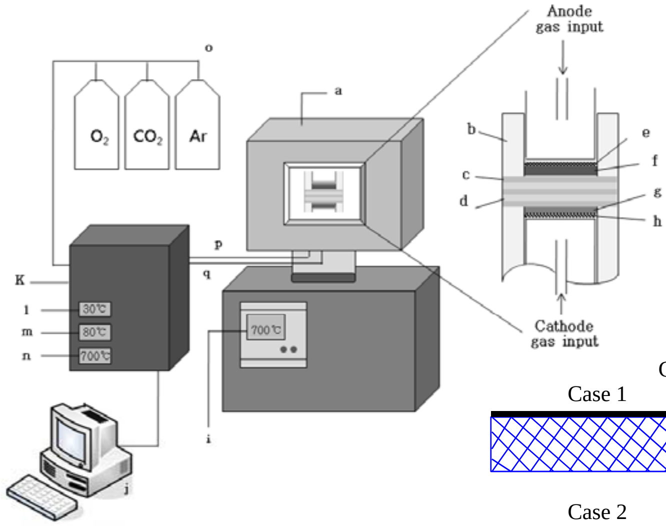
Ce (blue) oxygen (green), nickel (red)

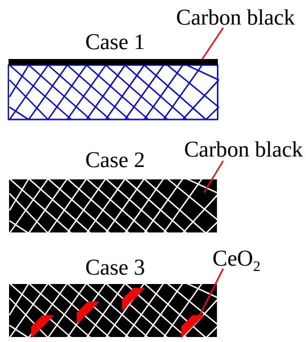


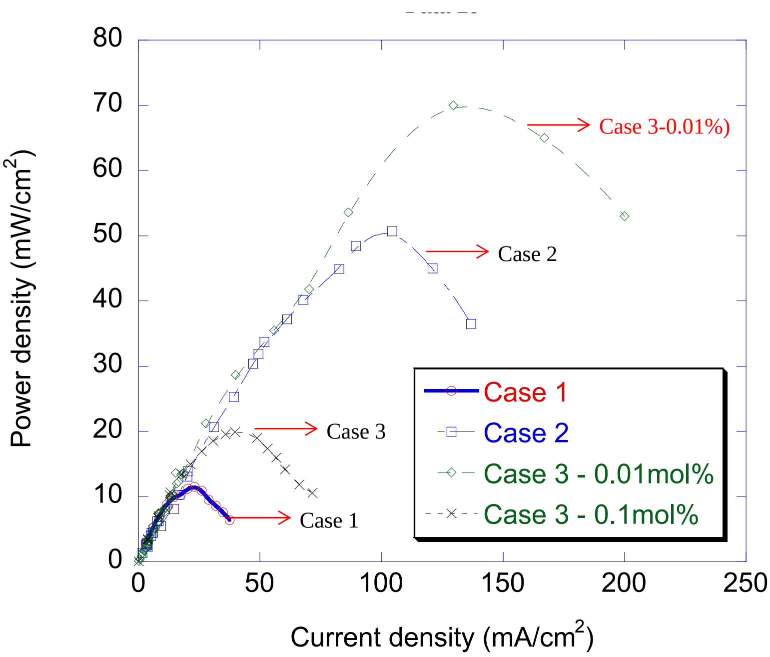


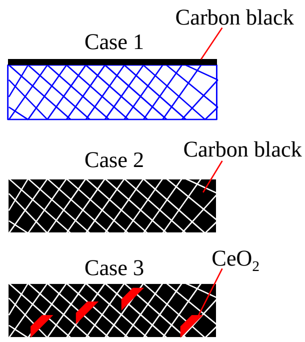










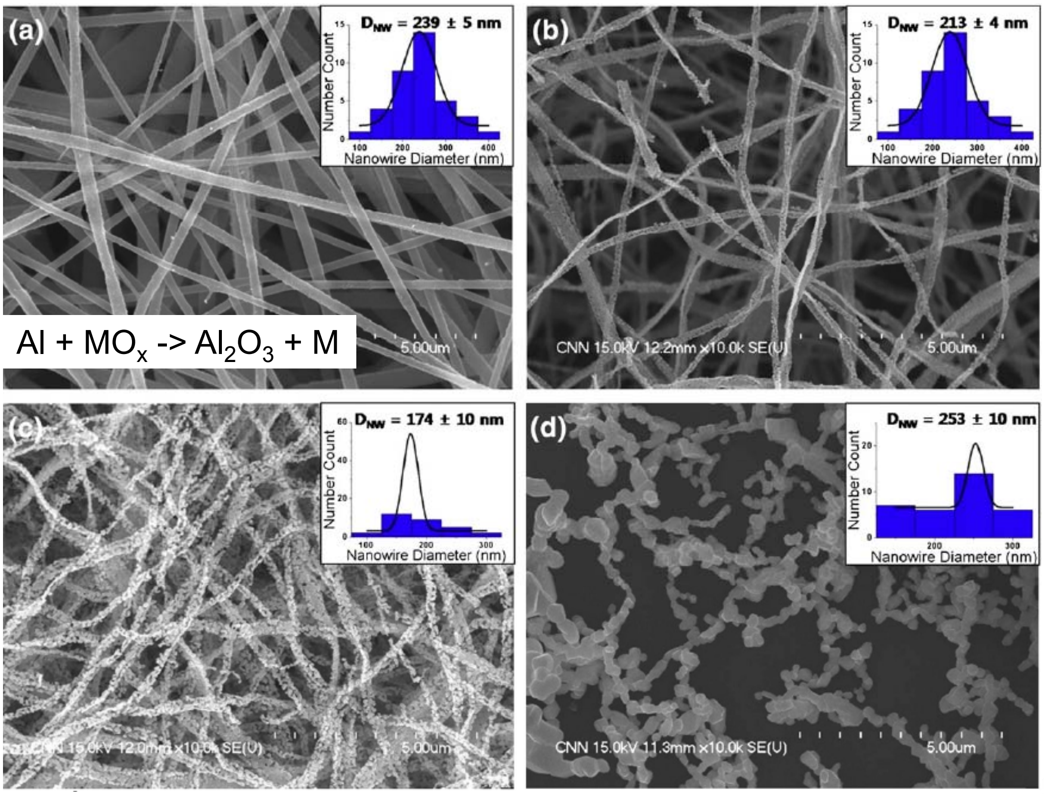


Improved max power density by
- maximizing triple-phase boundary
- enhancing electrode wetness

Further study
- Test for various coating materials
  (better conductivity & stability)

