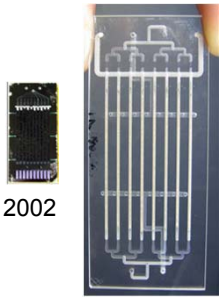
マイクロリアクターは化学プロセスに どう役立つか（過酸化水素製造を中心に）



2002

2008

2013

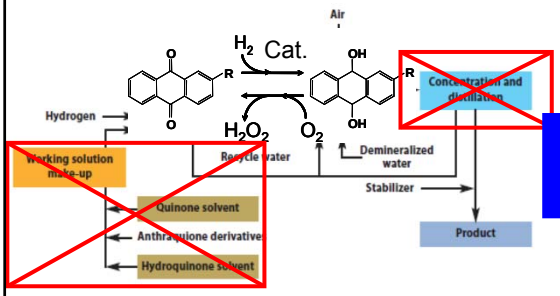
2014年7月4日
UMEMSME-AIST
井上　朋也

本日の話題

1. 背景～過酸化水素X直接製造Xマイクロリアクター
2. マイクロリアクター～デザインX触媒反応解析
3. まとめ、と、やりのこし

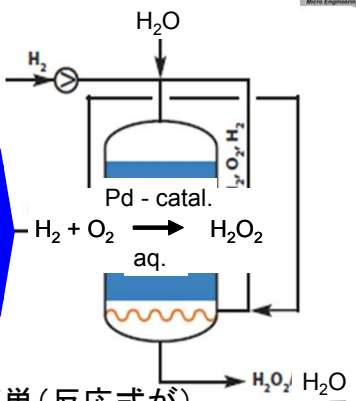
1. H_2O_2 – its process

アントラキノン法（もうそろそろ70歳）



-複雑。
-60%に濃縮して出荷。
コンビナート向き。
-有機物（炭素分）の除去が
課題の1つ。

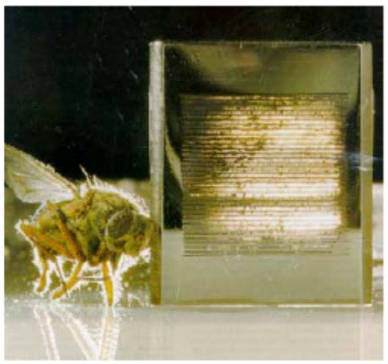
直接法
（まだ産まれてません）

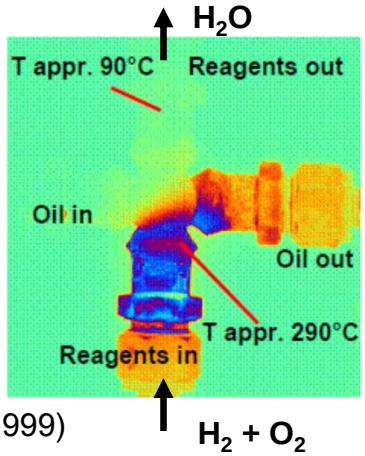


-簡単（反応式が）。
-オンサイト向き。
（そのまま使えれば）
-有機物は混入は防げる。
（溶媒次第）

Microreactor for…H_2-O_2 reaction

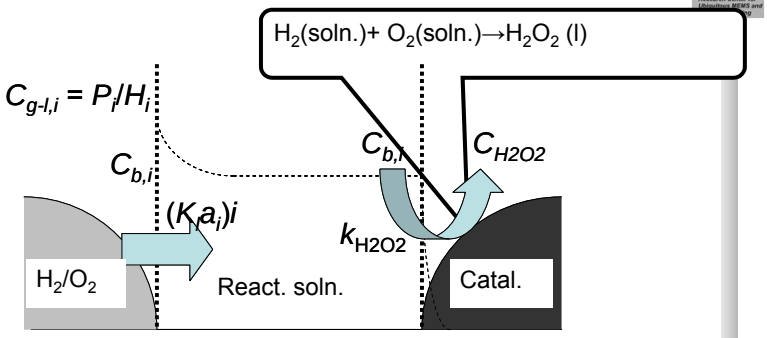
-幅300 μm マイクロチャンネルによる爆発反応の完全制御
(Max Planck　+ FZK, 1998)





