Electrochemical reactions of organic compounds in sub- and supercritical fluids

Mitsuru SASAKI[1], Takanari Oshikawa[1], Wahyudiono[1], Tsuyoshi Kiyan[1], Hidenori Akiyama[2], and Motonobu Goto[2]

[1]Graduate School of Science and Technology, Kumamoto University, Japan

[2]Bioelectrics Research Center, Kumamoto University, Japan

Acknowledgment

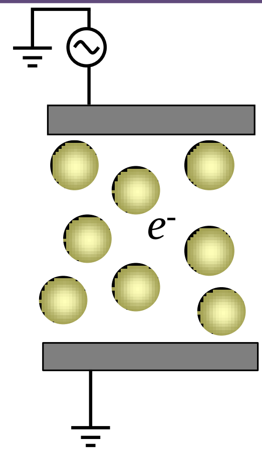
We would like to thank the Kumamoto University Global Center of Excellence (COE) Program “Global Initiative Center for Pulsed Power Engineering” and Ministry of Environment in Japan (K1904, K2049 and K2180) for their financial support.

Nano-pulsed arc discharge

Under high-pressures

-Electrons cannot be accelerated because of their collision with molecules

- No plasma generation due to lack of energy



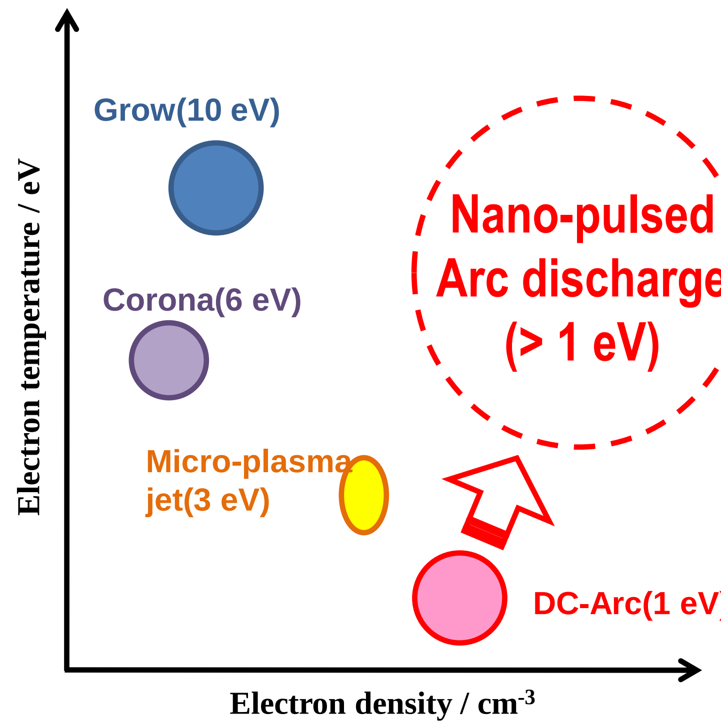
Solutions:
- **Reduce numbers of molecules**
- **Higher energy of each electron**

Impressed voltage at small space (Micro-plasma)

Impressed voltage within short time (This work)

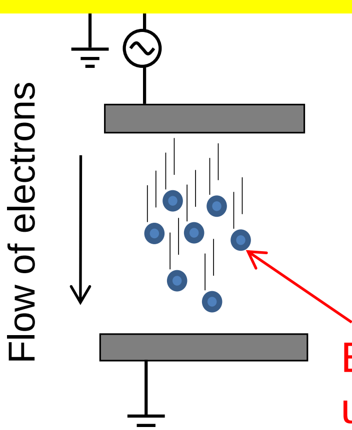
The atmosphere with high electron density and high activation energy

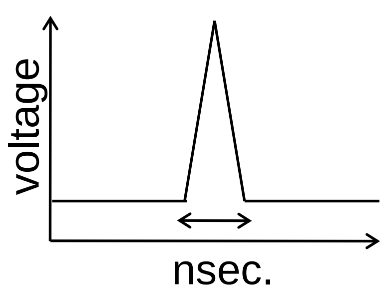
Electron temperature and density of plasmas[1]



Pulsed Power Technology

Enable to provide extremely high energy within nano-seconds





Electrons are accelerated under strong electric fields

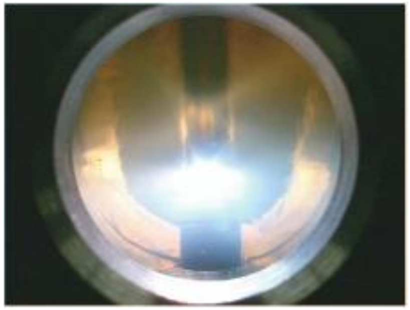
□電子が電場により加速されている
→高い電子温度（活性化エネルギー）を示す
□ナノ秒スケールの立ち上がり/下がり
→媒質に及ぼす熱的影響は少ない（非熱的）

(1) T. Nozaki *J.Plasma Fusion Res.*, 85 3 (2009) 129-130

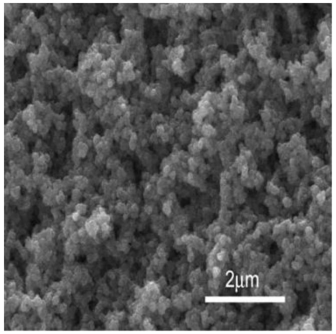
Material synthesis with SCF-Discharge plasma

Nano-sized particles have been synthesized with supercritical carbon dioxide and argon, etc.

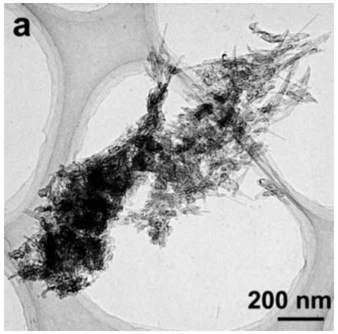
SCF-discharge plasma	・Higher electron density than gas phase discharge ・Improve crystallinity on the crystal growth step ・Lower plasma temperature than liquid plasma



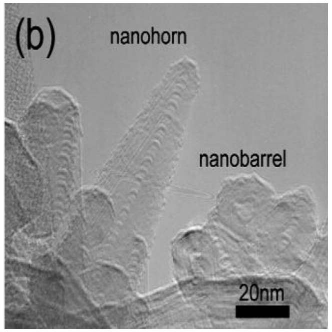
Discharge in supercritical argon



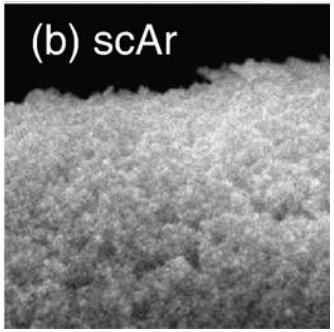
SC-CO2
Barrier discharge[(1)]



SC-CO2
Barrier discharge[(2)]



SC-CO2
Microplasma[(3)]



SC-Argon
Microplasma[(4)]

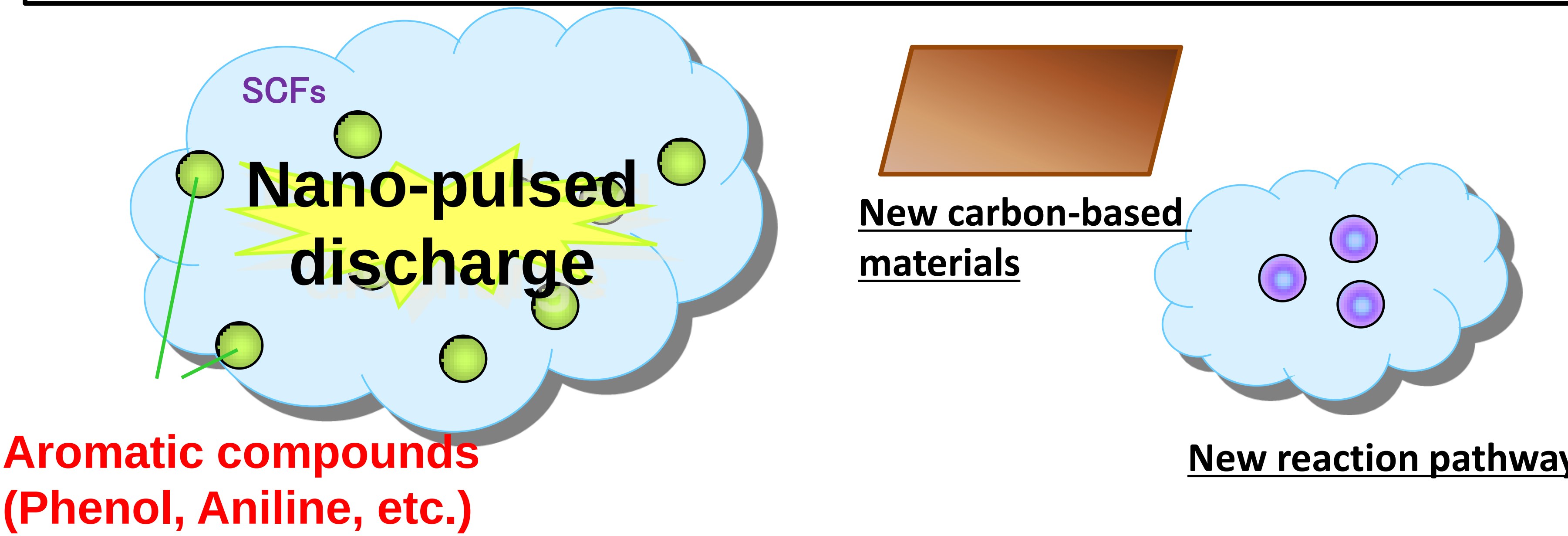
Recent problems

- Unknown reaction mechanism on the reactions in supercritical fluids with plasma
- A few researches have been reported

(1) T. Tomai et al., *Thin Solid Films*, **506-507** (2006) 409-413.
(2) T. Ito et al, *J. Mater. Chem.*, **14** (2004) 1513-1515.
(3) T. Tomai et al., *J. of Supercritical Fluids*, **41** (2007) 404-411.
(4) H. Kikuchi et al., *Thin Solid Films*, **516** (2008) 6677-6682.

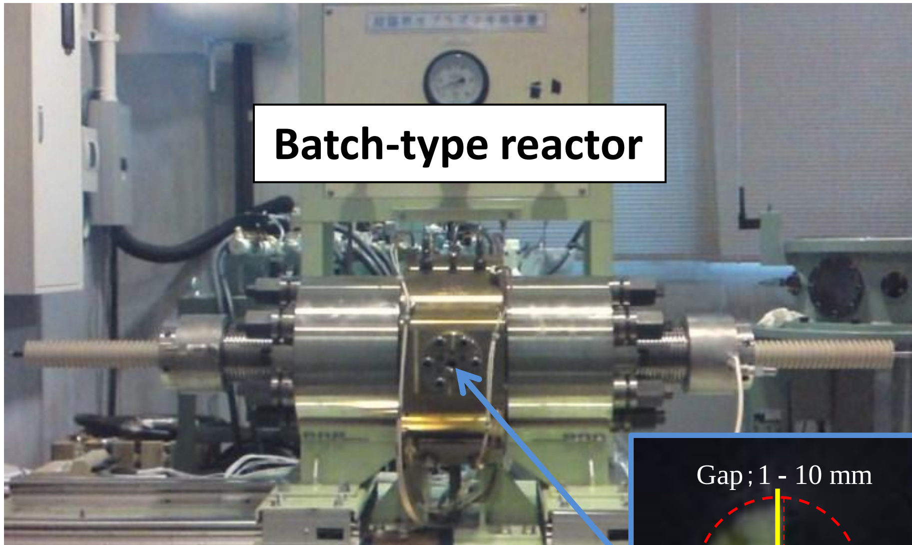
Purpose of this work

Development of a new method for useful carbon-based materials with pulsed discharge in sub- and supercritical fluids



1. **Nano-pulsed discharge reaction of organic compounds in supercritical Ar**
2. **Nano-pulsed discharge reaction of organic compounds in subcritical H_2O**

SCFs nano-pulsed discharge reactor



Material	:	SUS316
Max temp	:	360 °C
Max press	:	30 MPa
Volume	:	900 mL

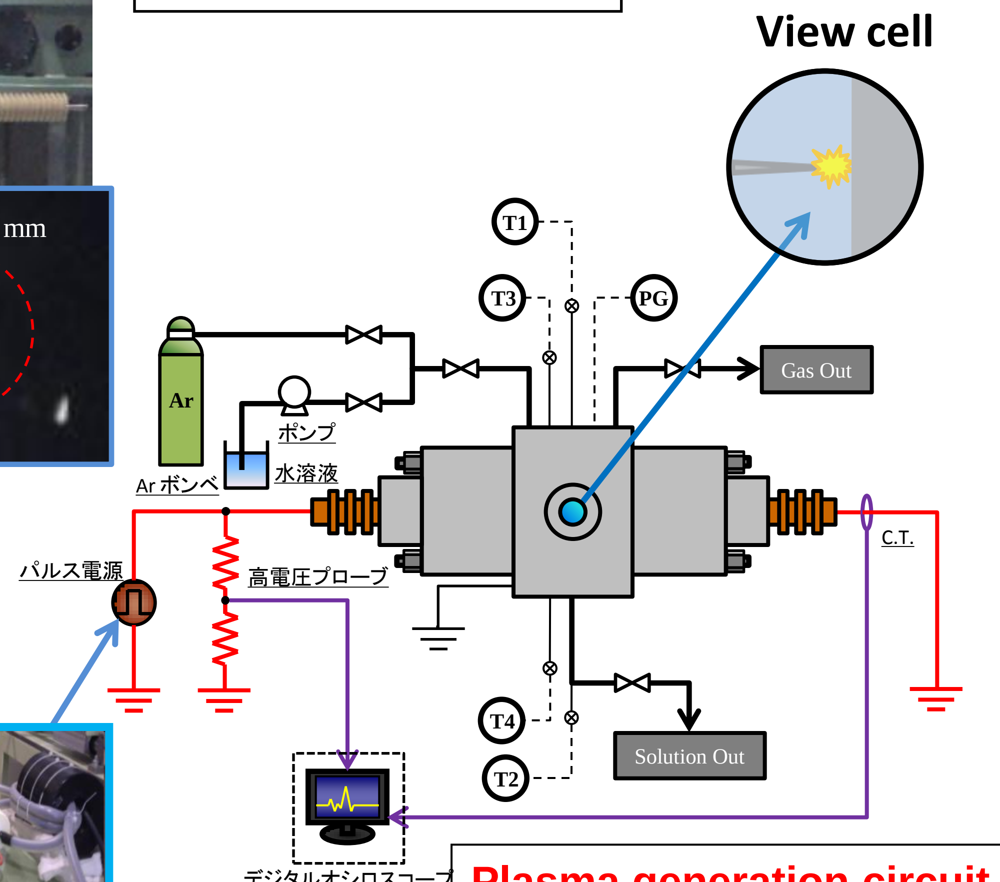
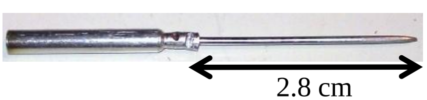
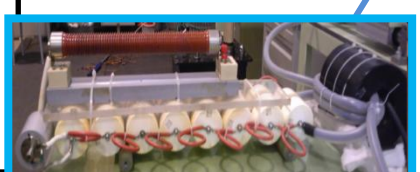


Plate electrode:
(Electro emission)
Stainless steel
(Fe, Cr, Ni, …)
Surface area: 3 cm^2



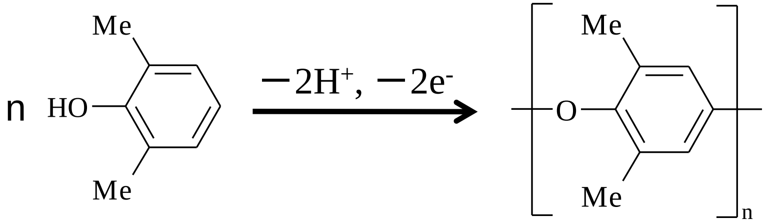
Needle-type electrode:
Tungsten (W)