1. Energy

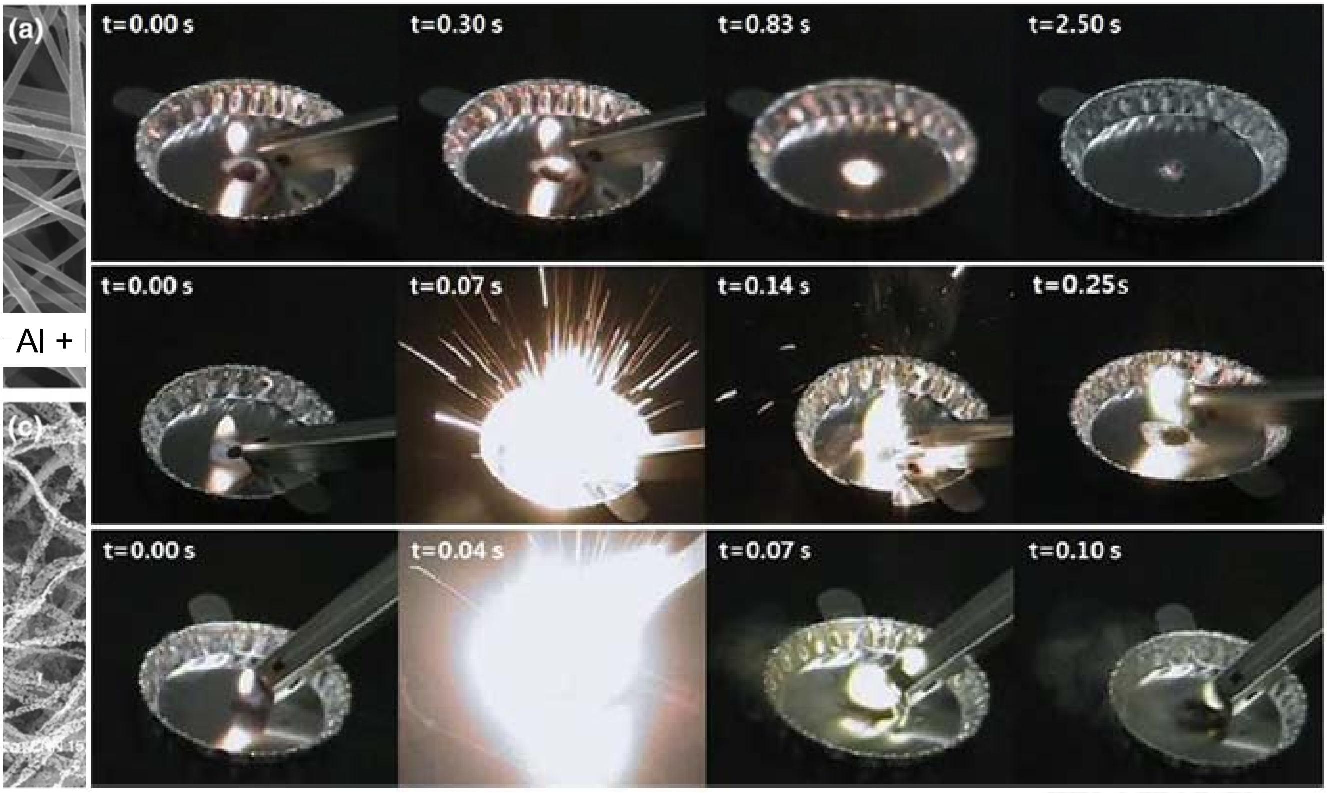
3) Energetic materials : Thermite

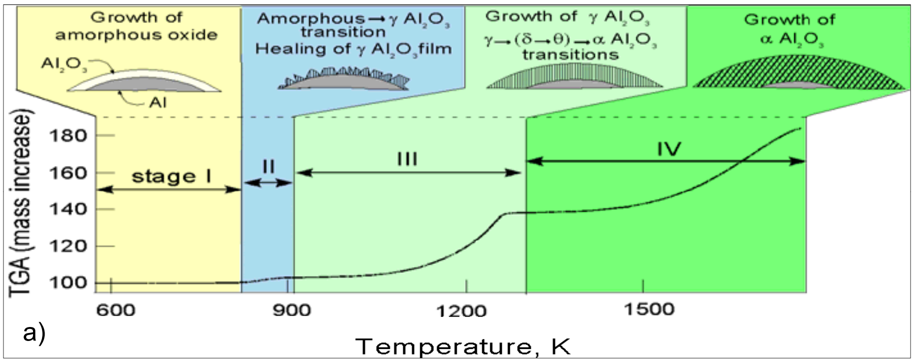


$Al + MO_x \rightarrow Al_2O_3 + M$

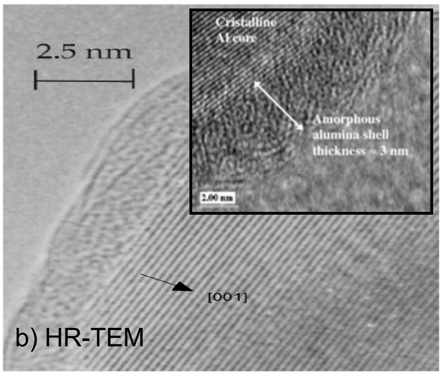
1. Energy

3) Energetic materials : Thermite

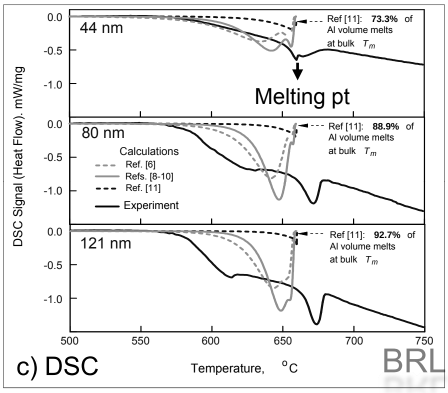




a)