(Max Planck Inst. Annual Report, 1999)
-触媒をコートしたマイクロチャンネル。

もちょっと複雑な直接製造法



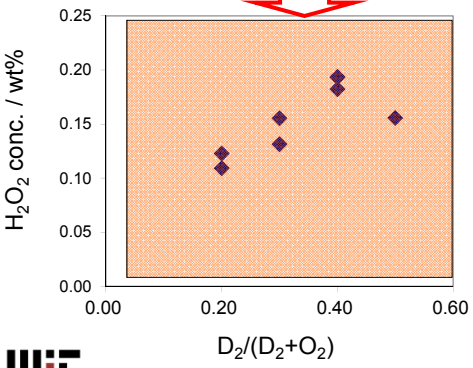
-実際には水素も酸素もいったん水に溶けて、溶存水素および酸素が触媒上で反応する(どちらも溶けづらいが)。
-気液固の共存は必須。
-物質移動効率は、高いほどよい。

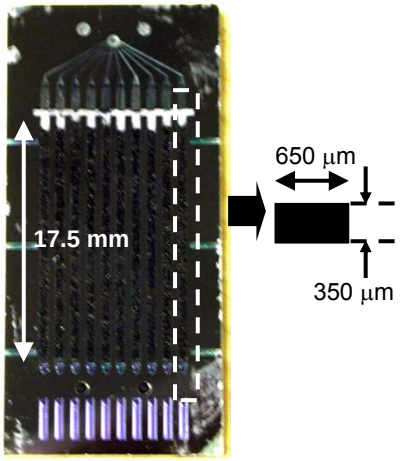
・・・どういう反応器がよいのか？

2. Microreactor - for the Direct H_2O_2

*Rapid heat removal (+ radical termination) at a channel wall = Perfectly controlled H_2-O_2 reaction

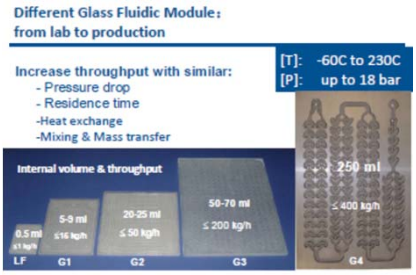
All conditions are in ***explosive region***.

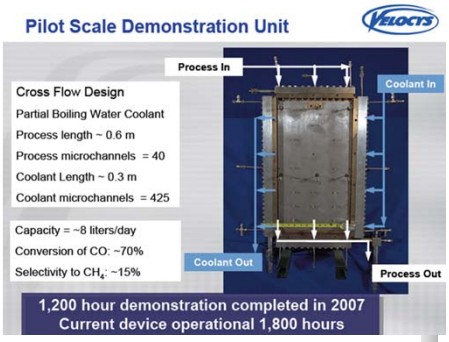




Inoue, T., et al.,IMRET7, (2003).
Inoue, T., et al., IECR 2007, **46**,1153.