Repetition frequency: 4 ~ 250 pps

Plasma generation circuit
Oscilloscope

Phenyleneoxide polymers



2,5-dimethoxy phenol

Polyphenylene ether

Conventional methods

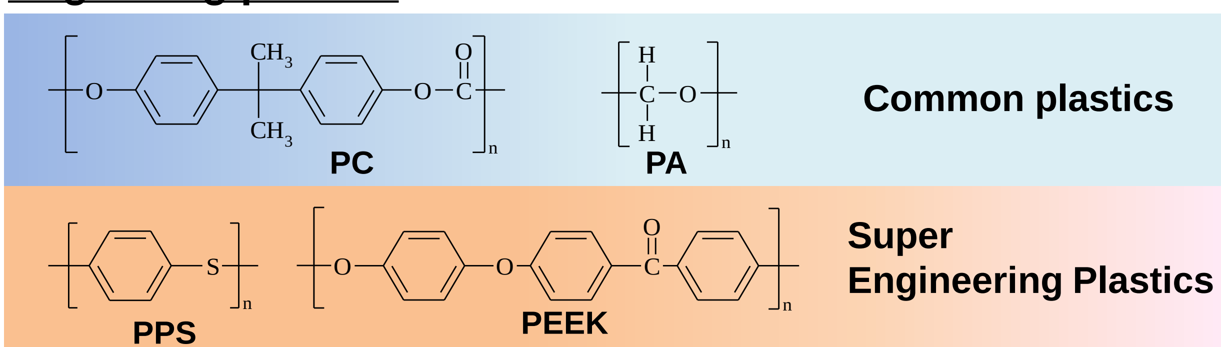
- ✓Polymerization with Cu cat.
- ✓Electric oxidation polymer.
- ✓Oxidation polymer. with transfer metal complex

⋮

Problems

- ✓Hard to control molecular weight distribution
- ✓Hard to separate products
- ✓Small-scale synthesis

Engieering plastics



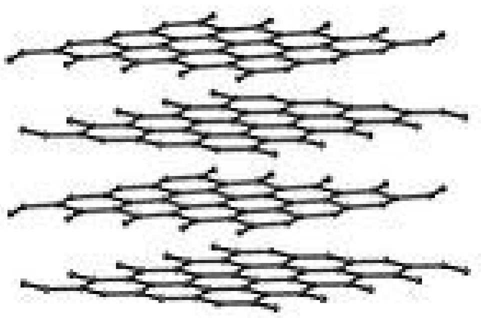
- High functionality
- Use in many fields

Target on the sc-Ar treatment

Carbon-based functional materials

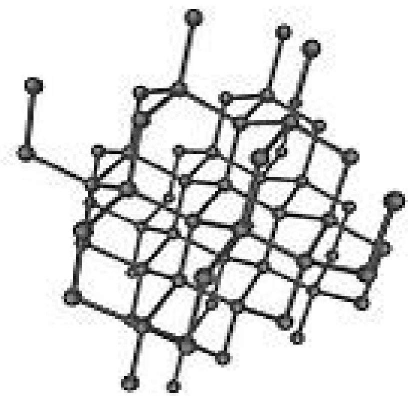
1st step **To prepare carbon-rich materials with pulsed discharge in sc-Ar**
To control the chemical structure of materials prepared

Graphene



Amorphous Carbon material

Diamond

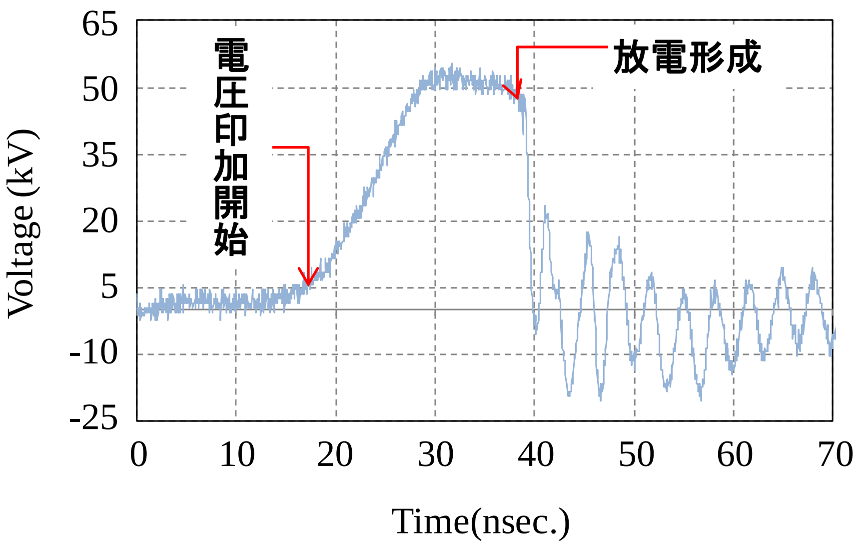


sp^2 ⟷ sp^3

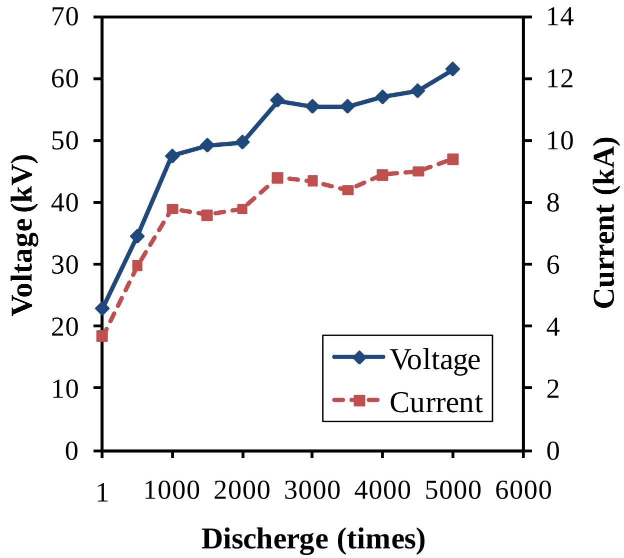
2nd step **To functionalize the materials with pulsed discharge in sub-H_2O, sub-NH_3 aq. soln. or other solvents.**

Pulsed discharge characterization in sub-H_2O

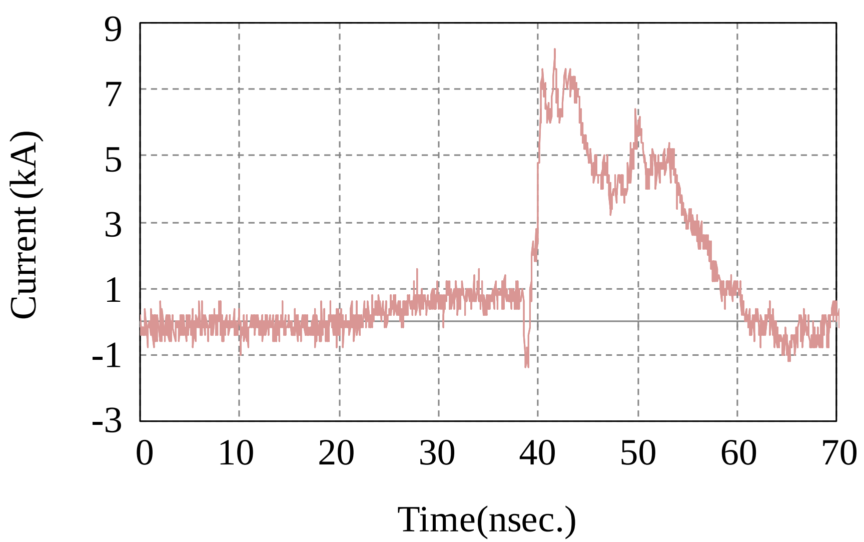
Voltage waveform



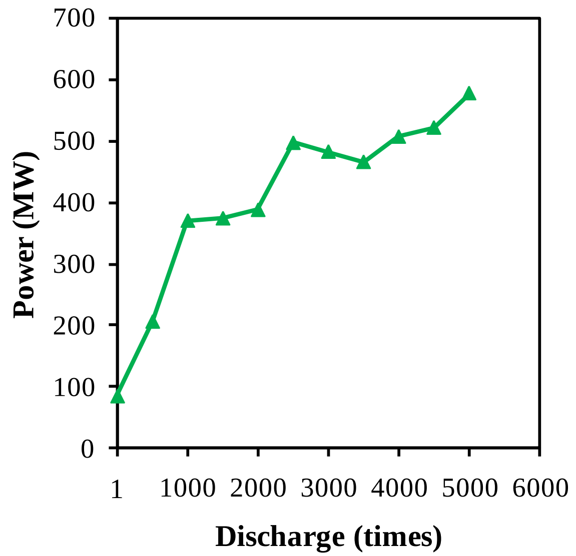
Voltage-Current profile



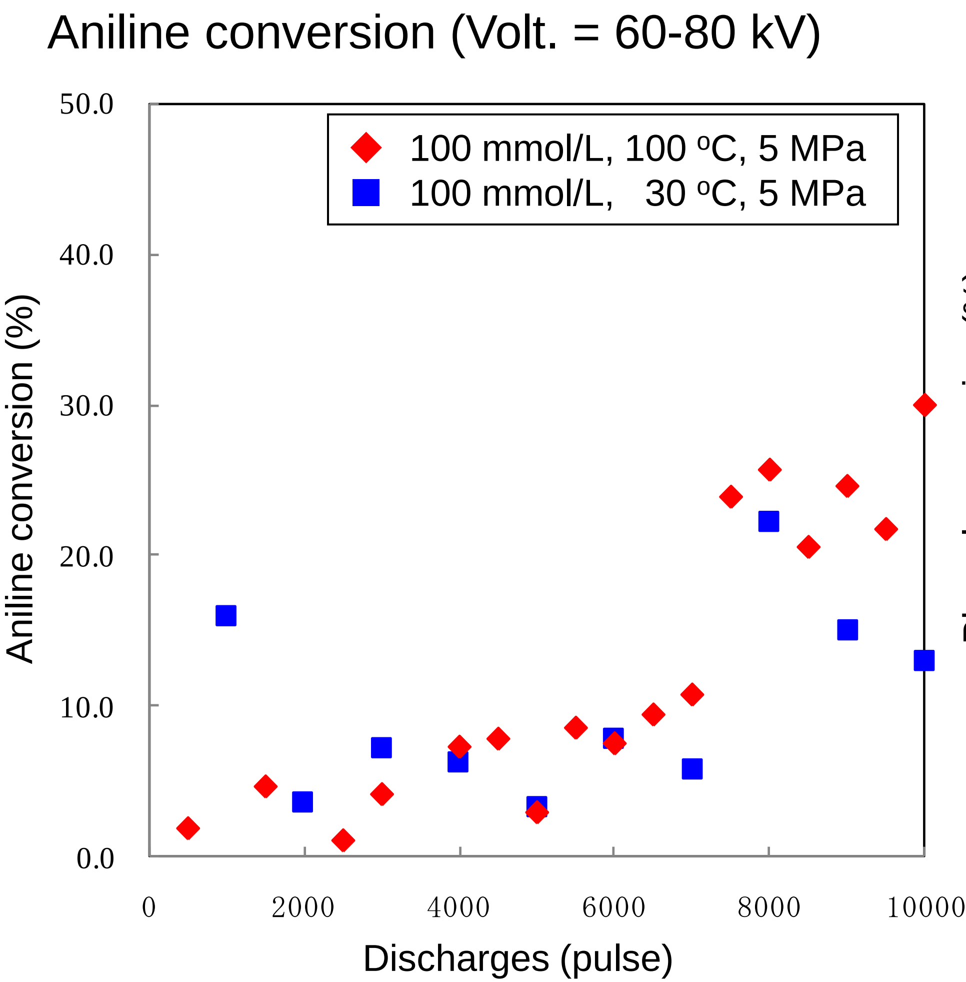
Current waveform

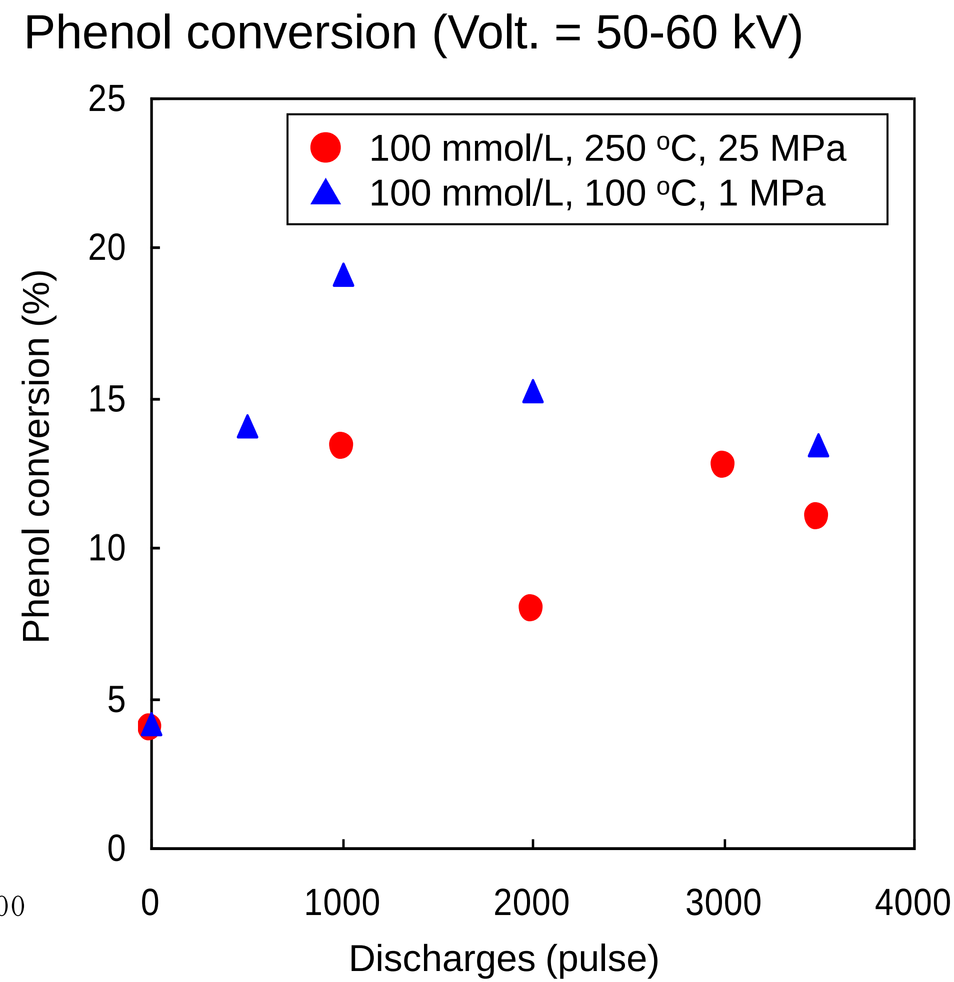


Power profile



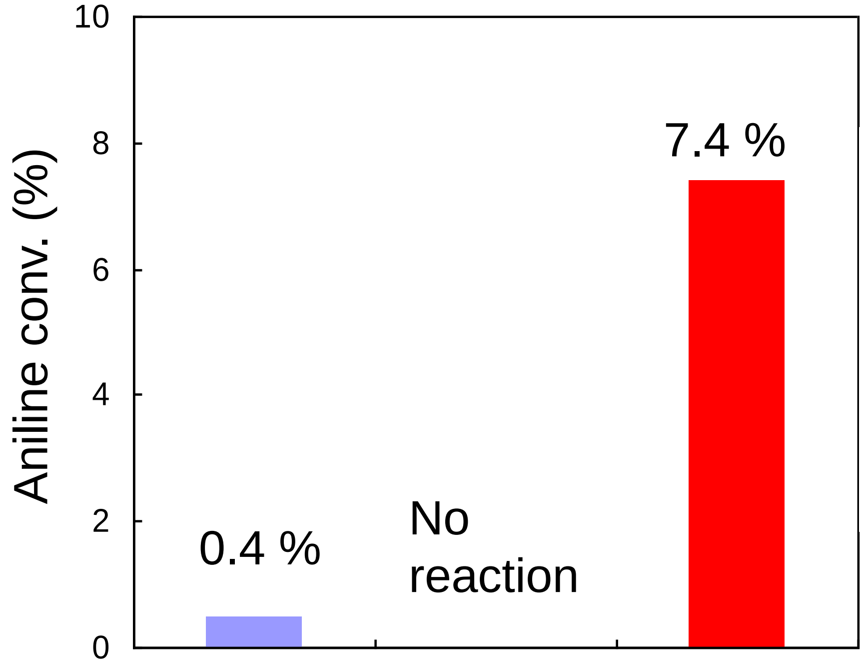
原料転化率と温度, 畜電圧および放電回数の関係

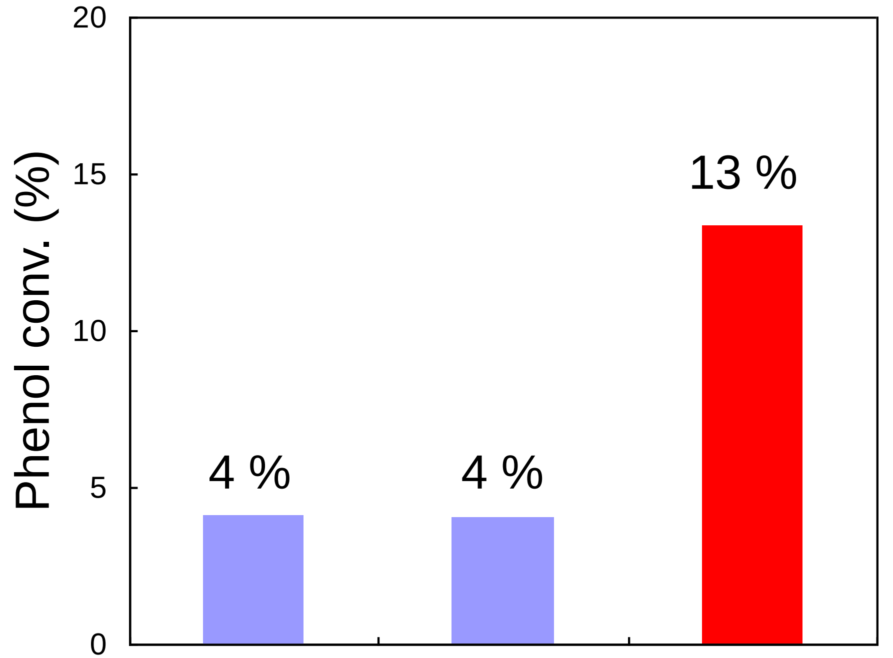




- 原料転化率に与える温度効果： 小 （ただし、30～250 ºC, 0.1～25 MPa）
- 転化に要する畜電圧 ： アニリン ＞ フェノール
- 放電回数 500～5000回の領域 ： 高温ほど転化が増大（最大30 %）