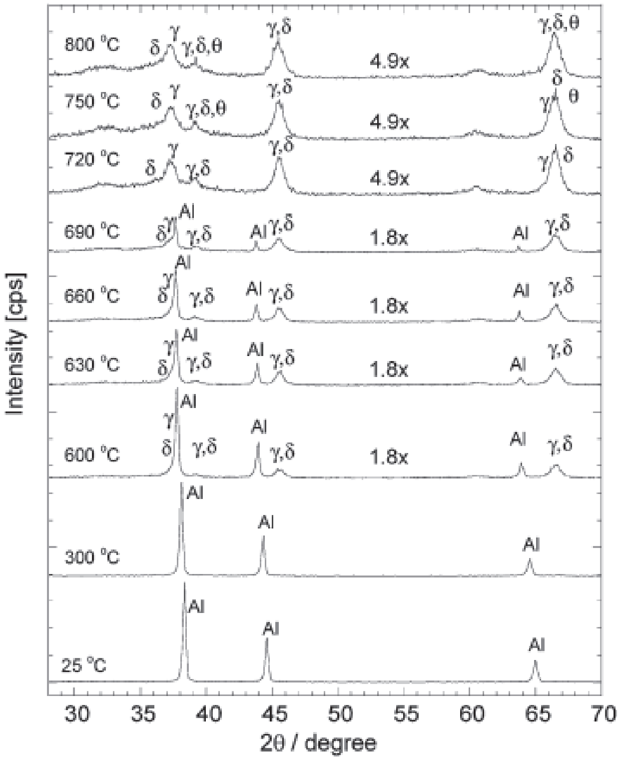


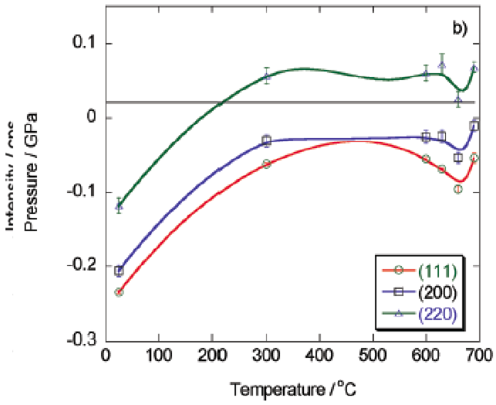
b) HR-TEM

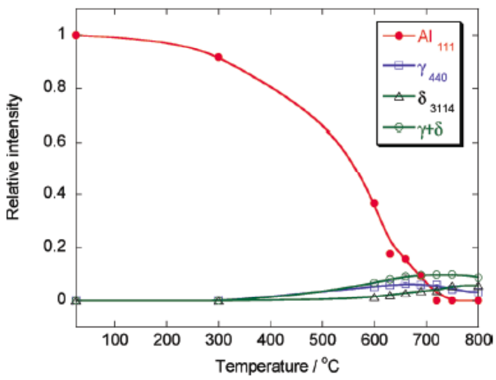


c) DSC

BRL ON DCFC

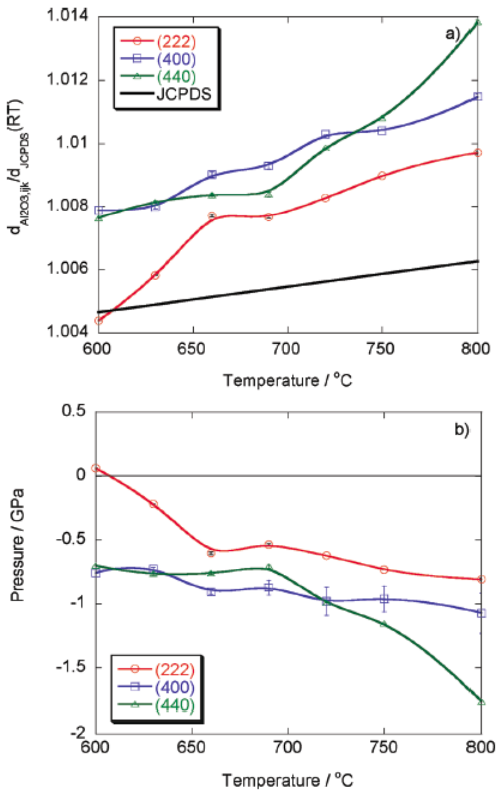


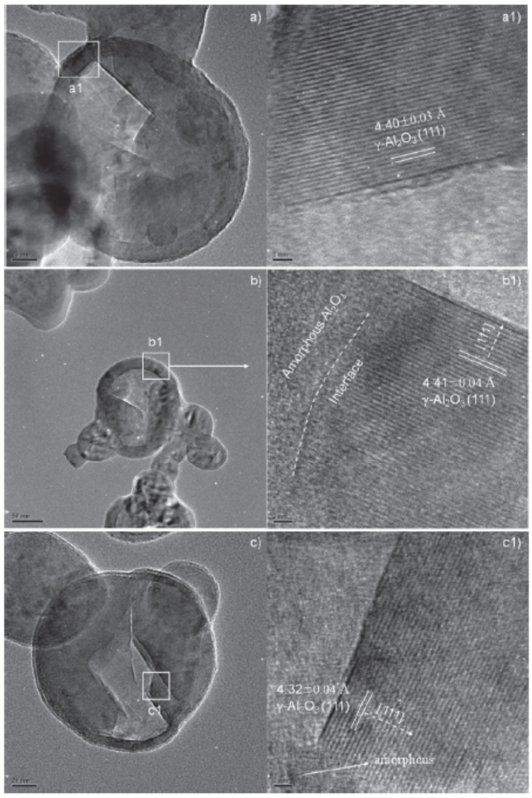




1. Energy

3) Energetic materials : Thermite





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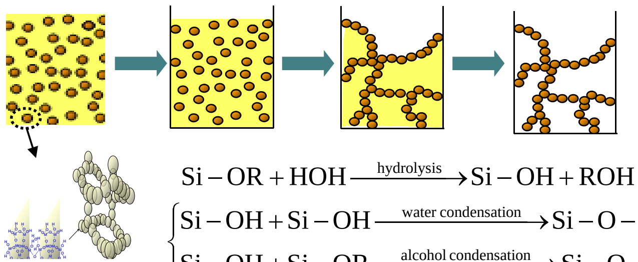
2. Environment

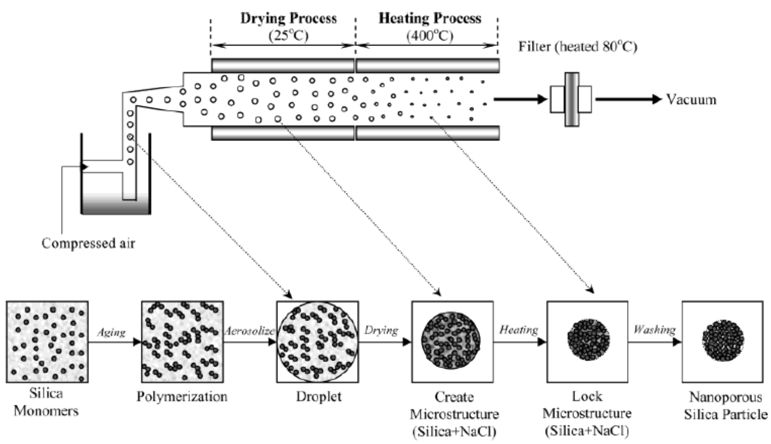
1) de-NOx catalysts

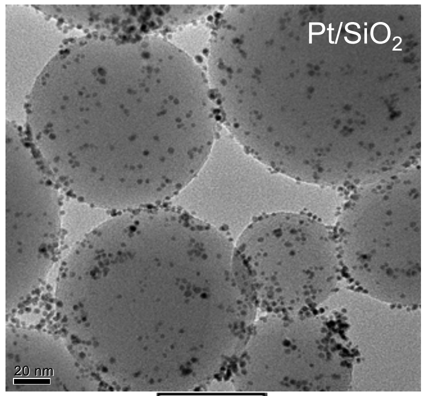
Aerosol-gel process to produce Pt/MOx

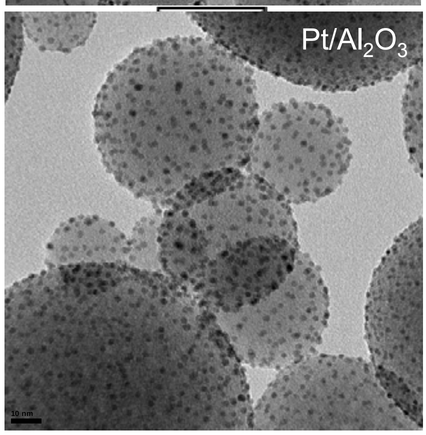


$$Si-OR + HOH \xrightarrow{\text{hydrolysis}} Si-OH + ROH$$

$$\begin{cases} Si-OH + Si-OH \xrightarrow{\text{water condensation}} Si-O-Si + HOH \\ Si-OH + Si-OR \xrightarrow{\text{alcohol condensation}} Si-O-Si + ROH \end{cases}$$





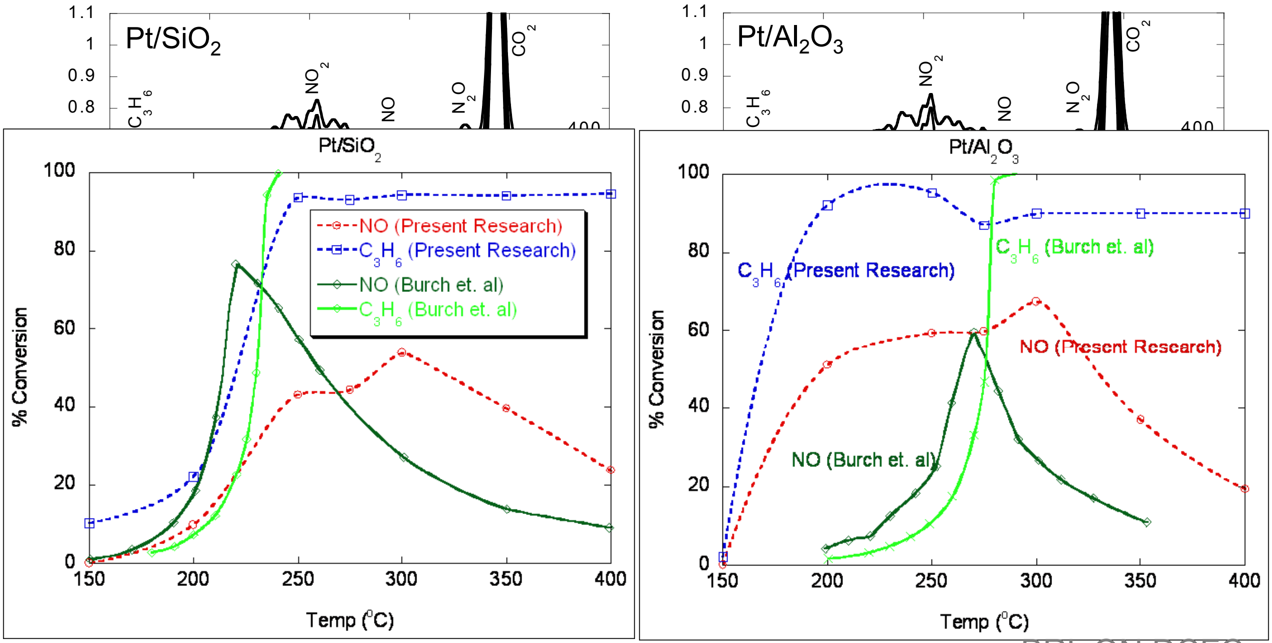


2. Environment

1) de-NOx catalysts

HydroCarbon-based Selective Catalytic Reduction :