誰かつくってくれませんか



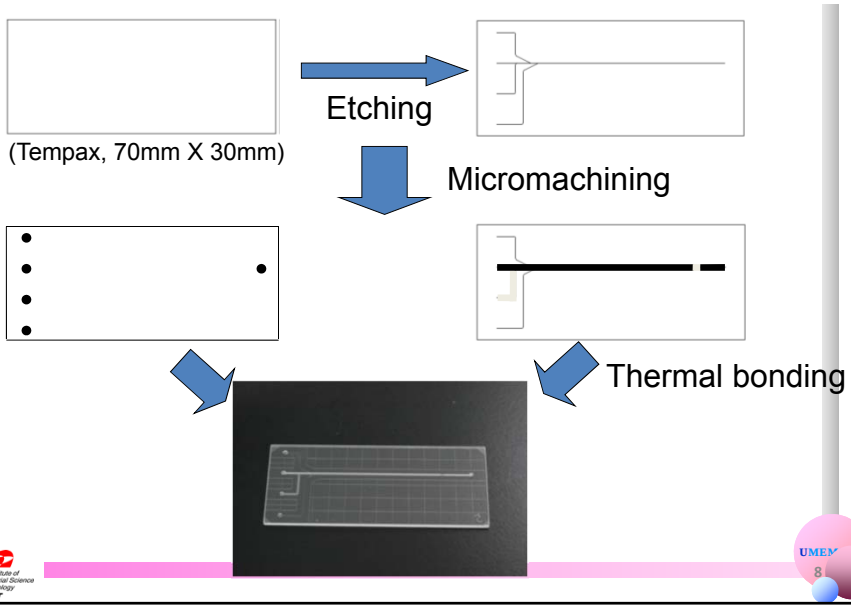


Corning: ものを詰めるのは不可。

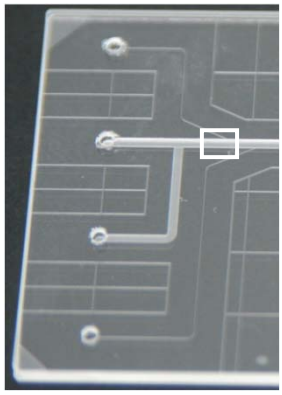
Velocys: 気相反応。いきなり購入するのも・・・

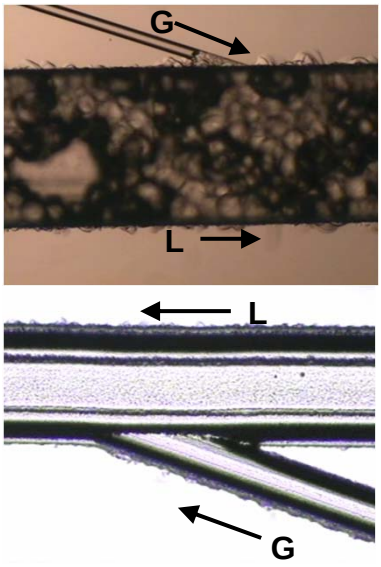
・・・やはり自分でつくります。

Reactor fabrication – for single bed



安定な“気液混相流”をつくる



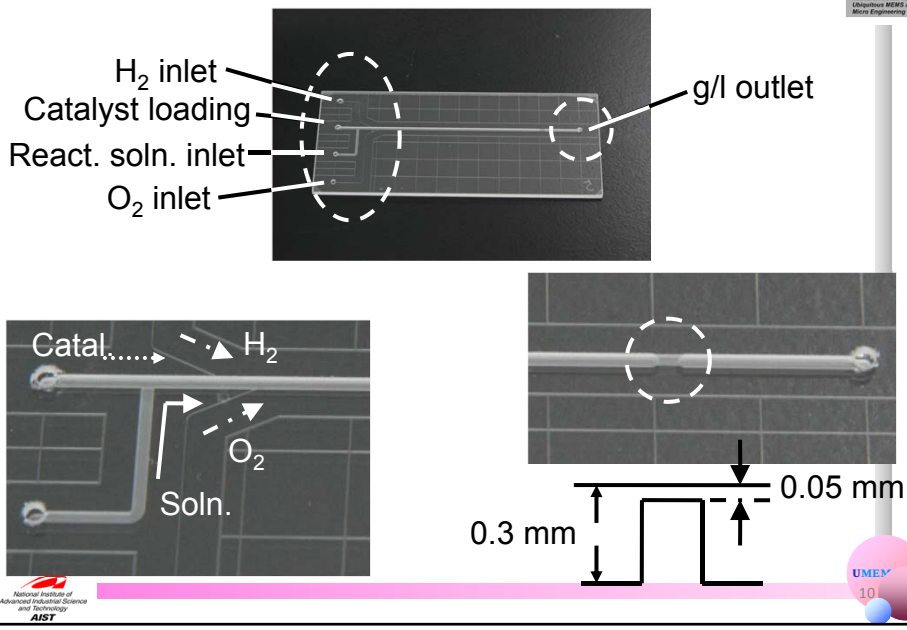


*$\Delta P \propto \mu, v_s$

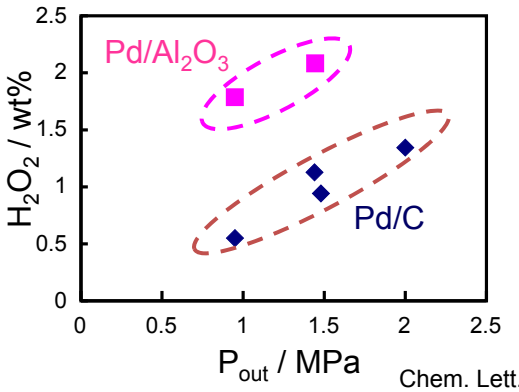
($\mu_g \sim 10^{-3}$cP, $\mu_l \sim 1$cP)

Chem. Eng. J., **160**, 909 (2010).