Comparison of reaction efficiency



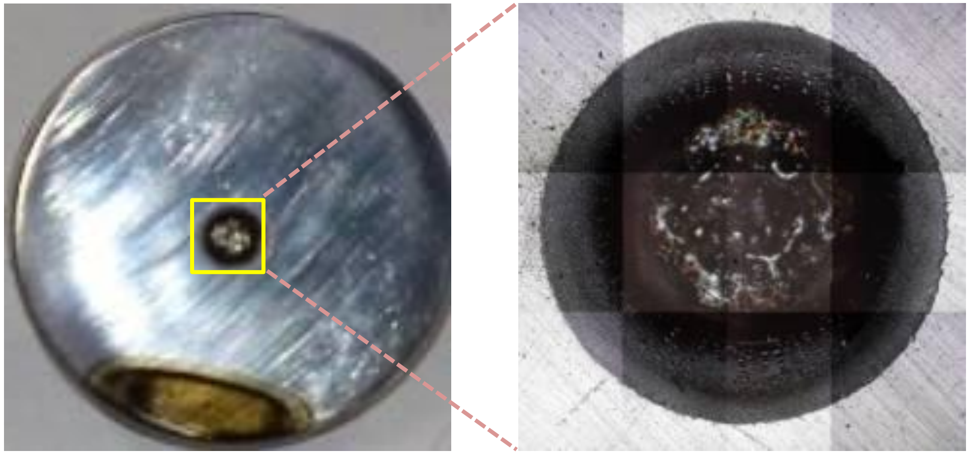


C_0 (mmol/L)	**100**	**100**	**100**	**100**	**100**	**100**
Temp. (^{o}C)	**250**	**35**	**100**	**260**	**28**	**100**
Pres. (MPa)	**5.0**	**0.1**	**5.0**	**10**	**0.1**	**1.0**
Discharge (pulse)	**0**	**4,000**	**4,000**	**0**	**10,000**	**4,000**
Reaction time (h)	**1.0**	**0.5**	**0.5**	**1.0**	**1.0**	**0.5**

➢At 100 ^{o}C and 5 (or 1) MPa, the conversions of aniline and phenol increased compared with the other treatments.

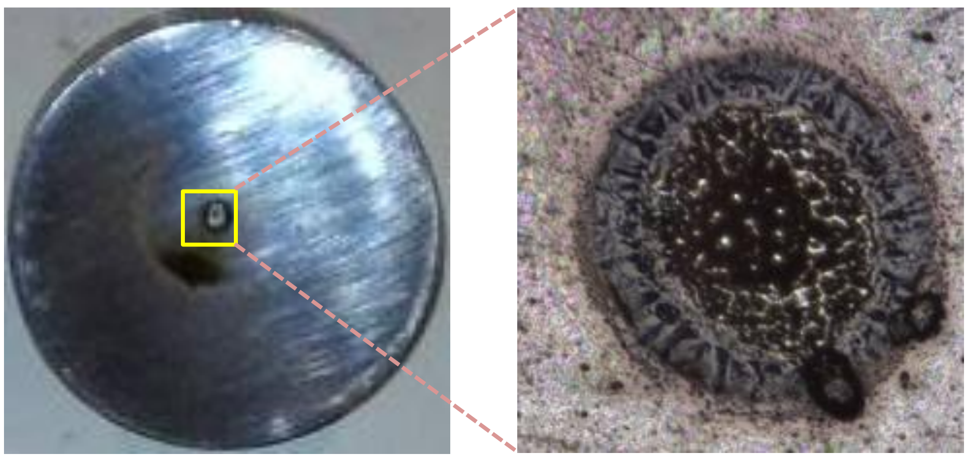
Plate electrode after sub-critical water discharge

B.P.F.N.



Electrical discharge radius:
1701.81 μm
Maximum depth: 95.03 μm

M.P.C.



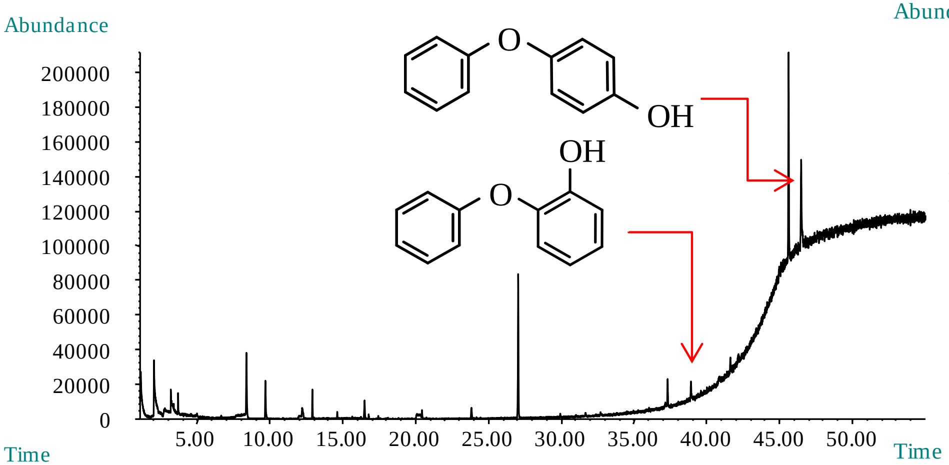
Electrical discharge radius:
927.63 μm
Maximum depth: 59.74 μm

協力：熊本県産業技術センター

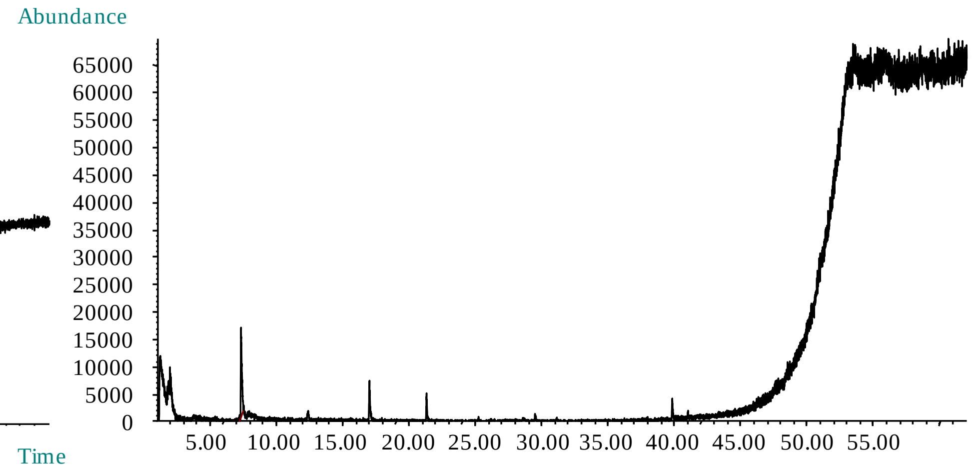
It was confirmed that electrical discharge occurred locally in case of B. P. F. N. compared with the case with M. P. C.

Production of phenolic oligomers

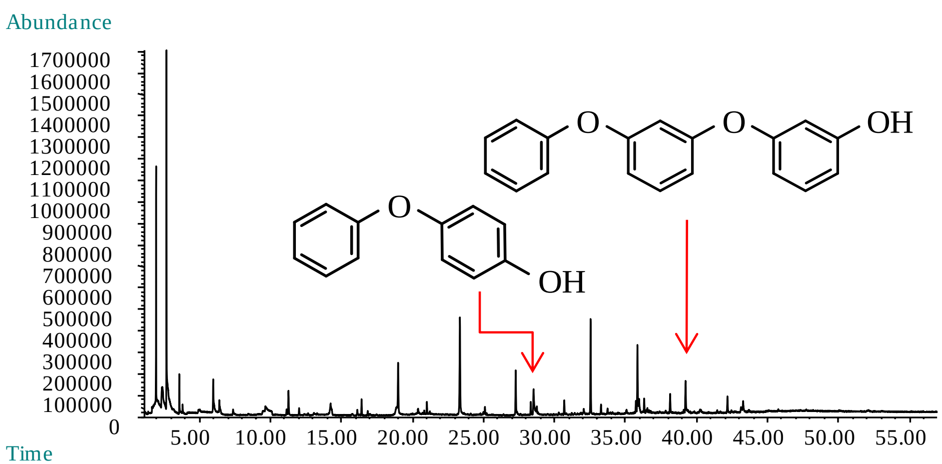
3500回



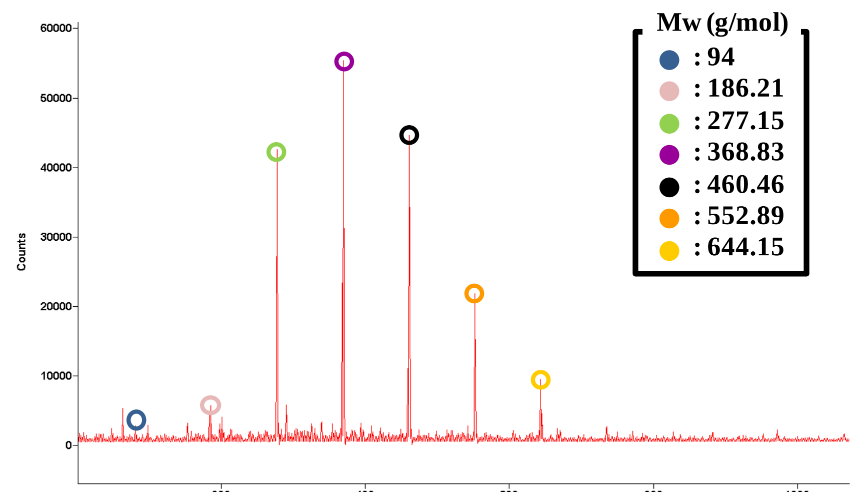
5000回



4000回



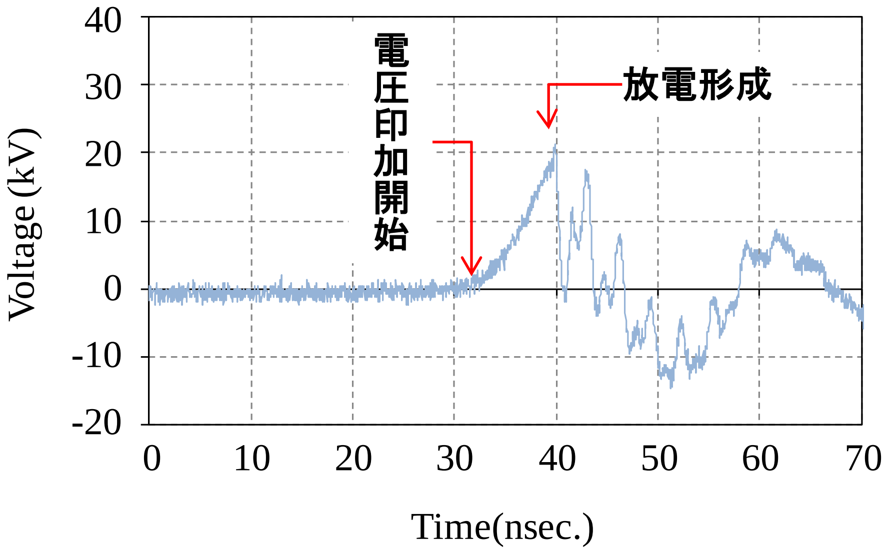
5000回（MALDI-TOF/MS）



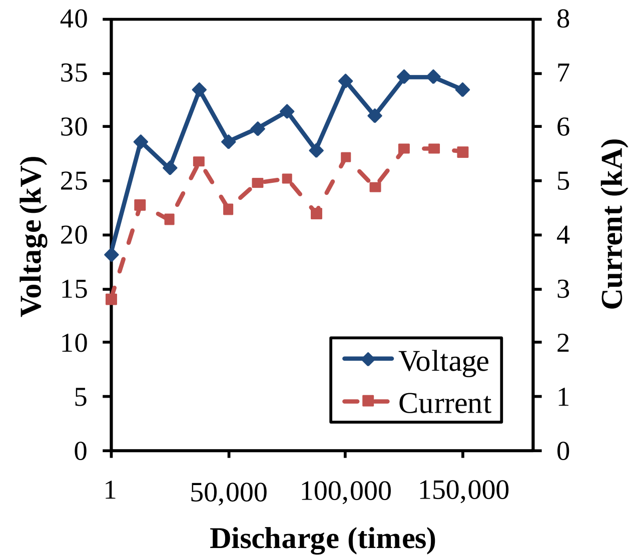
Oligomers (1-7 mers) was produced at 250 ºC in sub-critical water