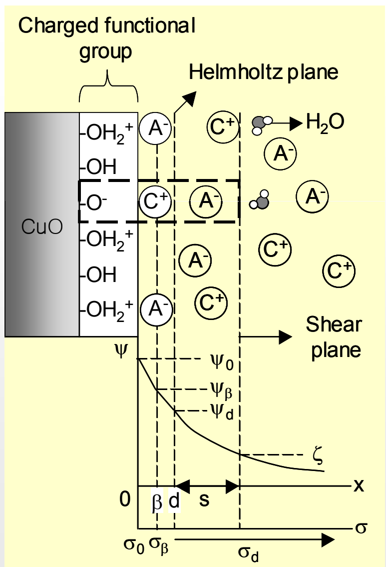
$a\mathrm{NO}+b\mathrm{C_3H_6}+c\mathrm{O_2} \rightarrow d\mathrm{N_2}+e\mathrm{NO_2}+f\mathrm{N_2O}+g\mathrm{H_2O}+h\mathrm{CO_2}$



2. Environment

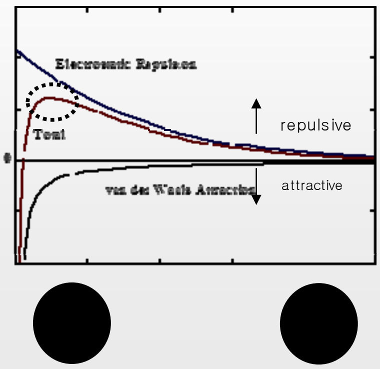
1-1) Colloidal system

Experimental parameters



Interaction between colloidal particles

- DLVO theory
- Electrostatic repulsion
- Van der Waals attraction
- Total interaction



Particle growth

- Suspension stability

$$W = 2r\int_0^\infty \exp\left(\frac{E_{tot}}{k_b T}\right)\frac{dx}{(2r+x)^2}$$

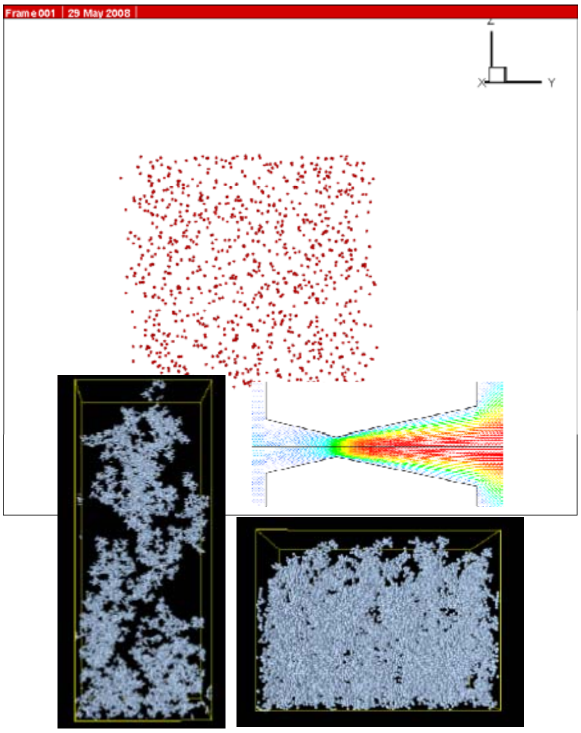
- Particle collision kinetics

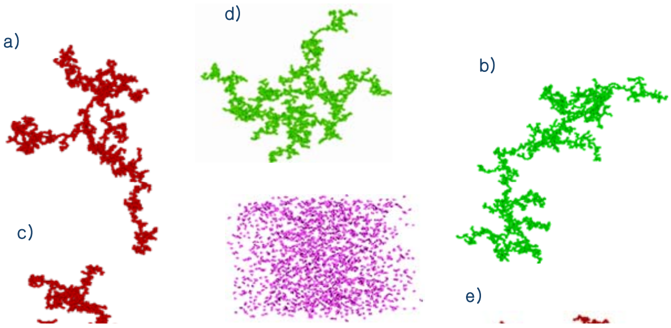
$$k = \alpha k_{diff} = \frac{k_{diff}}{W} = \frac{8k_b T}{3\eta W}$$

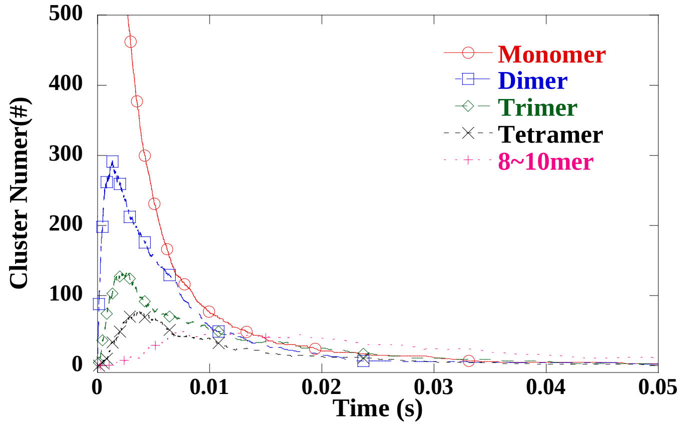
- Microstructure control

2. Environment

1-1) Colloidal system







2. Environment

1-2) Link systematic parameters w/ suspension stability

$$\sigma_0 = F\Gamma_{tot}\frac{10^{-0.566\Delta pH} - 10^{0.566\Delta pH}}{10^{PZC}/K_P + (10^{-0.566\Delta pH} + 10^{0.566\Delta pH})} \approx \frac{F\Gamma_{tot}K_p}{10^{PZC}}\left[10^{-0.566\Delta pH} - 10^{0.566\Delta pH}\right]$$

$$\sigma_s = \frac{F\Gamma_{tot}}{10^{PZC}/K_P + (10^{-0.566\Delta pH} + 10^{0.566\Delta pH})}\left[\frac{10^{-0.566\Delta pH}}{1+K_a a(A^-)10^{-0.434\Delta pH}} - \frac{10^{0.566\Delta pH}}{1+K_c a(C^+)10^{0.434\Delta pH}}\right]$$

$$\approx \frac{F\Gamma_{tot}K_p}{10^{PZC}}\left[\frac{10^{-0.566\Delta pH}}{1+K_a a(A^-)10^{-0.434\Delta pH}} - \frac{10^{0.566\Delta pH}}{1+K_c a(C^+)10^{0.434\Delta pH}}\right]$$

$$\sigma_s = -\sigma_d = -\frac{4000FI}{\kappa}\sinh\left(\frac{F\psi_d}{2RT}\right) \approx -\frac{1051.7\ F^3 I}{\kappa R^2 T^2}\psi_d^2$$