正しいシングルベッド



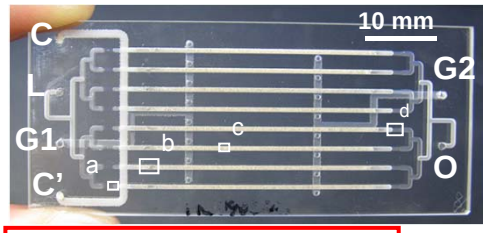
気液が正しく流れれば・・・

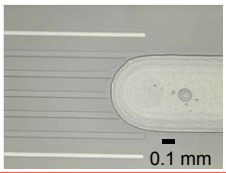


Chem. Lett. **38**, 820 (2009).
Chem. Eng. J. **160**, 909 (2010).

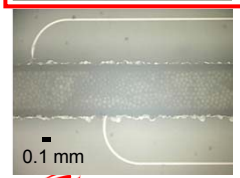
・・・マイクロリアクターは、“理想的な”反応場である。

Reactor design

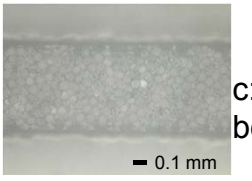




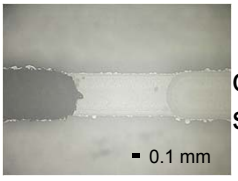
a: reaction solution distribution



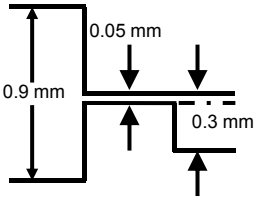
b: gas-liquid mixture



c: packed bed

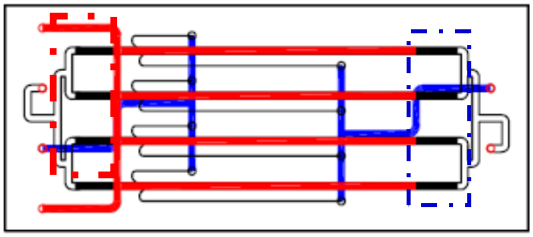


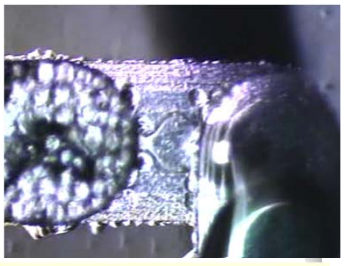
d: dam structure

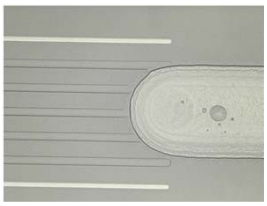


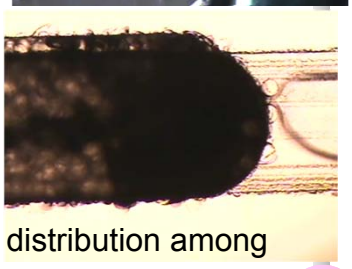
Go #-up successful

V_L=0.04 ml/min (0.01 x4)
V_G=2.0 sccm (0.5 x4)





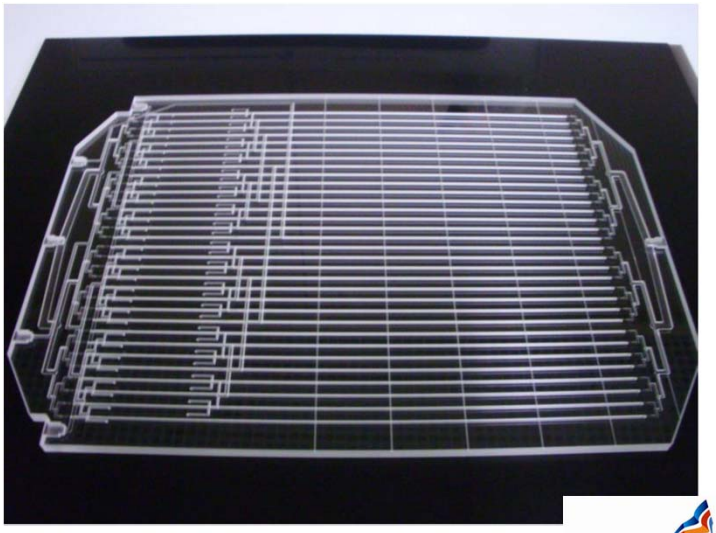




- Liquid distributor validates equal flow distribution among channels.