超臨界アルゴン中パルス放電特性

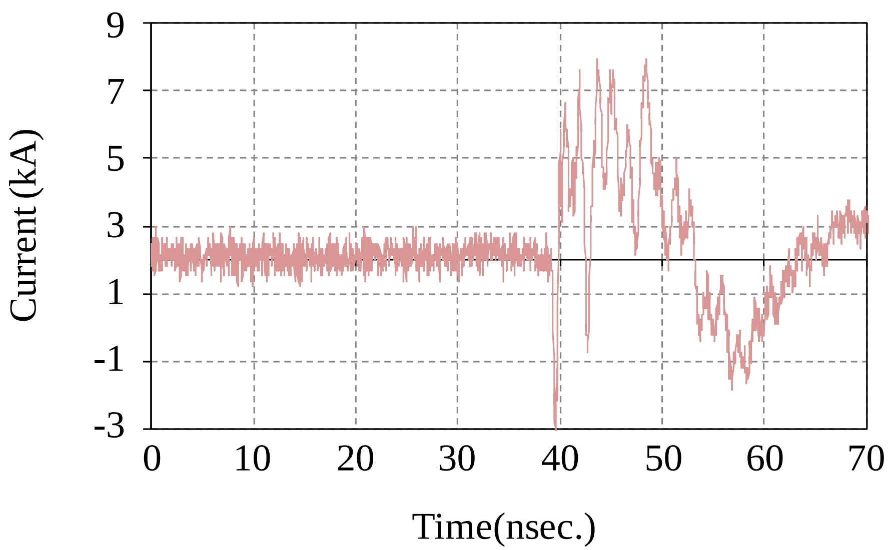
電圧波形



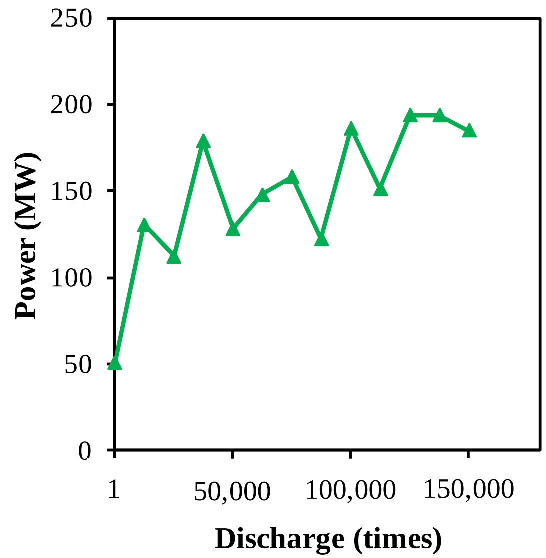
電圧・電流の変化



電流波形



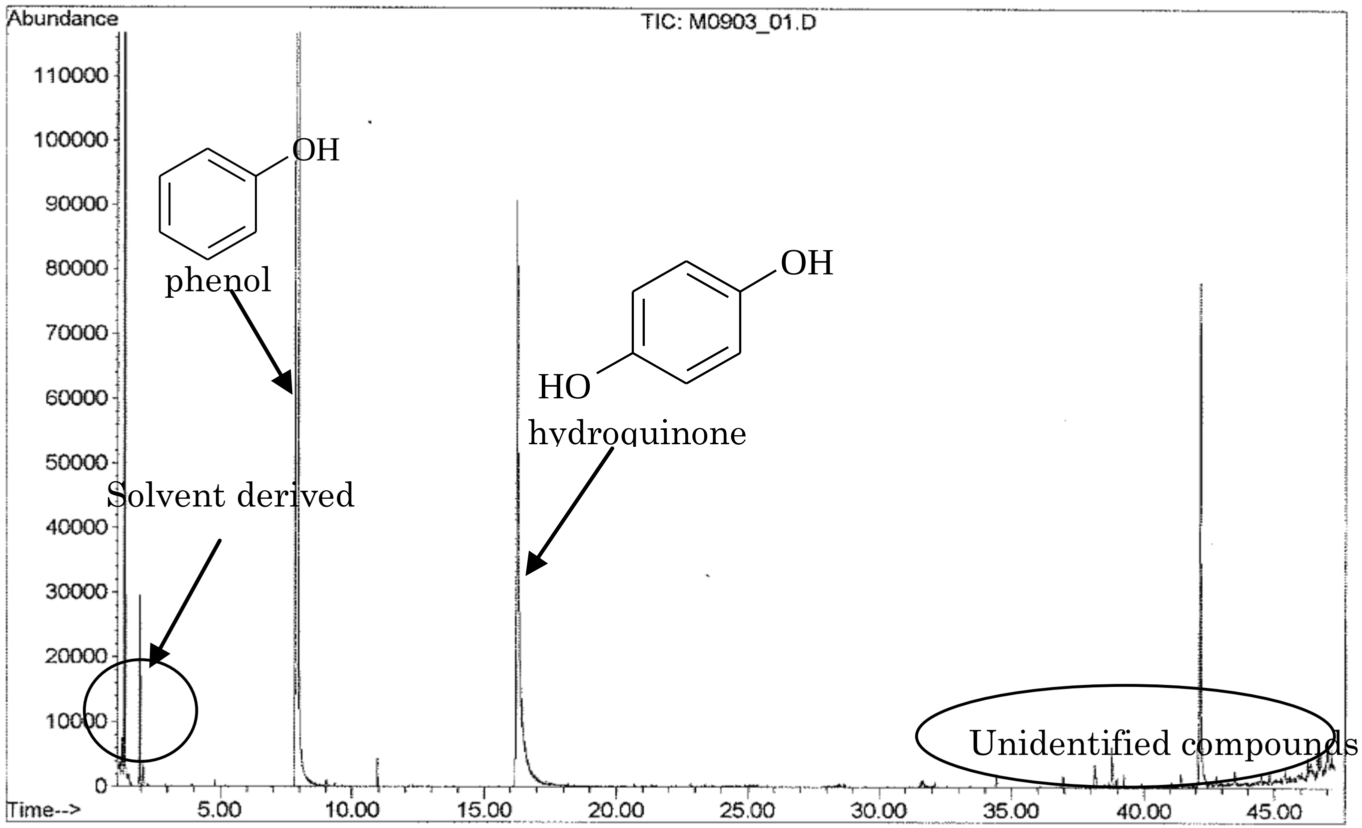
電力量の変化



Products after discharge treatment in sc-Ar

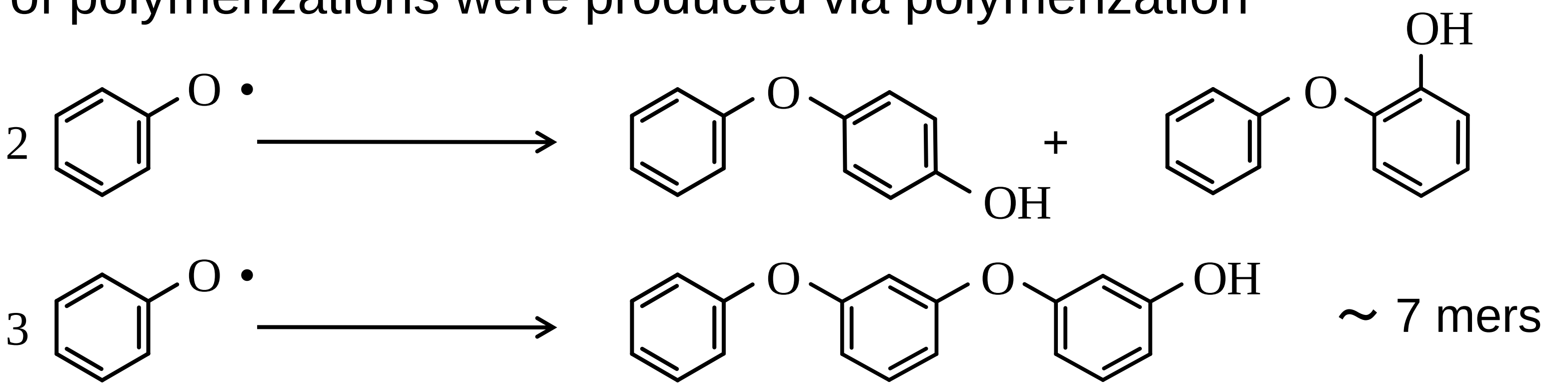
Addition reaction of OH group on phenol molecule occurred without any additives in supercritical argon

MeOH soluble fraction



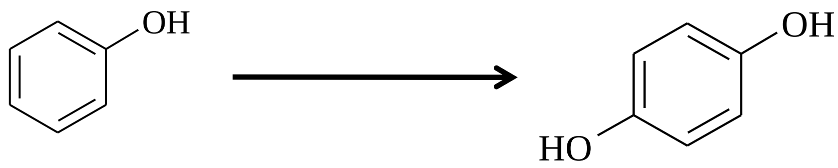
In sub-critical water:

✓Conversion of phenol reached about 30 % with this technique.
✓With increasing irradiation time, oligomers with higher degree of polymerizations were produced via polymerization

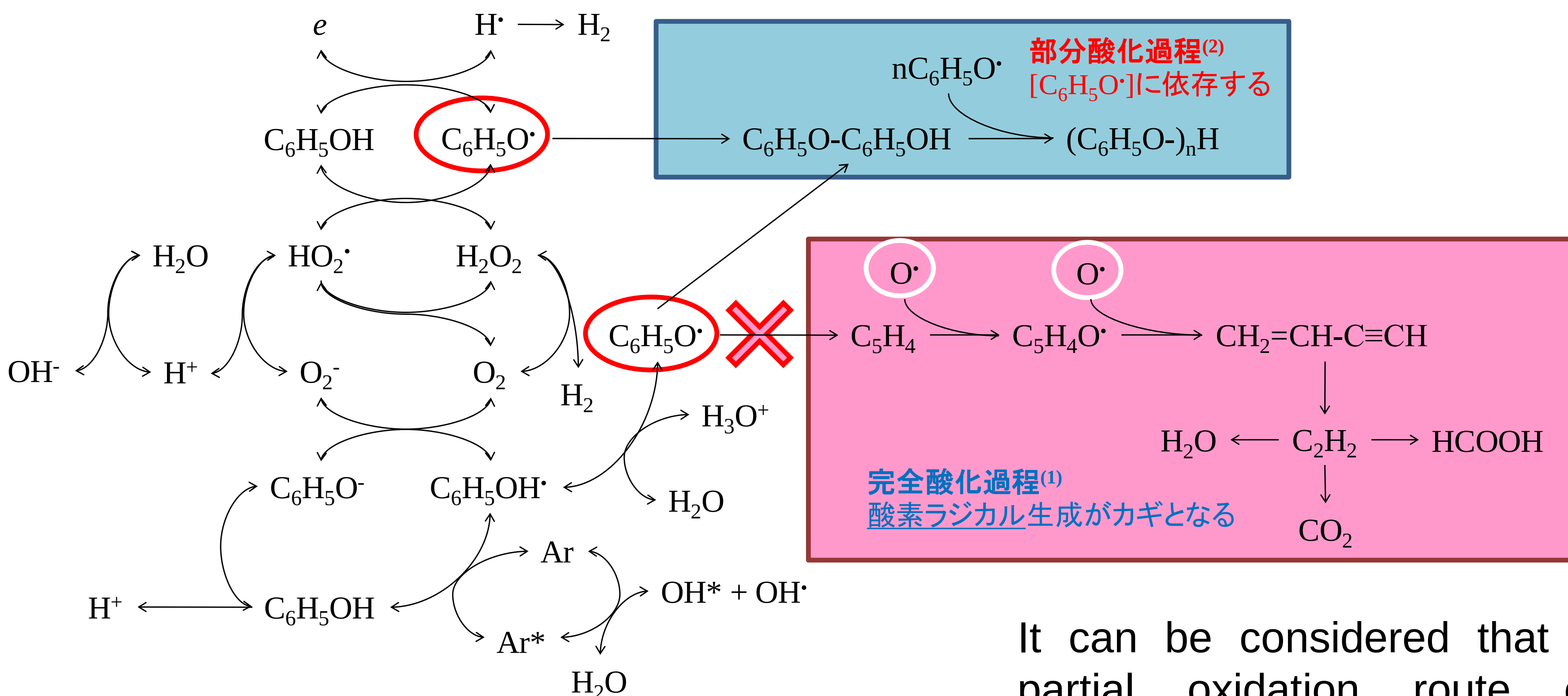


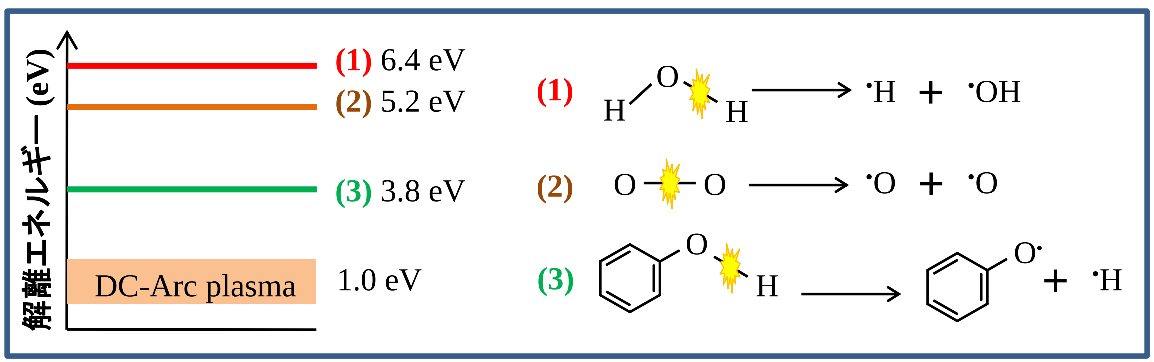
In supercritical argon:

✓OH addition to phenol to form dihidroxybenzene took place in supercritical argon, especially at longer irradiation time. No oligomers production was confirmed.



Phenol reaction in sub-critical water with pulsed plasma

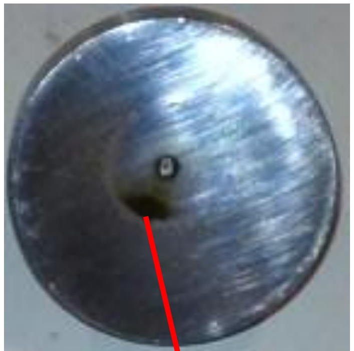


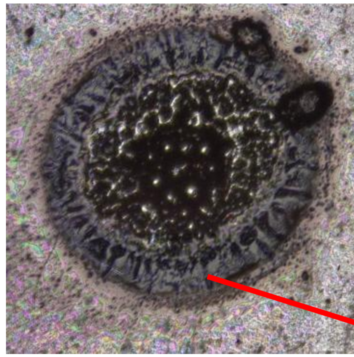


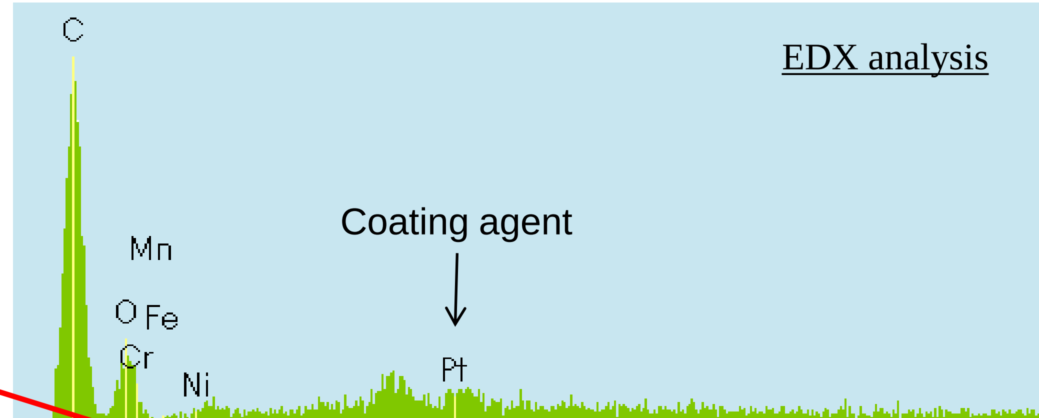
It can be considered that a partial oxidation route of phenol occurs with priority probably due to difficulty in generating O radicals.
→ Discharge energy was mainly consumed for dissociation of water.

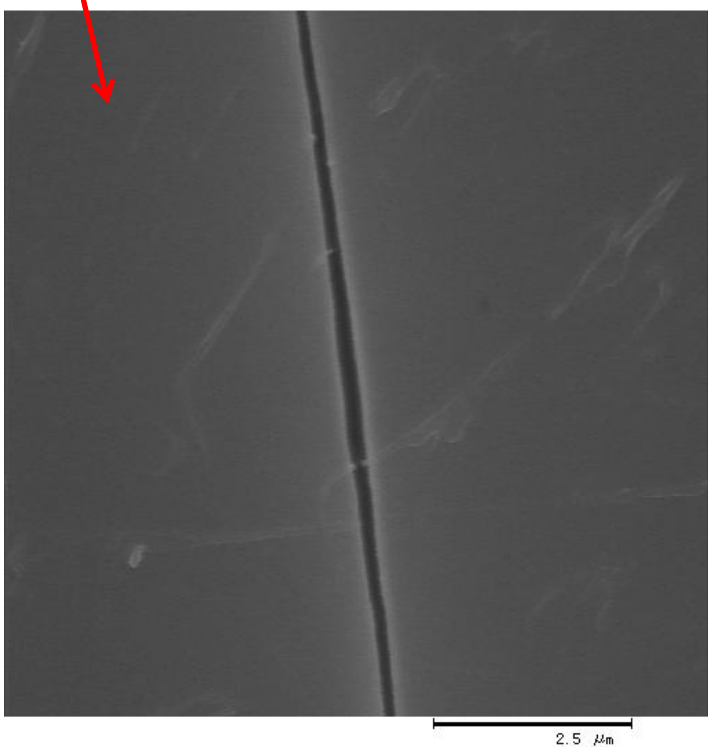
(1) H. Sekiguchi and M. Ando, *Kagaku kougaku Ronbunshu*, **30** (2004) 183.
(2) D. O. Cooney, Z. Xi, *J. AIChE*, **40** (1994) 361-364.