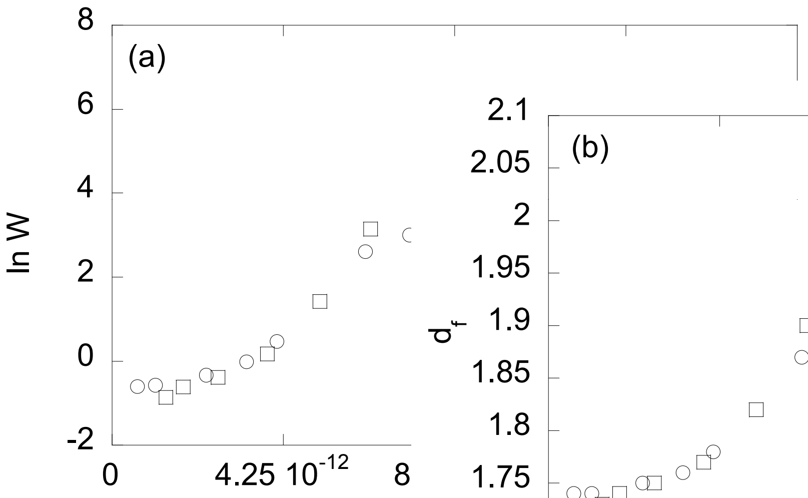
$$\psi_d^2 = \frac{\kappa R^2 T^2 \Gamma_{tot} K_P}{1051.7\, IF^2 10^{PZC}}\left[\frac{10^{-0.566\Delta pH}}{1+K_a a(A^-)10^{-0.434\Delta pH}} - \frac{10^{0.566\Delta pH}}{1+K_c a(C^+)10^{0.434\Delta pH}}\right]$$

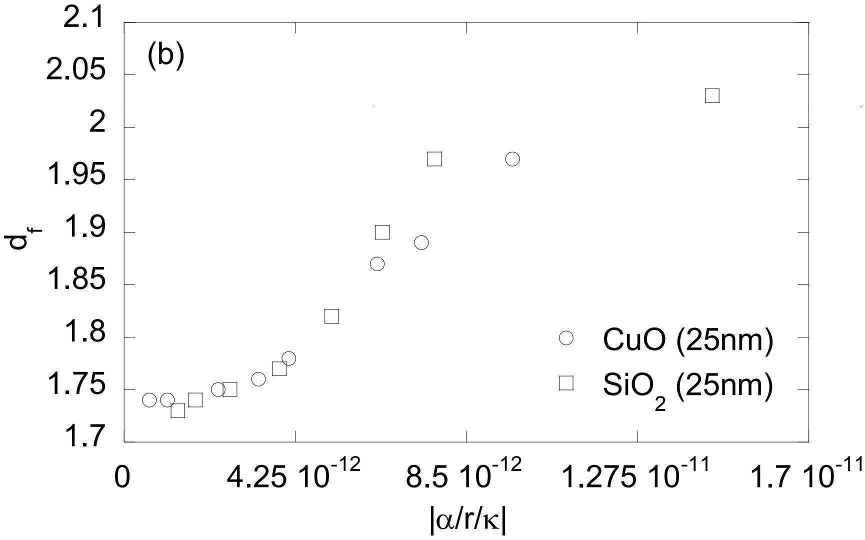
$$U^{el} = 2\pi\varepsilon_0\varepsilon_r r\psi_d^2\exp(-\kappa x)$$

$$U^{el} = \frac{3.803\pi rRT\Gamma_{tot}K_P}{10^{PZC}\kappa}\left[\frac{10^{-0.566\Delta pH}}{1+K_a a(A^-)10^{-0.434\Delta pH}} - \frac{10^{0.566\Delta pH}}{1+K_c a(C^+)10^{0.434\Delta pH}}\right]\exp(-\kappa x)$$

2. Environment

1-2) Link systematic parameters w/ suspension stability





$$U_{tot,max} \approx \frac{\alpha}{\kappa}(1-\kappa x_{max}) - \frac{\beta}{x_{max}}$$

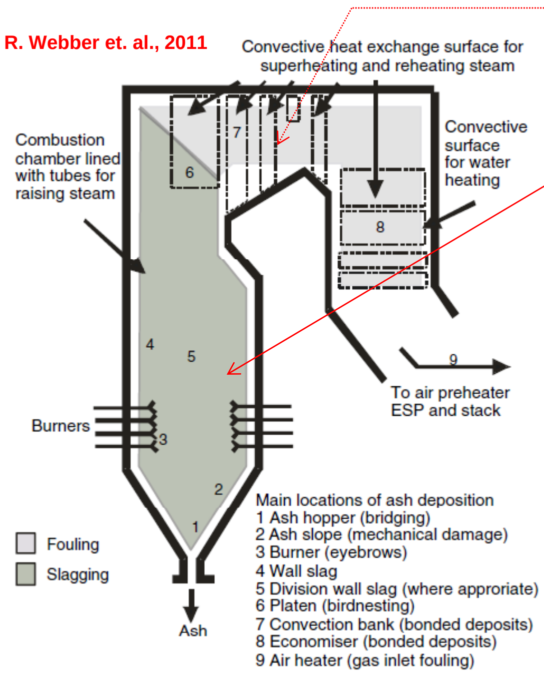
$$\ln(W) = \frac{U_{tot,max}}{k_b T} \approx \frac{1}{k_b T}\left(\frac{\alpha}{\kappa} - 2\sqrt{\alpha\beta}\right)$$

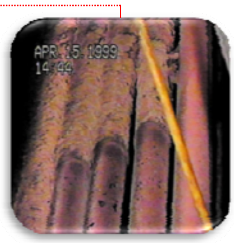
BRL ON DCFC

2. Environment

2) S effect on slagging

Slagging & Fouling Trouble at Pulverized Coal Fired Boiler





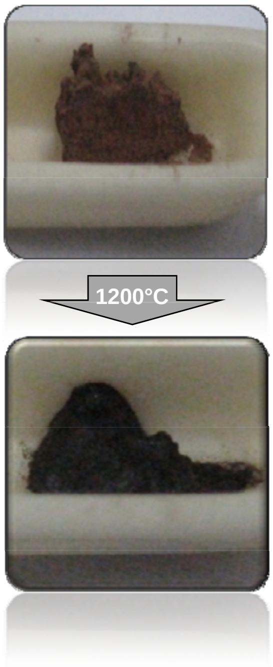
Ash deposition at furnace wall, super heater & reheater tube surface

- Degrade heat transfer efficiency
- Boiler damage by fallen clinker (5 tons)
- Blockage at the bottom of PC boiler

Need to understand the mechanism of the slagging & fouling & clinker formation

2. Environment

2) S effect on slagging



Ash composition

Species	Melting Point (°C)
Fe_2O_3	1566
SiO_2	1600
$CaSO_4$	1460
MgO	2852
Al_2O_3	2072
CaO	2572

ICP-AES

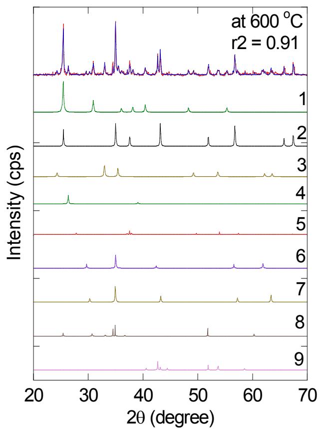
Element	Si	Fe	Al	Ca	K	Na
Atomic %	48	29	5.6	11.4	3.2	2.0

XRD

Phase	Fe_2O_3	Al_2O_3	$CaSO_4$
% Mol	58.4	8.6	33

Major species : glassy SiO_2 + Fe_2O_3+ $CaSO_4$

Minor species : Al_2O_3 + Alkali metal compounds



No.	Crystalline Phase	JCPDS No.
1	CaSO4	86-2270
2	Al2O3	88-0826
3	Fe2O3	84-0309
4	SiO2	87-2096
5	Ca2Fe2O5	18-0286
6	Fe3O4	82-1533
7	Fe2SiO4 [2]	80-1625
8	Fe2SiO4 [1]	87-0315
9	CaFe3O5	31-0274