Proc. mTAS. **2010**, 1694.
JJAP. **51**, 06FK11 (2012).

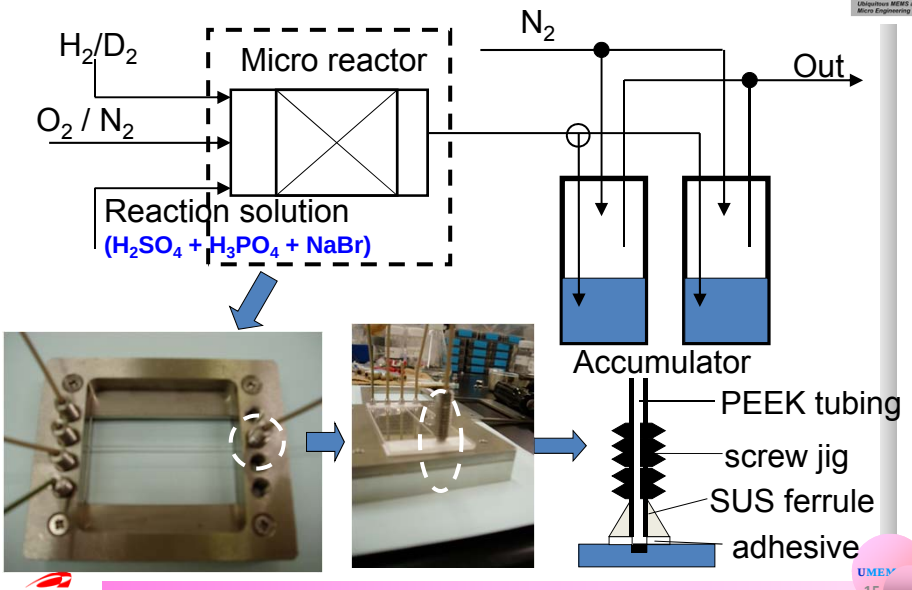
How 32ch reactor looks like?



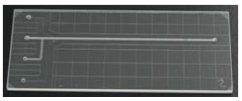
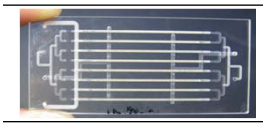
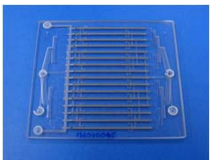
(to be in ナノテク展2014)

tecnisco

反応評価



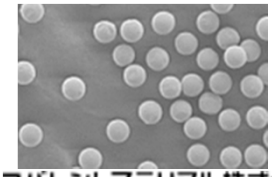
Reactor performances

Reactor (Pd1-Au0.7/TiO_2, Au/Pd=0.7) 1MPa, ca. 296 K	$H_2/(H_2+O_2)$ (Liq. rate [$mLmin^{-1}$], gas rate [sccm])	H_2O_2 C_{H2} [%]	S_{HO} [%]	W_{HO} [wt%]	Rate (cat. wt) [$10^{-4}molh^{-1}$ (g)]	T_{surf} [K]
	0.2 (0.01, 5.0)	15	86	2.9	3.6 (0.017)	295
	0.2 (0.08, 40)	30	90	2.8	39.2 (0.121)	297
	0.2 (0.16, 80)	49	68	4.4	123 (0.271)	*313*
	0.1 (0.16, 80)	24	79	1.5	41.4	296

・・・ちゃんと“ナンバリングアップ”できました。

触媒・・・

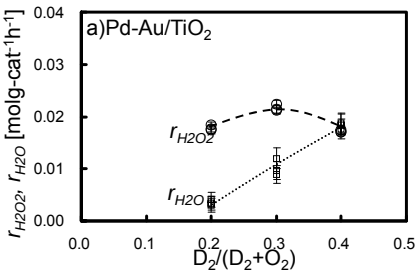
-Pd/Al_2O_3 was purchased from N. E. Chemcat Co. (5 wt%).
-Pd/TiO_2 and $Pd\text{-}Au/TiO_2$ were prepared by (co-) Impregnation, using chloride as metal resources.
-Support morphology: spherical, 0.06 mm diameter, monodispersed.