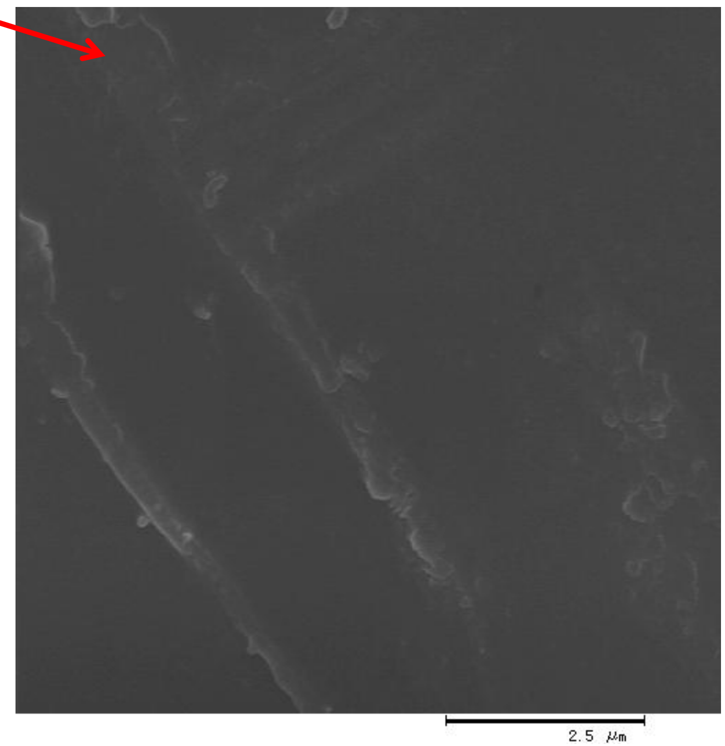
Surface of the electrode after sc-Ar discharge





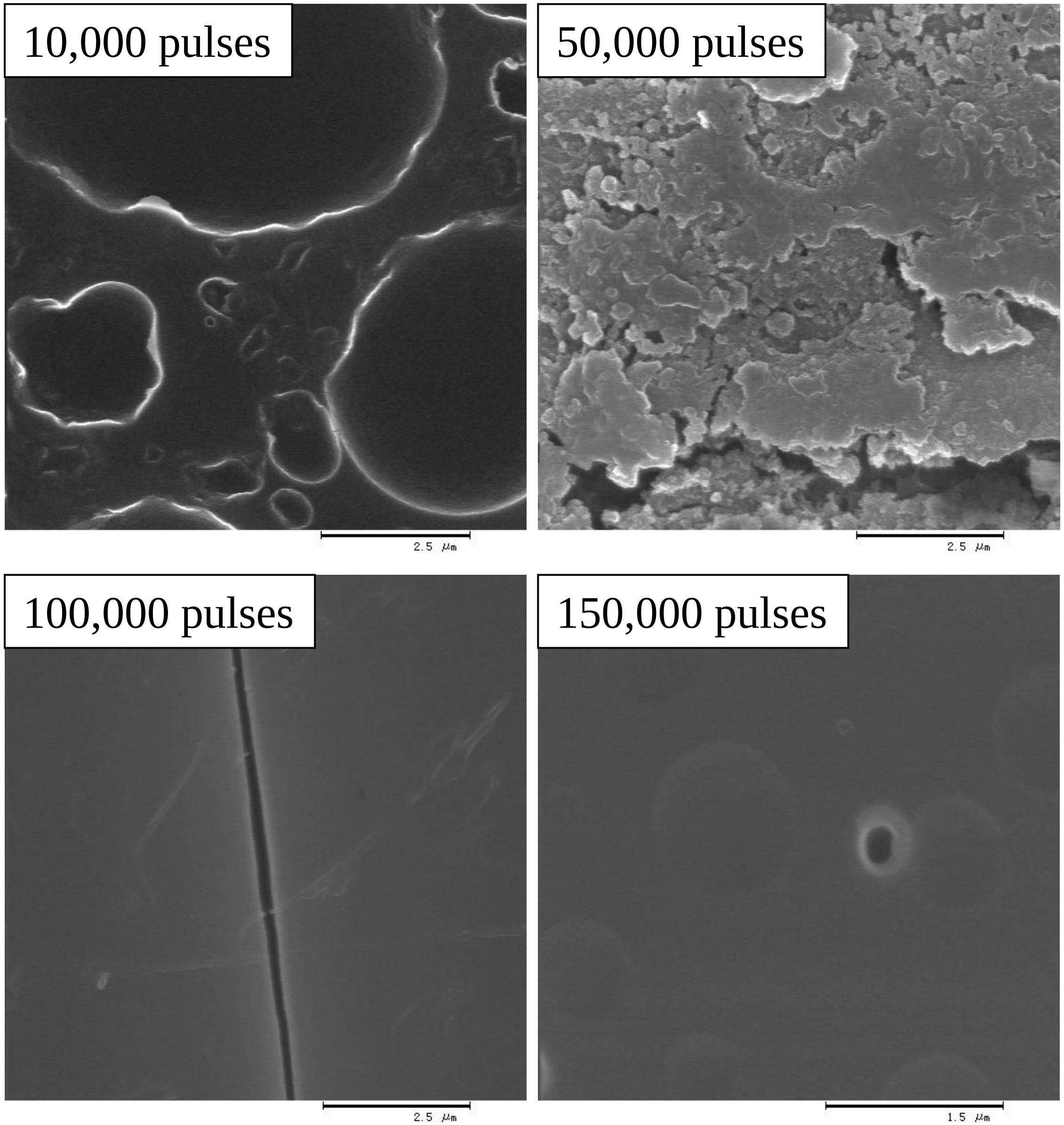




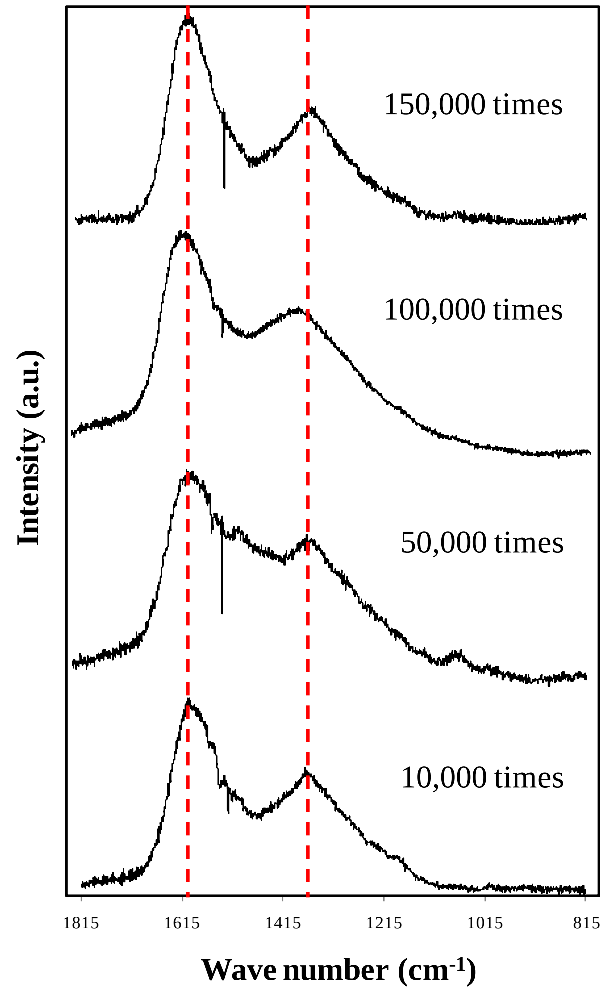


Carbon rich thin layer was produced

Effect of irradiation time on the product



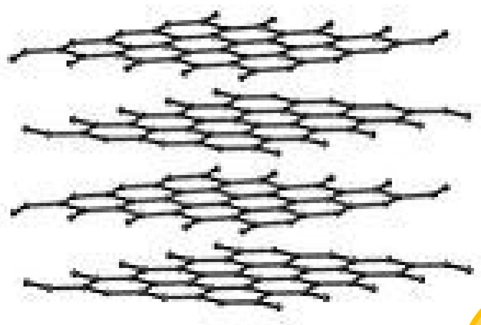
Raman spectroscopy



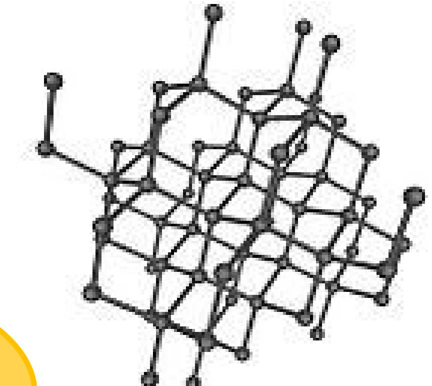
Two peaks were appeared in all the products

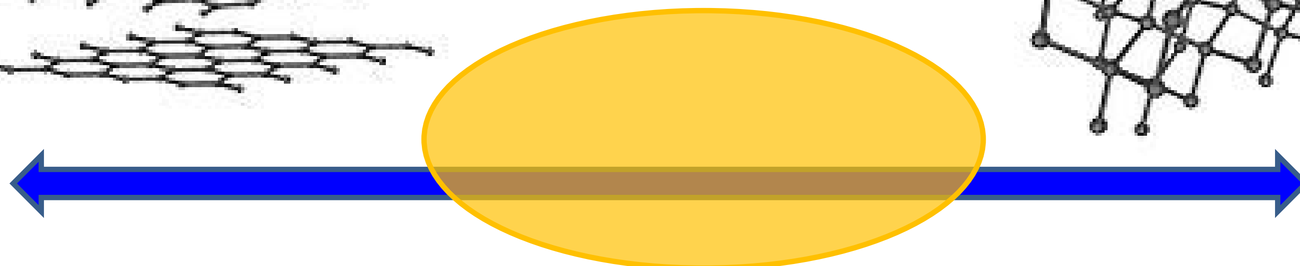
Raman spectroscopy of the samples

Graphene (or graphite

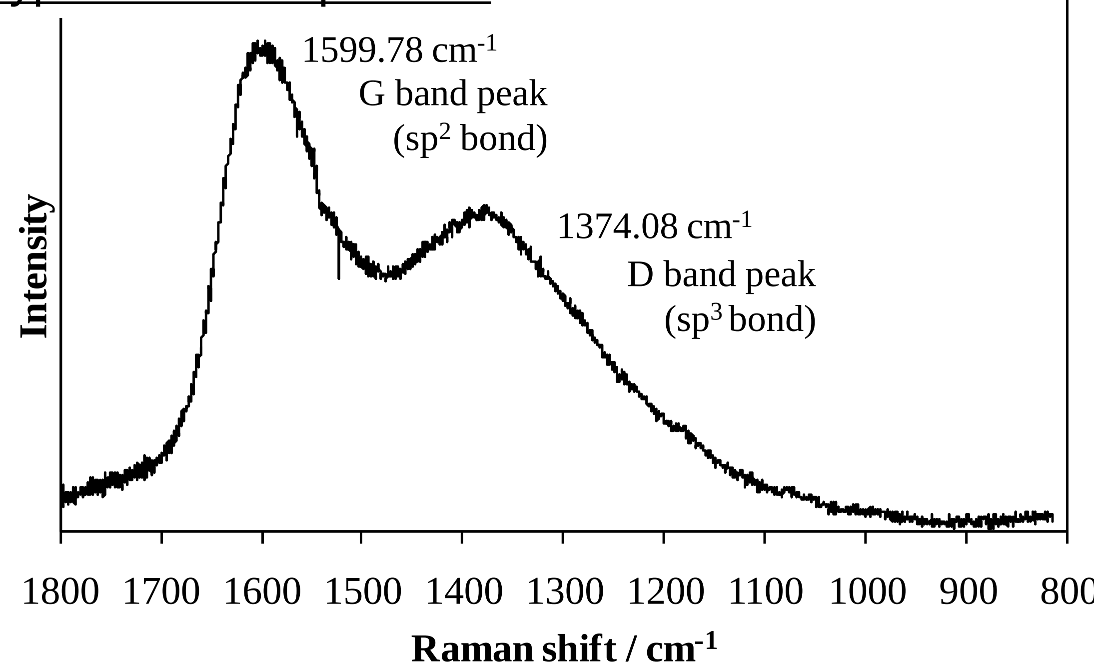


Artificial diamond



sp^2  sp^3

Typical raman spectrum



Amorphous structure

1580 cm^{-1}
sp^2結合に帰属されるGバンドピーク
1340 cm^{-1}
sp^3結合に帰属されるDバンドピーク

Conclusion-2

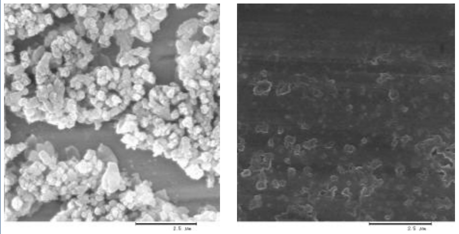
Nano-pulsed electric discharge in subcritical water

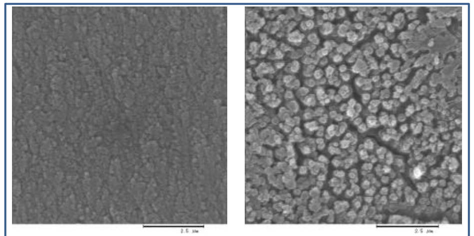
1. Phenolic oligomers (DP = 1 - 7) were obtained.
2. Phenol was probably activated by OH radicals which generated from H_2O degradation and polymerized.

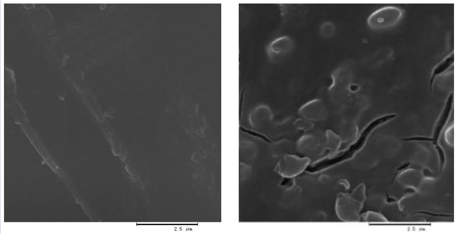
Nano-pulsed electric discharge in supercritical argon

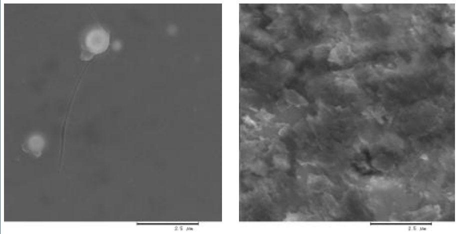
Carbon-based material with the following properties was synthesized.

1. Intermediate chemical structure between graphite and diamond
2. Main elements are C and O.
3. Multi-layers of graphene exist.


4 pps 250 pps
Effect of frequency

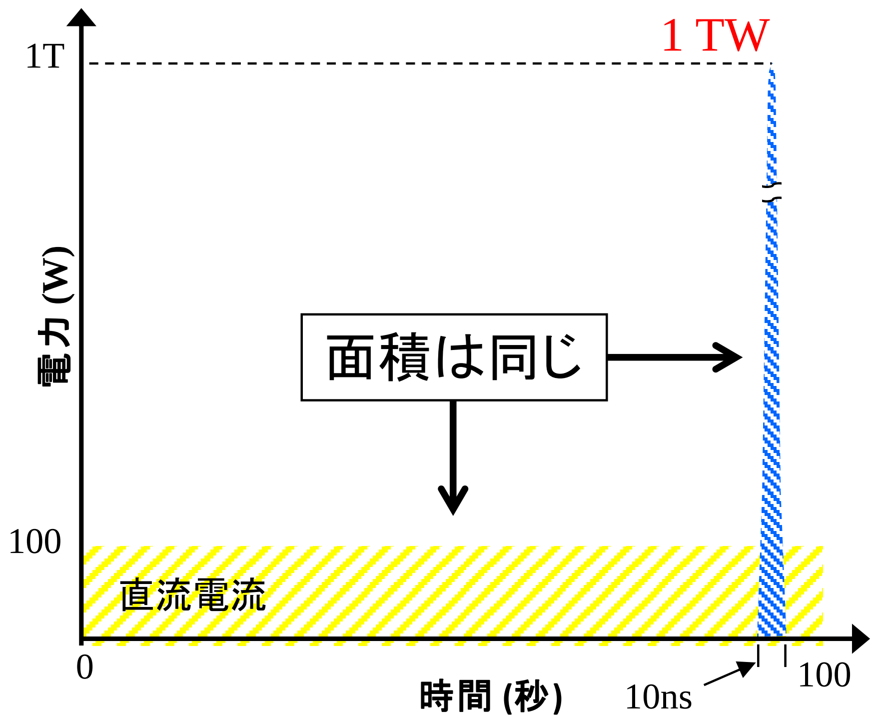

40 ^oC 50 ^oC
Effect of Temperature

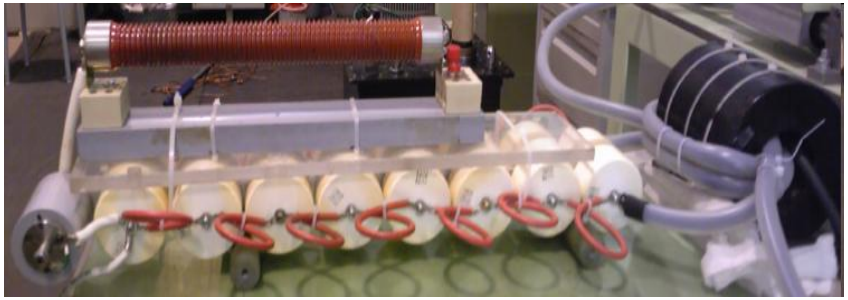

5 MPa 10 MPa
Effect of Pressure

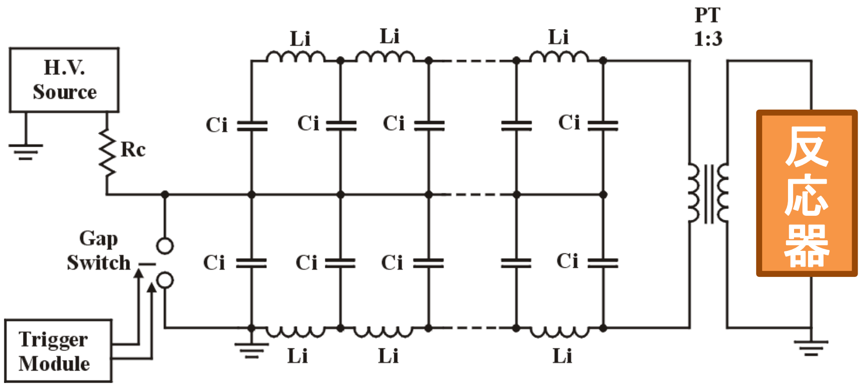

450 ml 900 ml
Effect of volume

Nano-pulsed power technology

Generation of extremely large power
for reduced power of chemical conversions



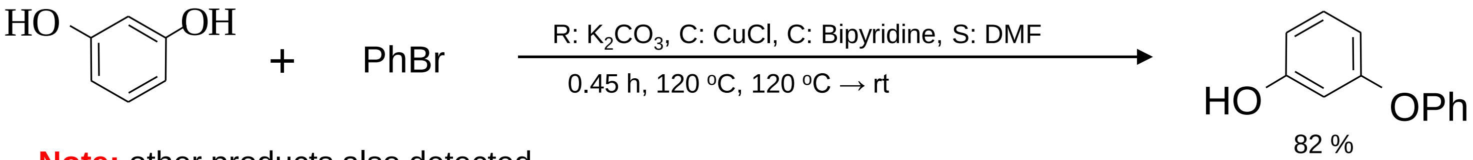




パルス電源回路図

Catalytic etherification process for preparing meta-phenoxyphenol from bromobenzene and resorcinol.