Peak observation w/ ramping T

↘ $CaSO_4$, Fe_2O_3, SiO_2

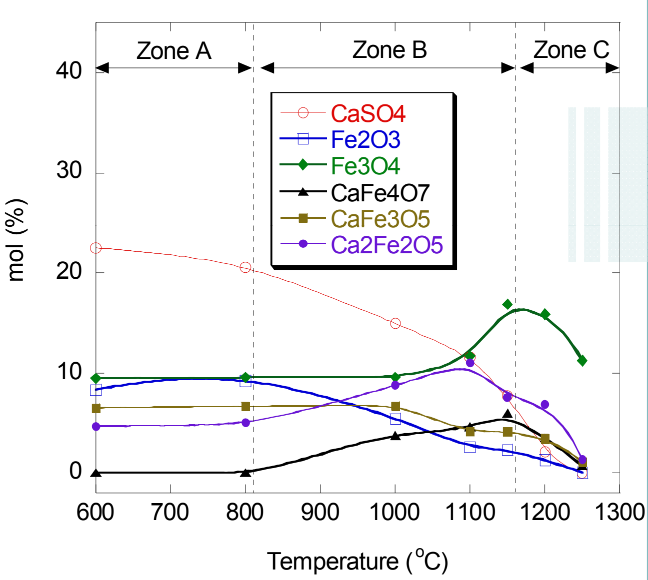
↗↘ $Ca_2Fe_2O_5$, $CaFe_3O_5$, $CaFe_4O7$, Fe_2SiO_4, Fe_3O_4 at 1100-1150°C

BRL ON DCFC

2. Environment

2) S effect on slagging

HT-XRD Indicates



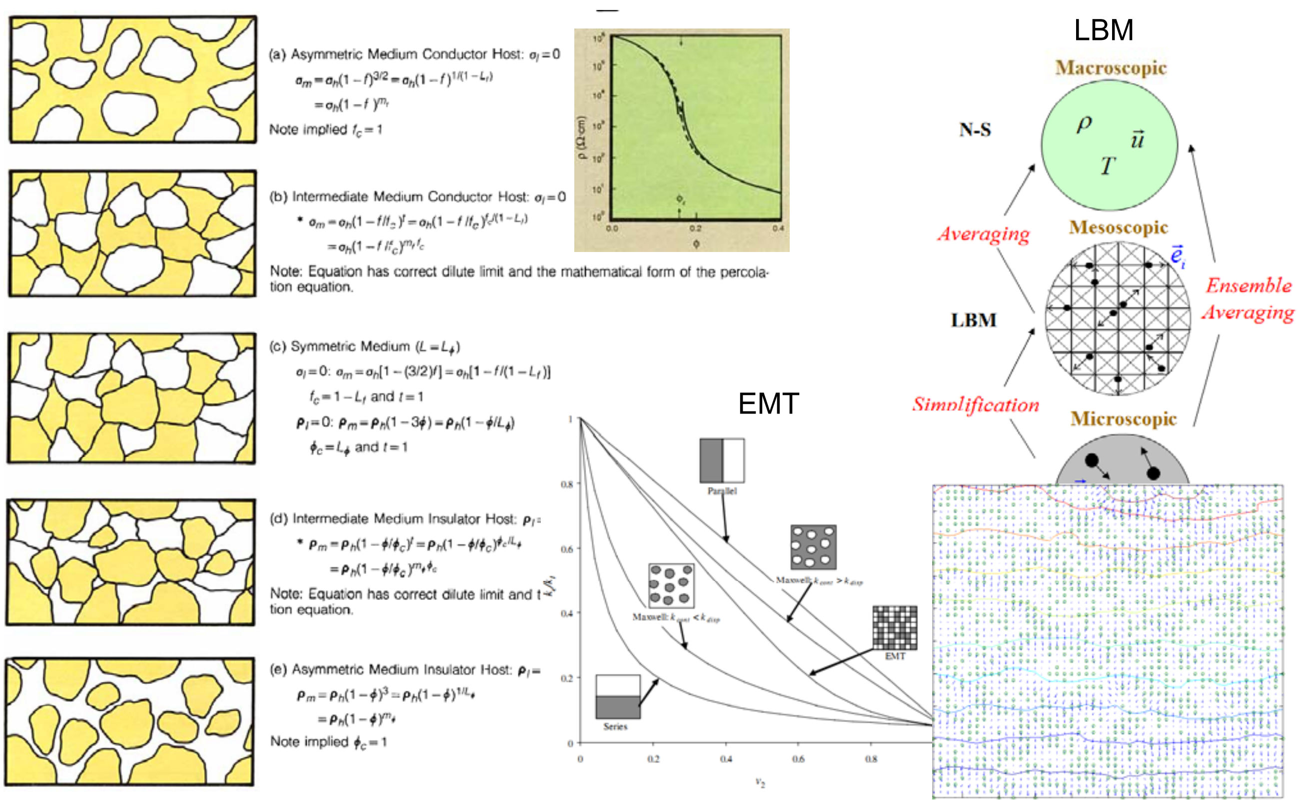
Zone A — Below Reaction Zone: < 800°C

Zone B — Reaction Zone: 800~1150°C
$CaSO_4$ reacts w/ Fe_2O_3 to form various forms of Calcium ferrite formation

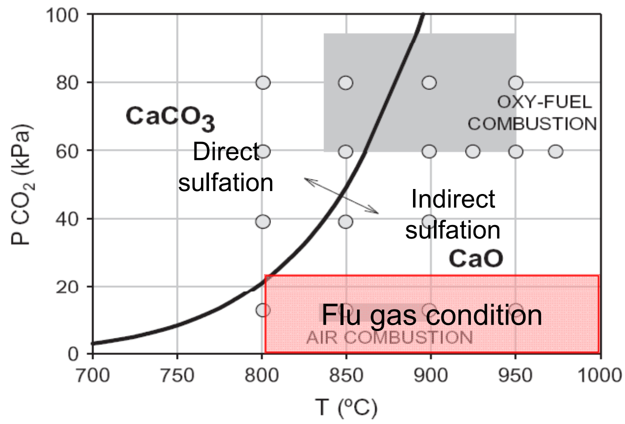
Zone C — Melting Zone: > 1200°C
Calcium ferrite begins to melt

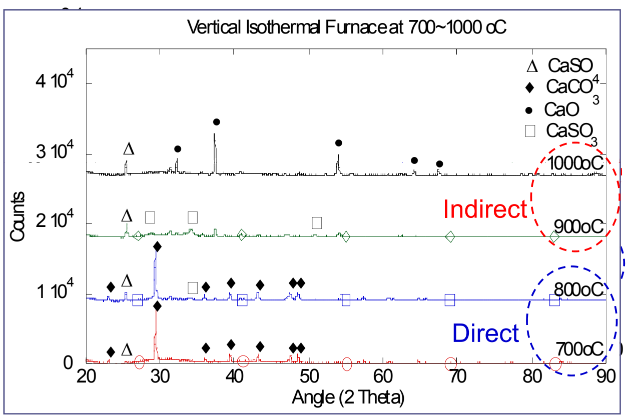
Potential Reaction pathway

1. $CaSO_4 + 3Fe_2O_3 \rightarrow CaF_3O_5 + Fe_3O_4 + SO_2 + O_2$
2. $CaSO_4 + 2Fe_2O_3 \rightarrow CaFe_4O_7 + SO_2 + 0.5O_2$
3. $2CaSO_4+Fe_2O_3 \rightarrow Ca_2Fe_2O_5+SO_2+2O_2$
4. $2CaSO_4+4Fe_2O_3 \rightarrow Ca_2Fe_2O_5+2Fe_3O_4+SO_2+2.5O_2$