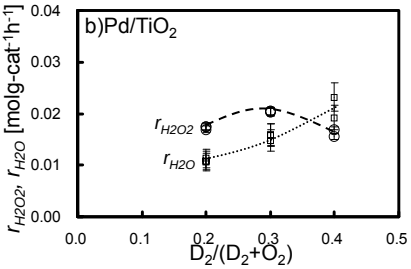


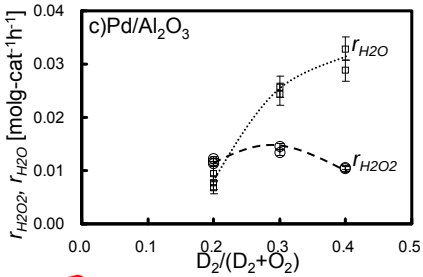
コバレントマテリアル株式会社

	Productivity	⊿P	Stability	S. A.
TiO_2	◎ (10%)	◎(<0.1 MPa)	○	△($16m^2g^{-1}$)
C	△ (1-2%)	× (>0.4MPa)	× (burn off)	◎ ($200m^2g^{-1}$)
Al_2O_3	○ (6%)	◎(<0.1 MPa)	◎	◎

What is different?







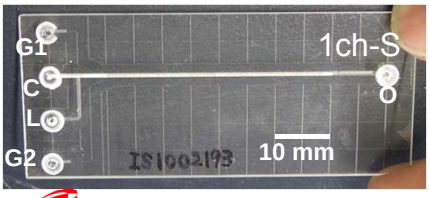
-Reaction scheme:
1: $H_2+O_2 \rightarrow H_2O_2$
2: $H_2O_2+H_2 \rightarrow 2H_2O$

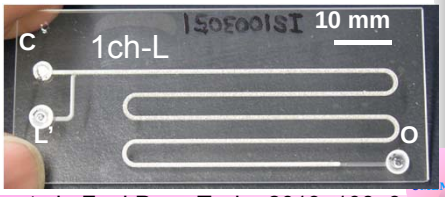
-TiO_2 supported catalyst suppresses 2, also with Au modification.

Fuel Proc. **108**, 8 (2013).

Reactor performances @ 1 MPa, RT.

Catalyst / reactor	Inlet condition $D_2/(D_2+O_2)$ (f_L, f_G)	D_2 conversion / D_2O_2 (H_2O_2) production			
		C [%]	*S* [%]	*W* [wt%]	rate[b]
Pd/Al_2O_3 (N. E., 5 wt%)					
8ch-S	0.1 (0.01, 40)	48	20	*6.3*	10.2 (0.7)
Pd/TiO_2					
1ch-S+1ch-L	0.3 (0.01, 5.0)	81	46	*10.4*	14.9 (1.2)
Pd-Au/TiO_2 (Pd1-Au0.5)					
8ch-S	0.175 (0.01, 40)	22	50	*11.7*	20.5 (1.5)
1ch-S+1ch-L	0.3 (0.01, 5.0)	80	45	*9.9*	14.4 (1.2)





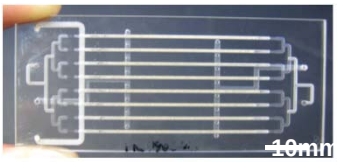
Inoue, T., et al., Fuel Proc. Tech., 2013, 108, 8.

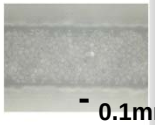
3. まとめ・・・

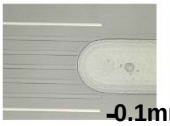
Conventional

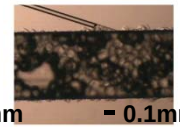
- Batch / CSTR
- 5.0～9.5 MPa
- H_2: 3.6 vol. %

AIST









-Reaction conditions become moderate, by *intensified heat/mass transfer.*

- PFR / Fixed-bed
- 1.0 MPa↓
- H_2: 10 vol. %↑