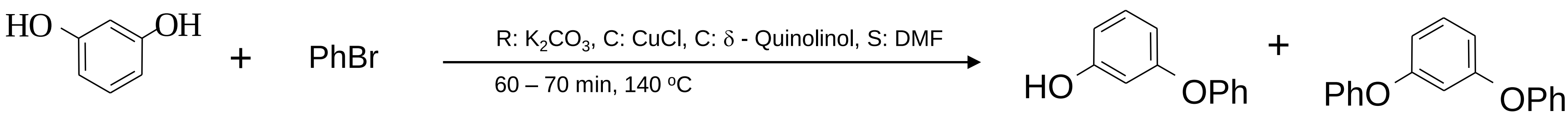
Mil'to, V. I.; Orlov, V. Yu. (OOO "Meta-FF", Russia). Russ. (2006), 4pp. CODEN: RUXXE7 RU 2287516 C1 20061120 Patent written in Russian. Application: RU 2005-119464 20050616. Priority: . CAN 145:488993 AN 2006:1216261 CAPLUS



Note: other products also detected ,
Reactants: 2 , Reagents: 1 , Catalysts: 2 , Solvents: 1 , Steps: 1 , Stages: 1

Technology of m-phenoxy-phenol synthesis.

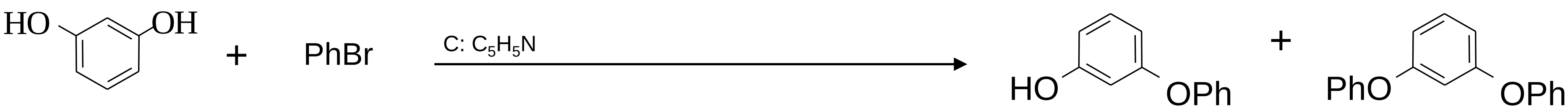
Mil'to, V. I.; Orlov, V. Yu.; Mironov, G. S. Yarosl. Gos. Univ. im. P. G. Demidova, Russia. Khimicheskaya Tekhnologiya (Moscow, Russian Federation) (2004), (1), 24-26. Publisher: OOO Nauka i Tekhnologii, CODEN: KTMRAG Journal written in Russian. CAN 141:379673 AN 2004:153231 CAPLUS



Note: green chem , optimization study , optimized on ratio of the starting substances , amount of the catalyst , reaction time ,
Reactants : 2 , Reagents : 1 , Catalysts : 2 , Solvents : 1 , Step : 1 , Stages : 1

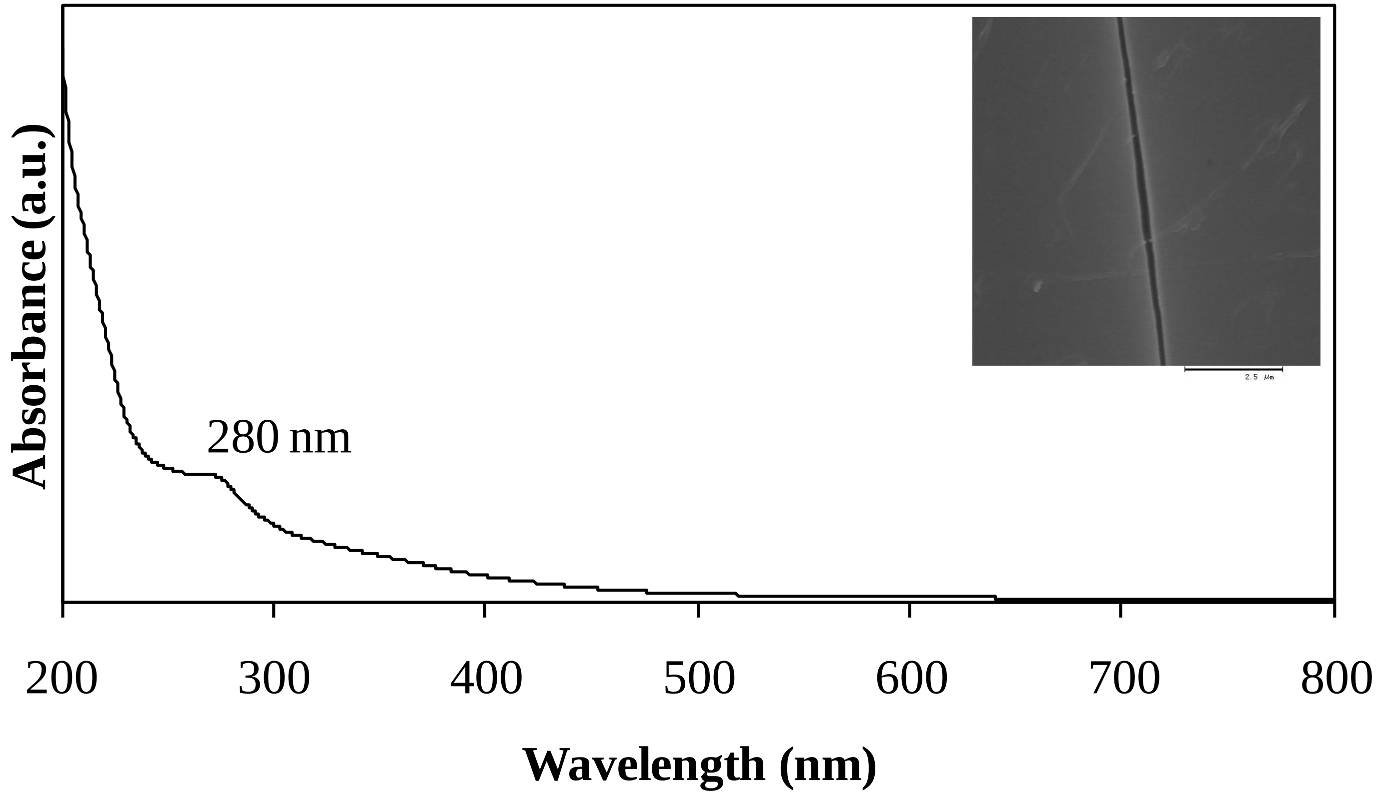
Solvent-assisted Ullmann ether synthesis. Reactions of dihydric phenols.

Williams, Albert Lloyd; Kinney, R. E.; Bridger, Robert F. Central Res. Div. Lab., Mobil Oil Corp., Princeton, NJ, USA. Journal of Organic Chemistry (1967), 32(8), 2501-5. CODEN: JOCEAH ISSN: 0022-3263. Journal written in English. CAN 67:63969 AN 1967:463969 CAPLUS



Note: Classification : O-Arylation ; # Conditions : NaOMe pyridine ; /N2 ; CuCl PhBr ;
Rf / N2 3 h , Reactants : 2 , Solvents: 1 , Steps : 1 , Stages : 1