Indirect sulfation	Direct sulfation
$CaCO_3 \leftrightharpoons CaO + CO_2\uparrow$--------- Decomposition $CaO + SO_2 + 1/2O_2 \leftrightharpoons CaSO_4$---- Sulfation	$CaCO_3 + SO_2 + 1/2O_2 \leftrightharpoons CaSO_4 + CO_2\uparrow$



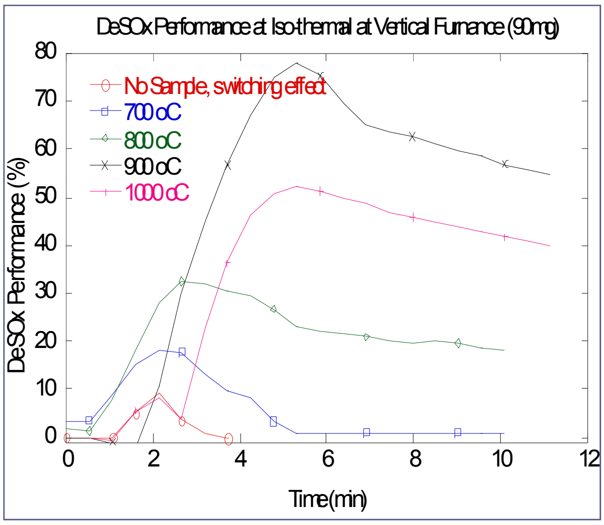


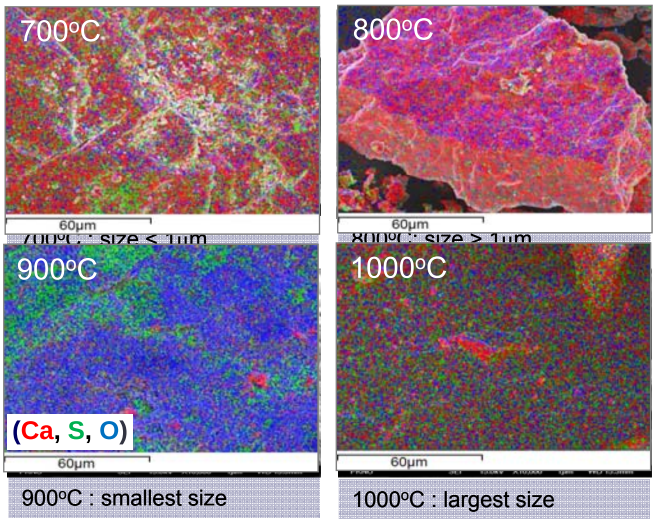
Flu gas condition
- T : 800～1500°C
- CO_2 : 23%
- O_2 : 5~6%
- N_2 : 70~75%

- TGA indicates that T > 800°C to decompose $CaCO_3$
- XRD indicates that below 800°C, Direct sulfation occurs
- above 900°C, Indirect sulfation occurs w/ $CaSO_3$ formation

2. Environment

3) de-SOx catalysts





$$CaCO_3 \xrightarrow{T \geq 800^\circ C} CaO + SO_2 \xrightarrow{T \leq 900^\circ C} CaSO_3 + 1/2O_2 \xrightarrow{T \leq 1000^\circ C} CaSO_4 \xrightarrow{T \geq 1000^\circ C} CaO$$

When T > 1000°C,

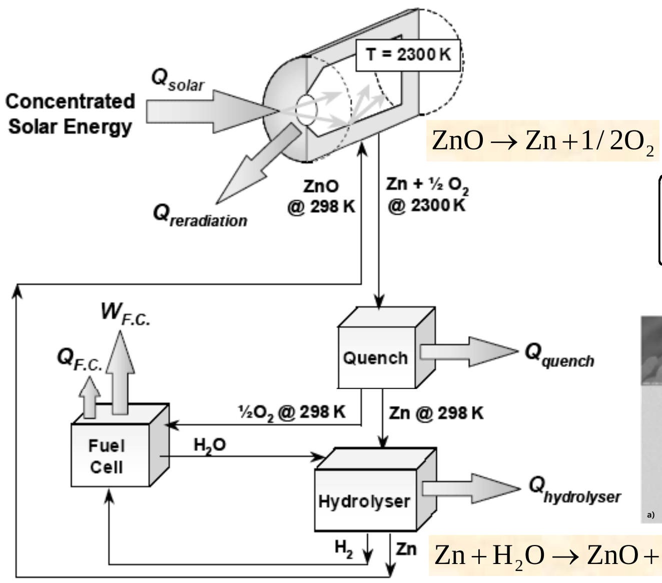
de-SOx (indirect sulfation) efficiency degraded due to sintering & decomposition of $CaSO_4$

2. Environment

4) C-free H_2 production

Concept of two-step thermo-chemical cycle

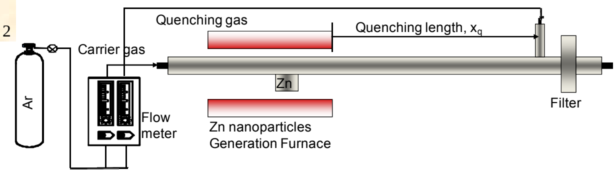
- Easy scale-up like CFB + CYRO
- Low-temperature splitting is possible
- Various MOx can be used

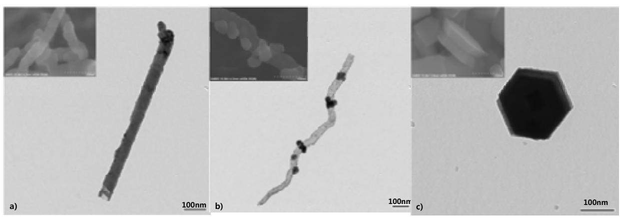


$ZnO \rightarrow Zn + 1/2O_2$

$Zn + H_2O \rightarrow ZnO + H_2$

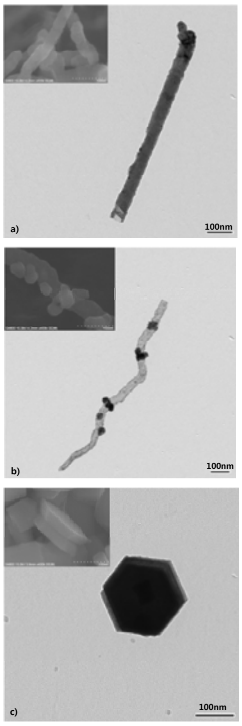
$Zn + \beta CO_2 + (1-\beta)H_2O \rightarrow ZnO + \beta CO + (1-\beta)H_2$

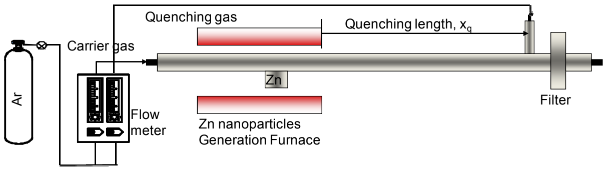


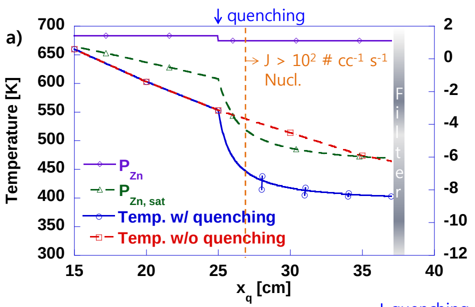


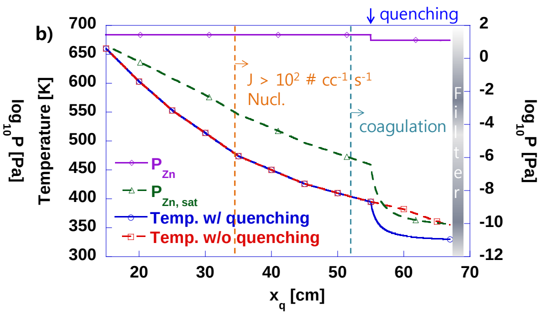
2. Environment

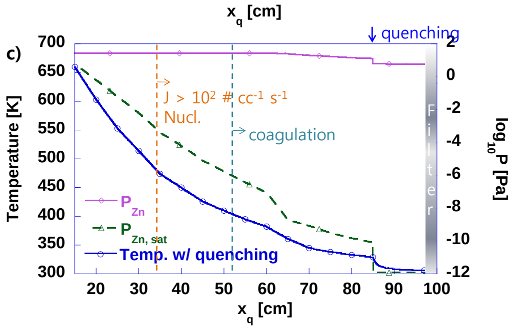
4) C-free H_2 production









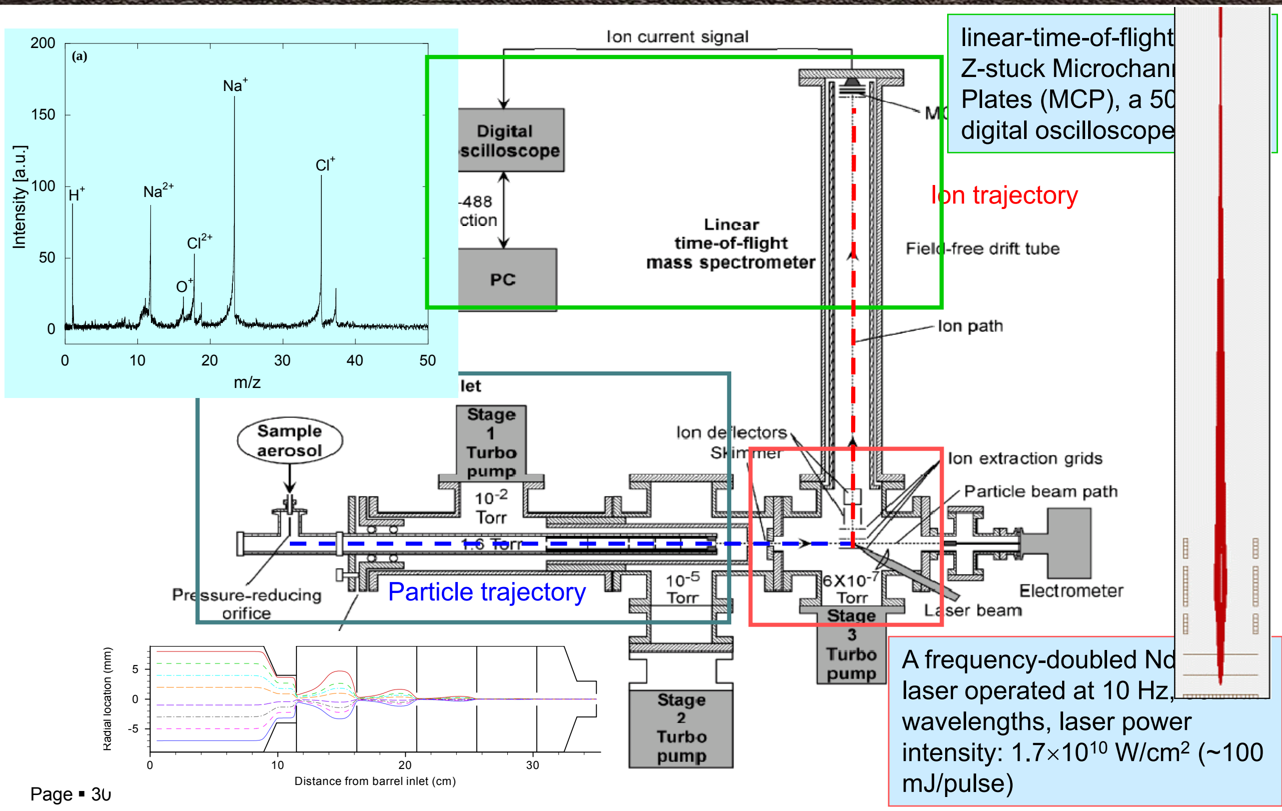


- 25cm : nucleation & condensation
- 55cm : nucleation & coagulation
- 85cm : sintered hexahedral crystal

BRL ON DCFC

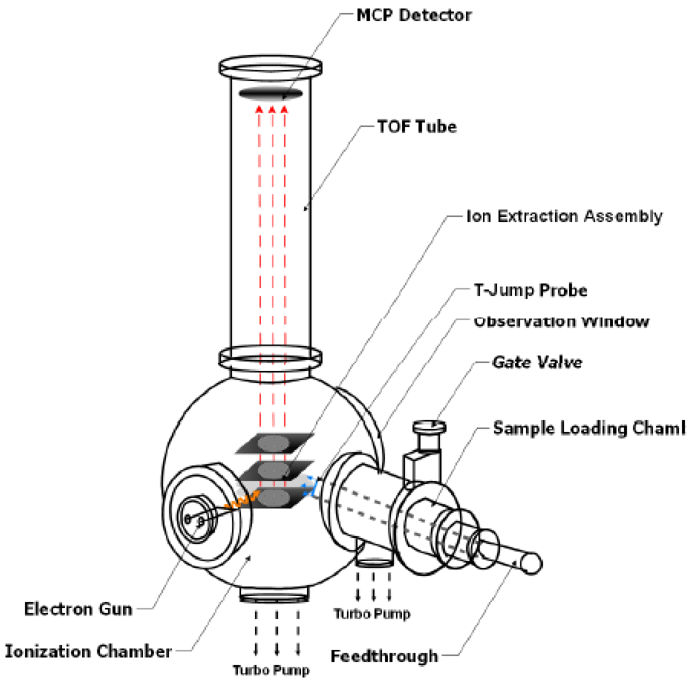
3. Instrumentation

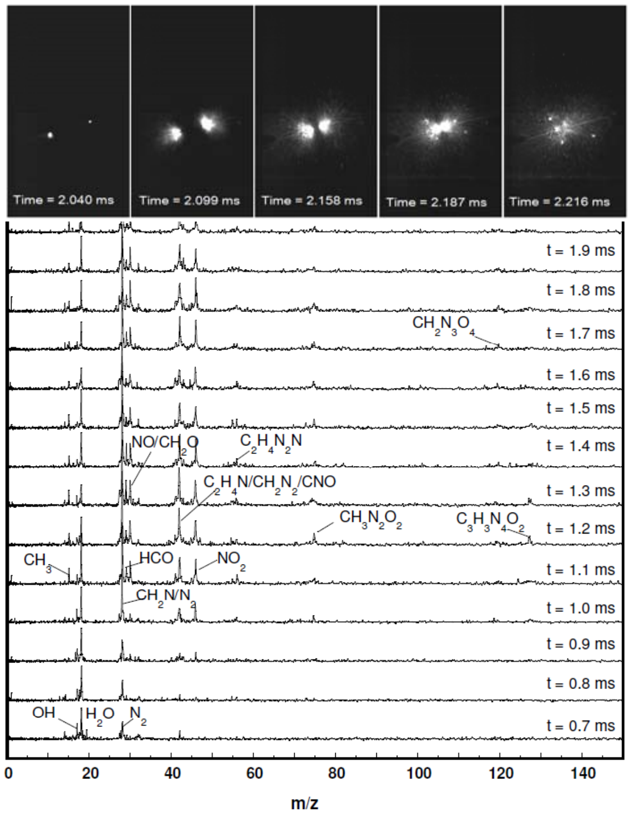
1) SPMS



3. Instrumentation

2) T-jump MS





Acknowledgement