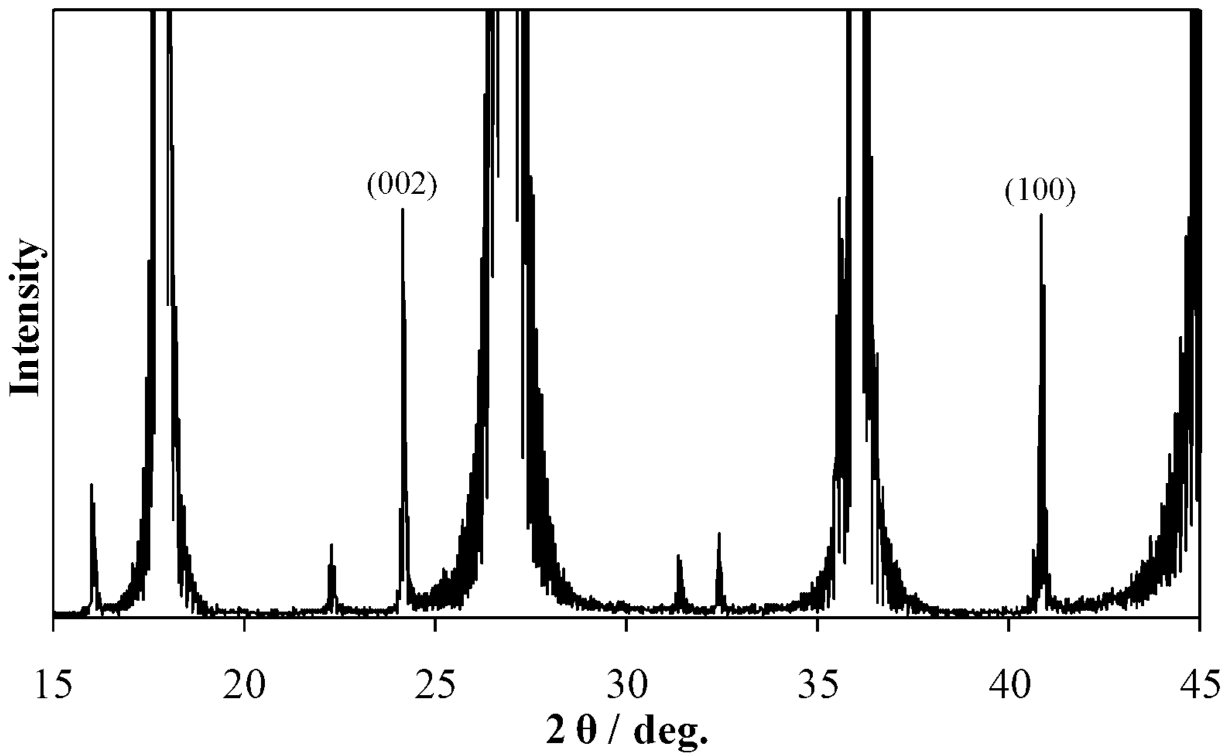
UVスペクトル



280 nm付近にC=O結合のn → π*遷移に起因するショルダーピークを確認できた

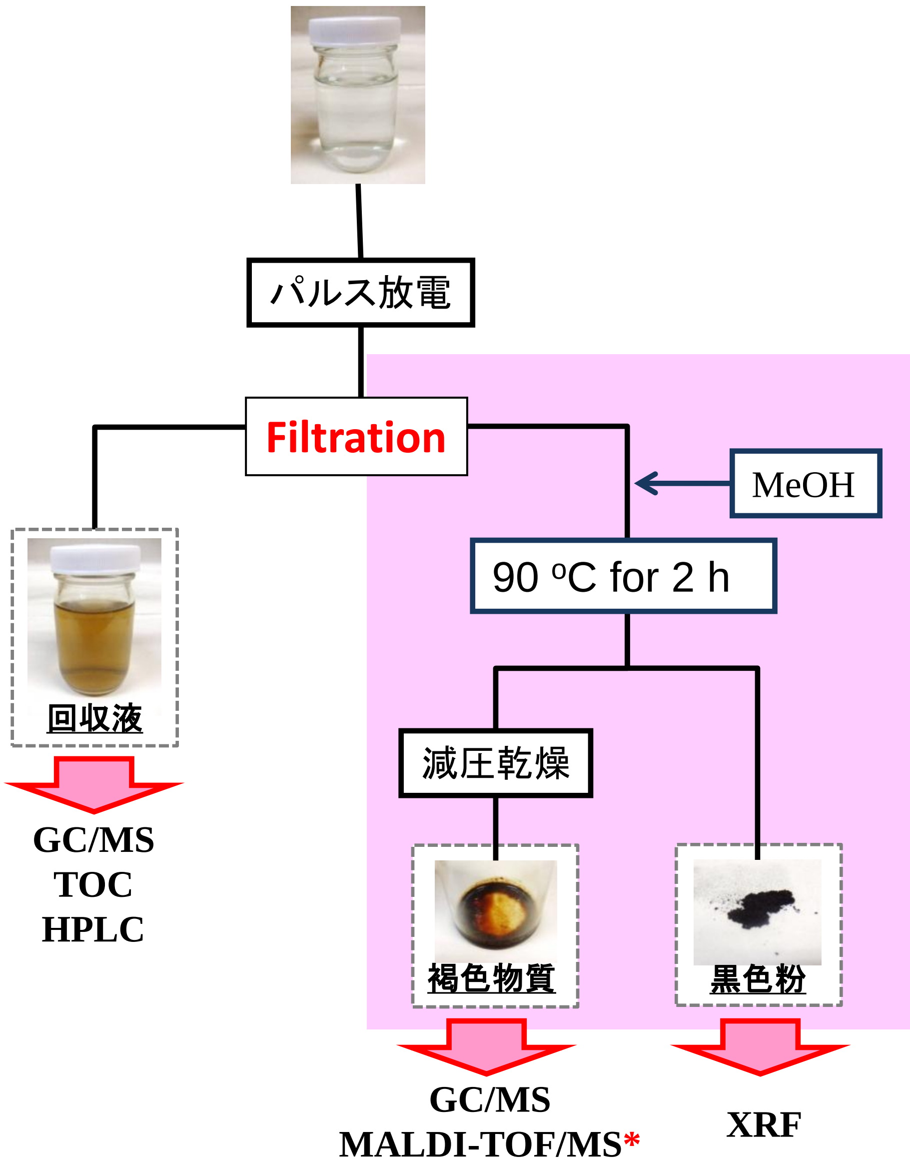
<u>**C=O結合を有するアモルファス構造の炭素膜**</u>

膜状物質のXRDパターン

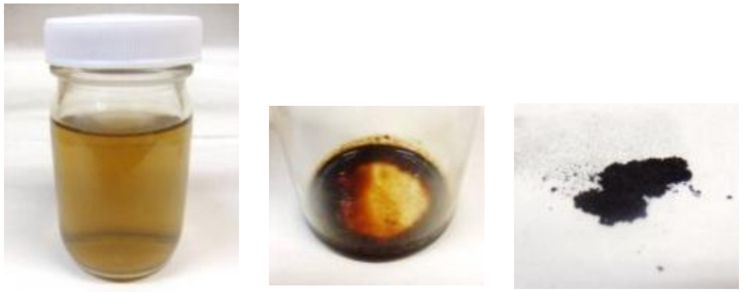


グラファイトの(002)面、(100)面を確認

(亜臨界水パルス放電)回収サンプル



*5000回放電時回収サンプルのみ



回収液　褐色物質　黒色粉

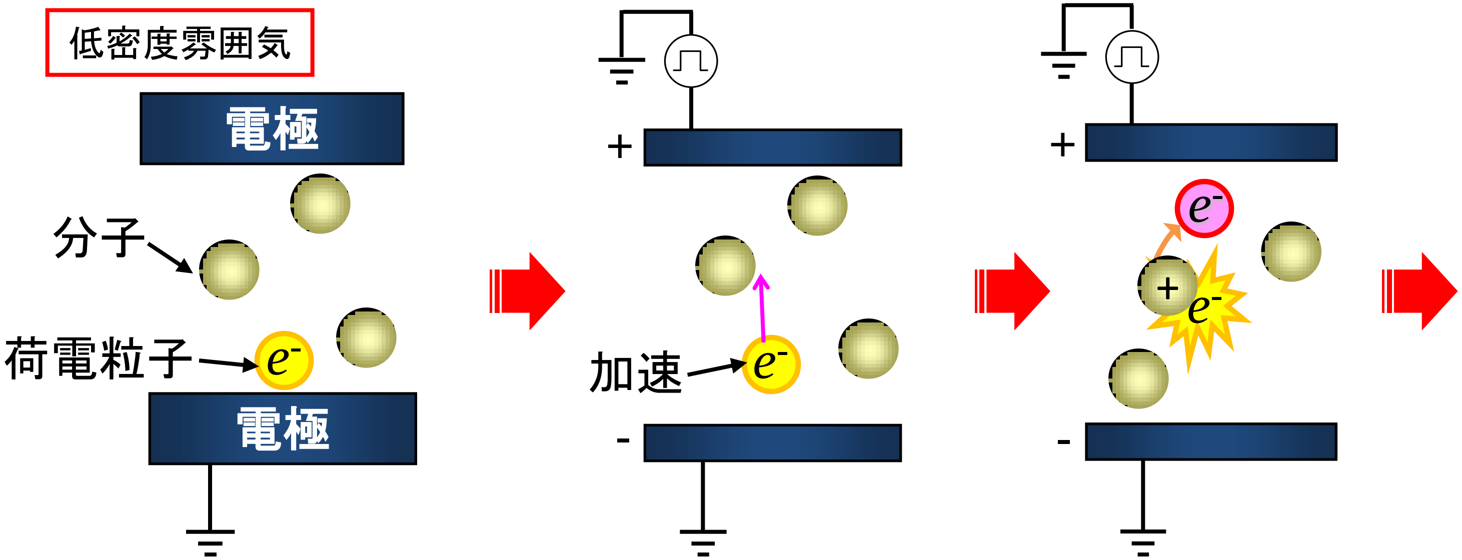
黒色粉のXRF分析結果

Elements	Content (%)
Fe	46.46
Cr	13.25
W	33.82
Ni	5.22
Mn	1.25

黒色粉は電極由来の物質である

放電開始電圧

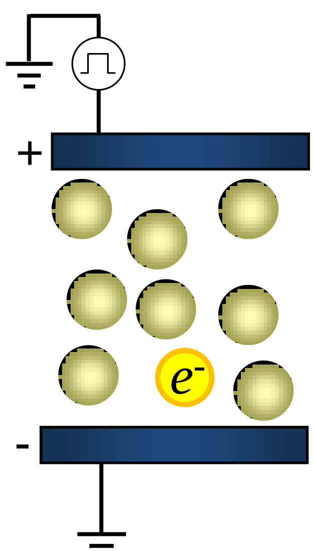
低密度雰囲気



衝突を繰り返し、
電極間にプラズマ
が発生する

低電圧でも
放電が起こる

高密度雰囲気



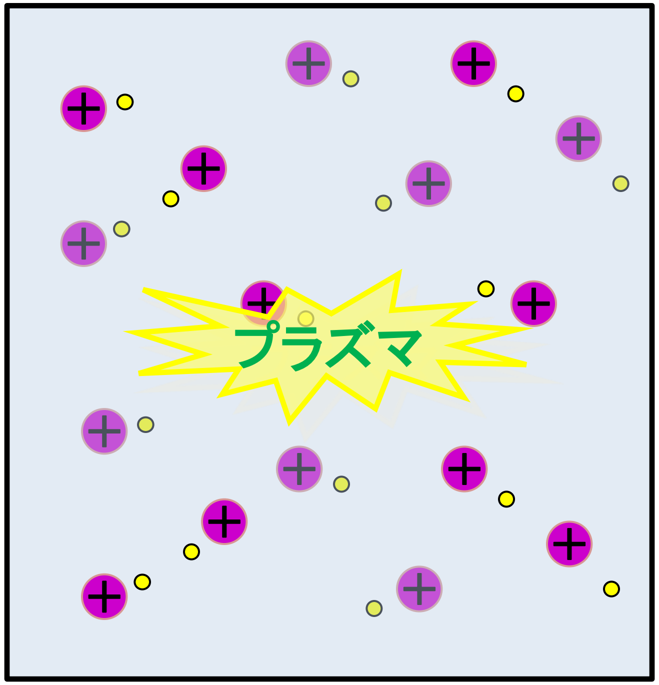
十分加速されないうちに
周りの分子と衝突してしまう

電子のエネルギー不足が
起こりプラズマ形成が困難

超臨界流体中において
　　　プラズマを形成するには..

<u>電子の持つエネルギーを高める必要がある</u>

プラズマ



プラズマ
多くの活性種(ラジカル・電子など)から構成される<u>電離した流体</u>

投入電圧を変化させることで様々な種類のプラズマを形成することができる

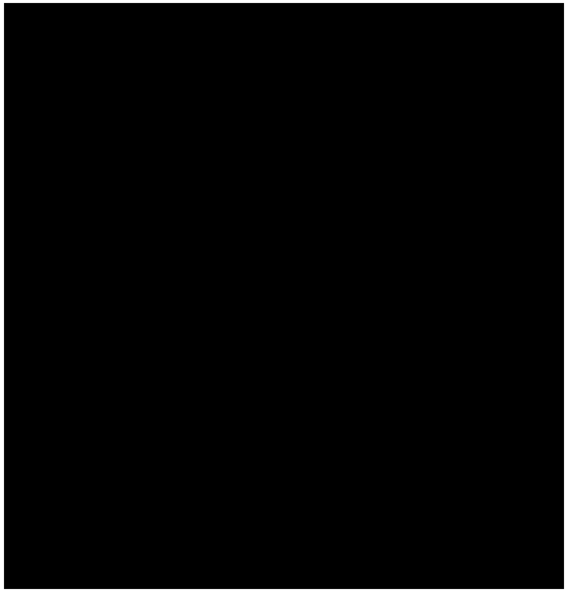
放電プラズマの種類

コロナ放電

熱発生量;少量
安定性;低い

アーク放電

熱発生量;多量
安定性;高い



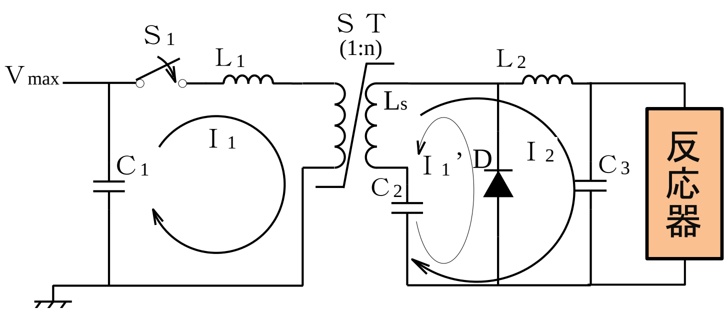
液中プラズマ放電(コロナプラズマ→アークプラズマ)

M.P.C.電源

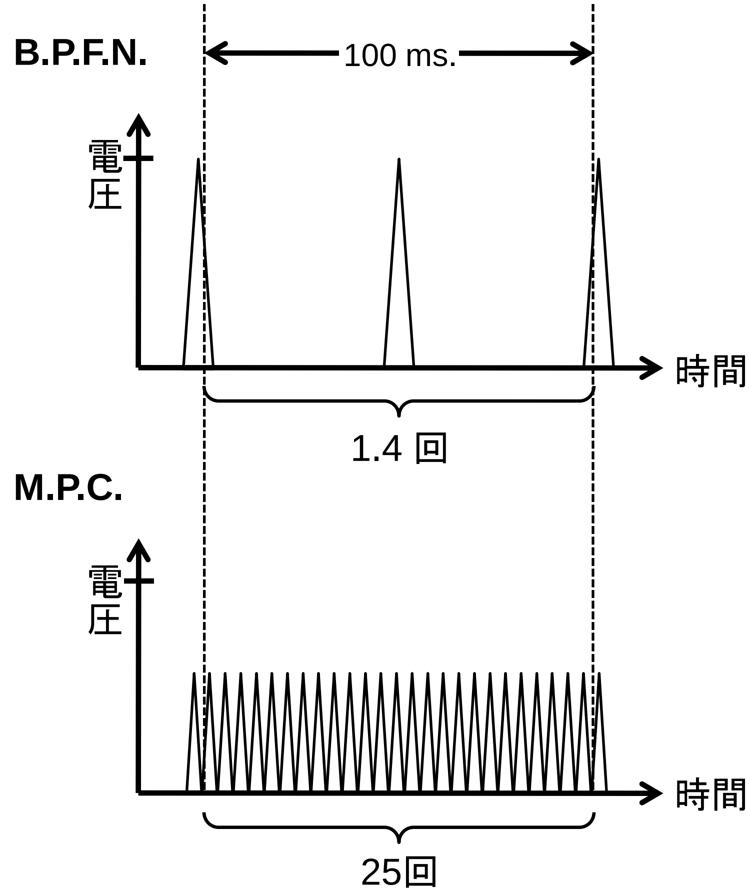
M.P.C.電源のプラズマ放電高繰り返しを利用し、フェノール反応の高効率化を目指す

M.P.C. (Magnetic Pulse Compression)

MPC2000S, Suematsu Electronics Co. Ltd., Japan



✓半導体素子によるスイッチング
✓パルスの立ち上がりが早い
✓安定で長寿命
✓**高繰り返しが可能**



B.P.F.N.電源に比べ数十倍以上の
プラズマ放電を流体中に印加できる

亜臨界水中プラズマ実験

実験条件

試料 : フェノール水溶液（0.1 M）
温度 : 250 ºC
圧力 : 25 MPa
放電 : ~ 5,000 回

実験操作

1. 反応器内をArガスに置換する
2. 反応器内に試料を加える
3. 所定圧力･温度に上げる
4. プラズマ放電
5. 反応液回収（褐色溶液）
6. 洗浄過程: MeOH, 90 ºC, 2時間で洗浄
7. 洗浄過程: 洗浄液回収（褐色溶液）

分析条件

GC/MS	Column	:	HP-5 MS capillary column system
	Detector (MS)	:	HP model 6890 series GC system 5973 mass selective detector
	Temp. program	:	5 K/min. (318 K to 543 K)
	Carrier Gas	:	Helium (1.5 mL / min.)
HPLC	Column	:	Inertsil ODS-3
	Detector	:	UV – VIS (280 nm)
	Flow rate	:	1.0 mL/min
	Mobile phase	:	CH_3CN / H_2O = 20 / 80
MALDI -TOF/MS	Acceleration (V)	:	+ 25 kV
	Nitrogen laser	:	337 nm 3 ns pulse width
	Laser probe	:	Laser Probe Rm-3700 Universal Radiometer
	Matrix	:	2,5-Dihydroxybenzoic acid (DHB)
TOC	TOC – 5050A (Shimadzu Corporation)		
XRF (X-Ray Fluorescence)	Current	:	3 uA
	Voltage	:	50 kV
	Detector	:	Si (Li) semiconductor detector
	Analyze	:	SEA-2001 (Seiko Instruments Inc,)

Equations

$$Conversion\ (\%) = \left(1 - \frac{Recoverd\ (AREA)}{Initial\ \ Sample\ (AREA)}\right) \times 100$$

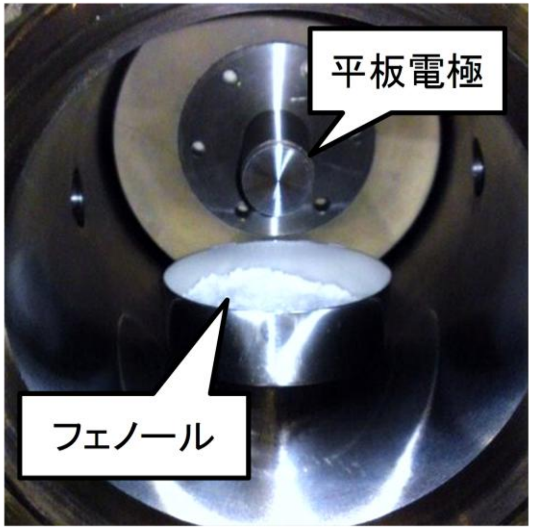
$$Residual\ ratio\ (\%) = \left(\frac{Recoverd\ (ppm)}{Initial\ \ Sample\ (ppm)}\right) \times 100$$

超臨界アルゴンプラズマ実験

実験条件

試料 : フェノール（10 g）
温度 : 40 ºC
圧力 : 5 MPa
放電 :
10,000回 , 50,000回, 100,000回, 150,000回

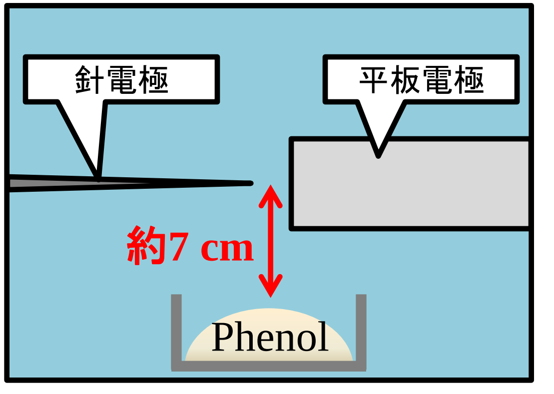
アルゴン（臨界点）
T_c ; -120 ºC, P_c ; 4.8 MPa



反応器内サンプル設置の様子

実験操作

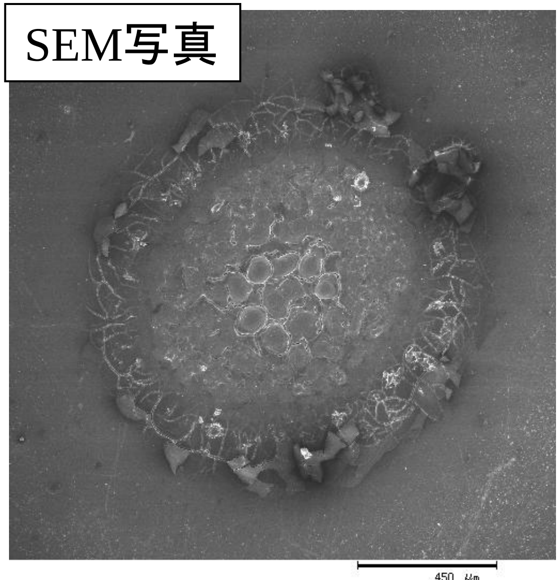
反応器内に試料を加える
↓
反応器内をArガスに置換する
↓
所定圧力･温度に上げる
↓
プラズマ放電開始
↓
平板電極回収 ⇒ SEM観察 / EDX分析 / ラマン分光 / UV-vis測定
↓
洗浄過程:
MeOH, 90 ºC, 2時間で洗浄
↓
反応器洗浄液回収 ⇒ GC/MS分析



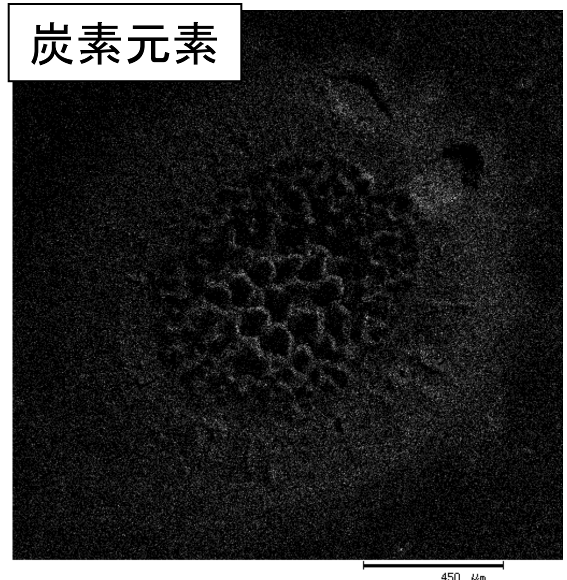
反応器内サンプル設置の模式図

SEM/EDX分析

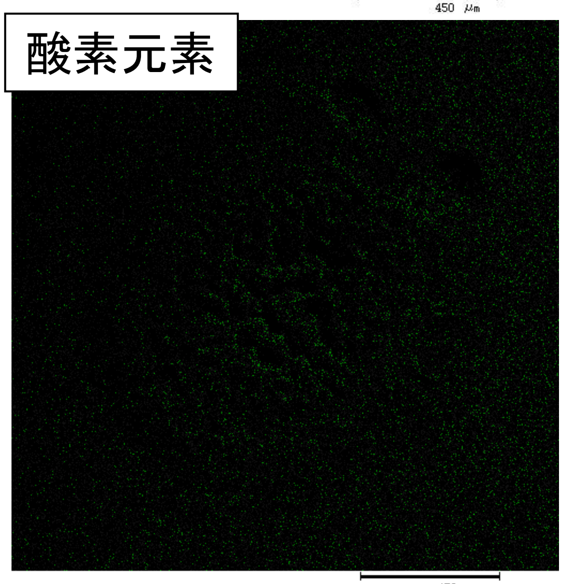
SEM写真



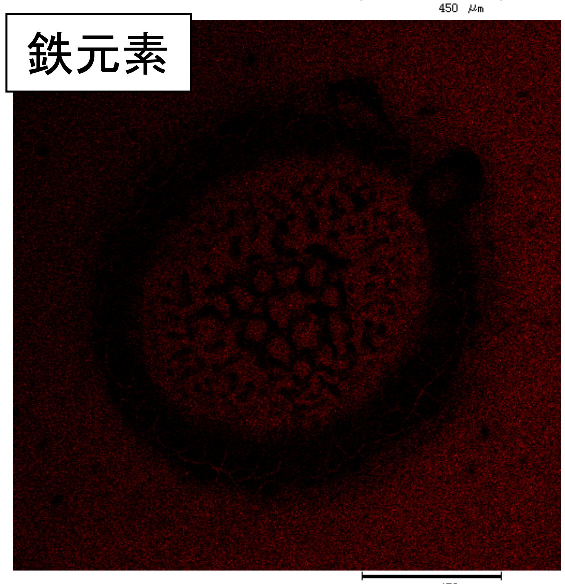
炭素元素



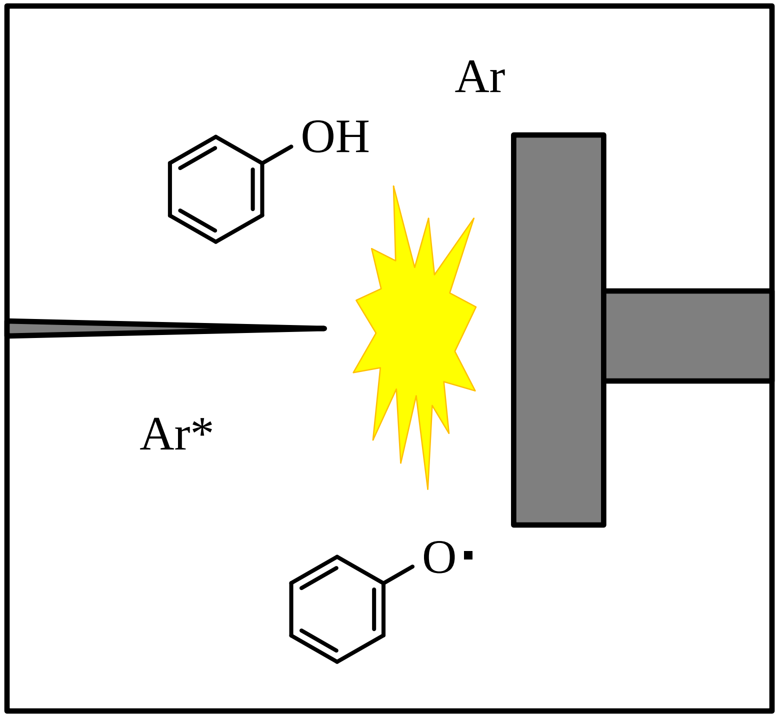
酸素元素

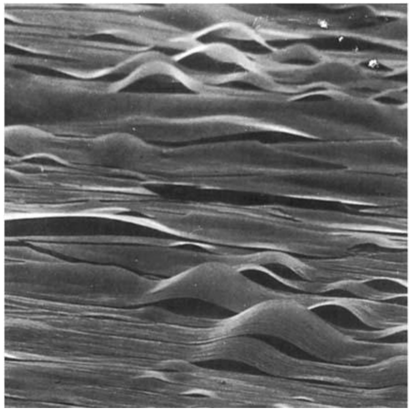


鉄元素



Purpose of our study





(2)Poly (2-alyl) phenylene oxide film (SEM image)

<u>フェノール性高分子のSEM画像</u>

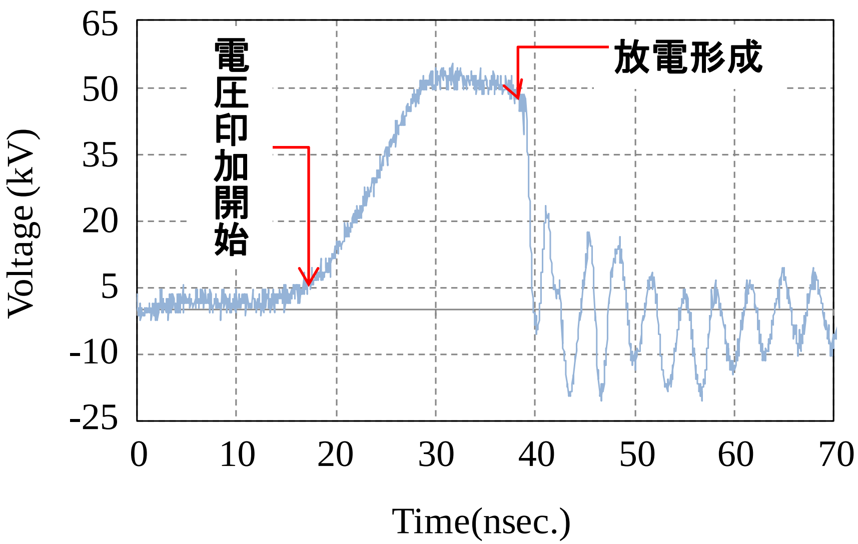
急峻な過電圧を印加できるナノパルス技術を応用し、
<u>超臨界アルゴン中で高活性種密度の高活性化エネルギー反応場</u>
を創成する。

フェノキシラジカルを多量に生成させ、フェノール性材料を合成する。
（耐熱・耐薬品性・導電性に優れた材料）

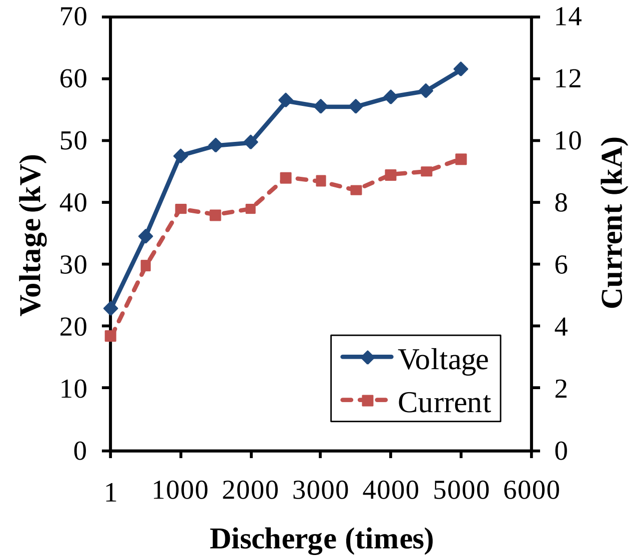
(1) J. Marsh et al. *J. Appl. Polym. Sci.*, **59** (1996) 897-903

亜臨界水中パルス放電特性

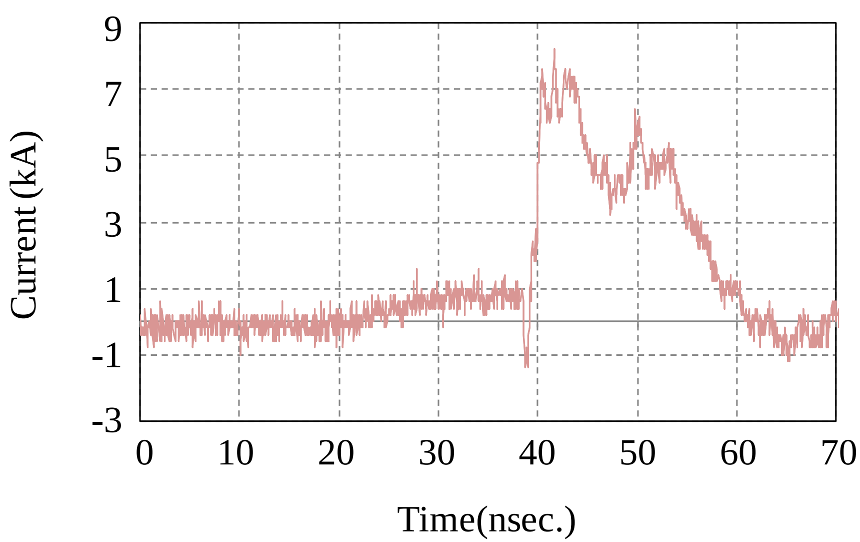
電圧波形



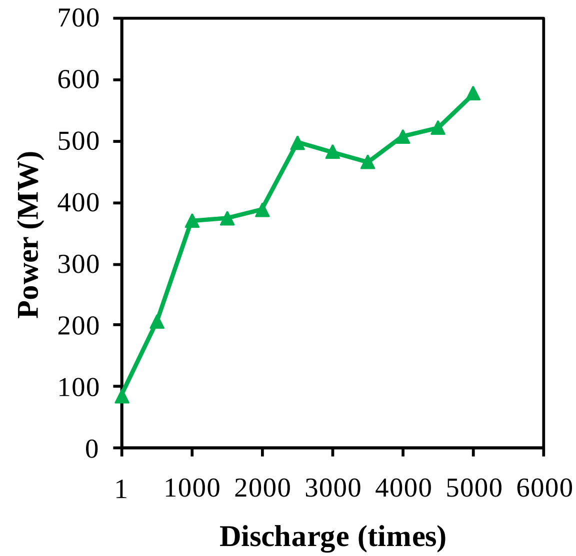
電圧・電流の変化



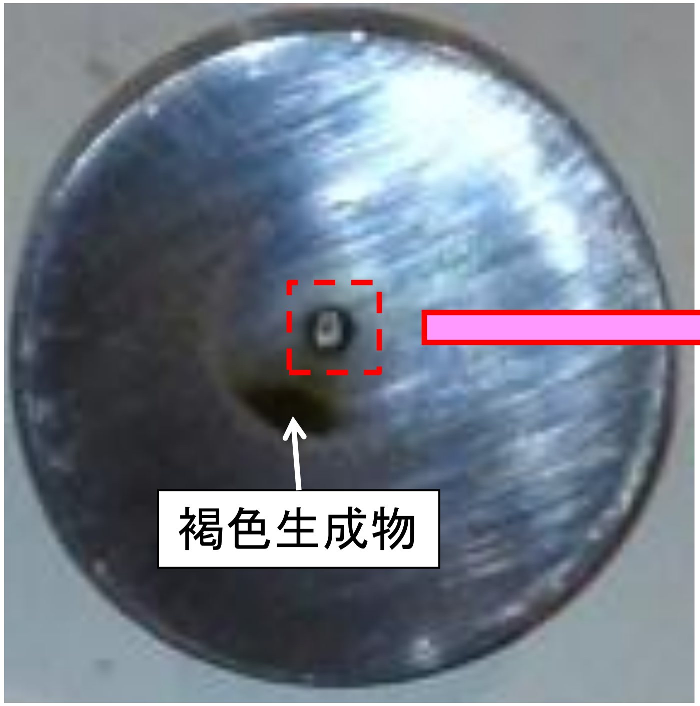
電流波形



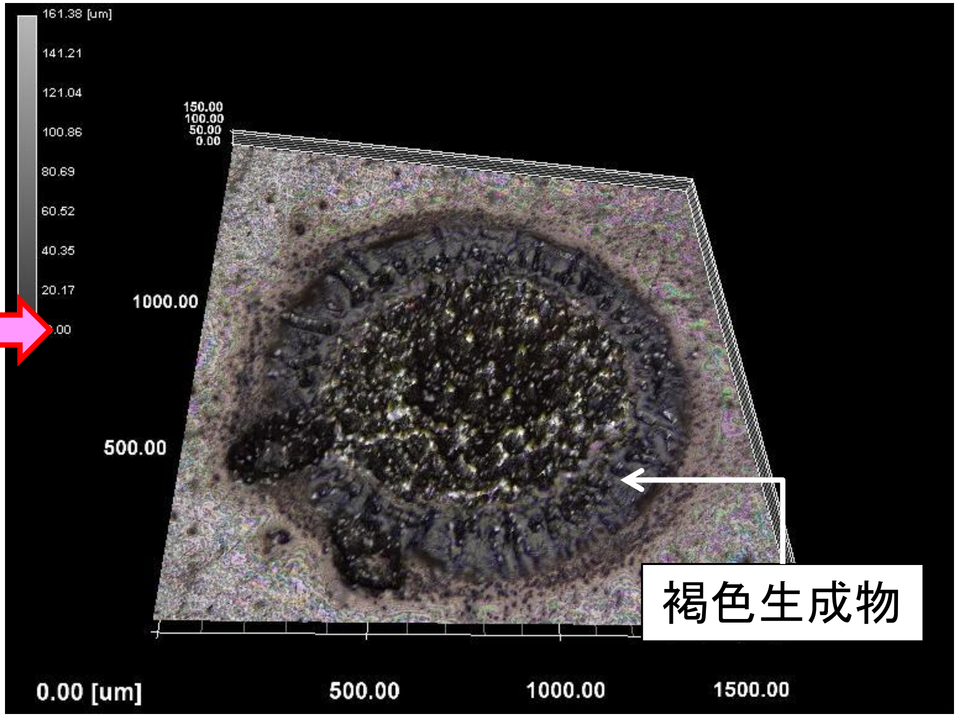
電力量の変化



超臨界Ar中パルス放電後の平板電極



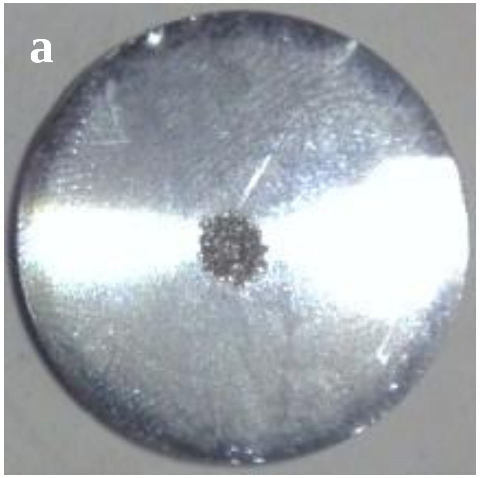
回収電極写真(100,000回放電時)

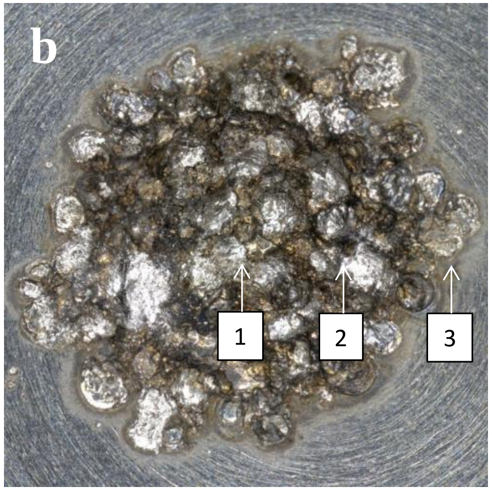


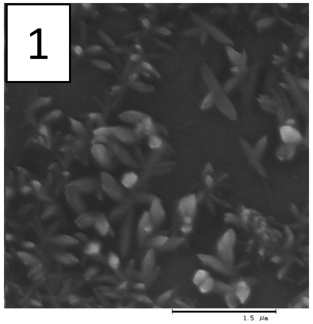
放電痕レーザー顕微鏡写真(20倍)

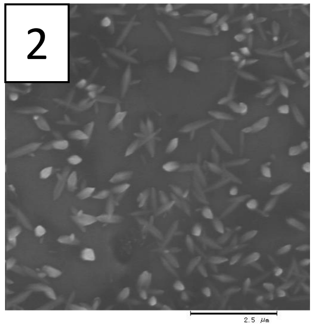
<u>**放電痕:ナノパルス放電で形成されるクレーターのような陥没**</u>

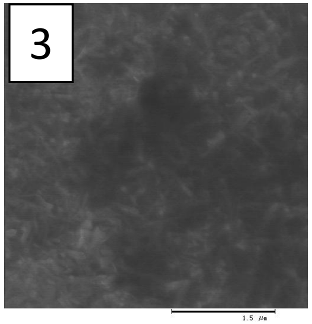
回収電極(亜臨界水プラズマ実験)

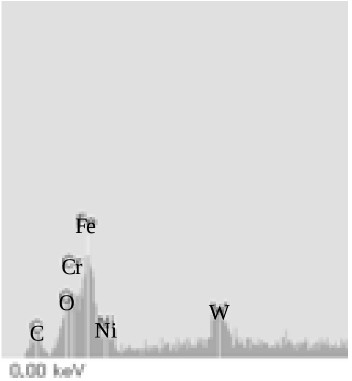


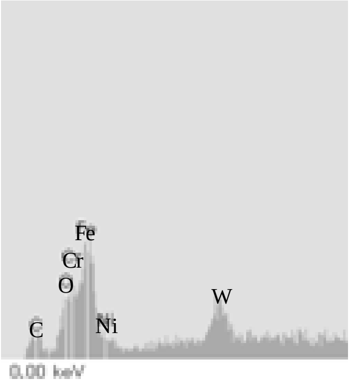


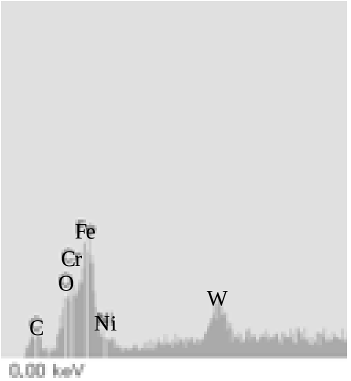




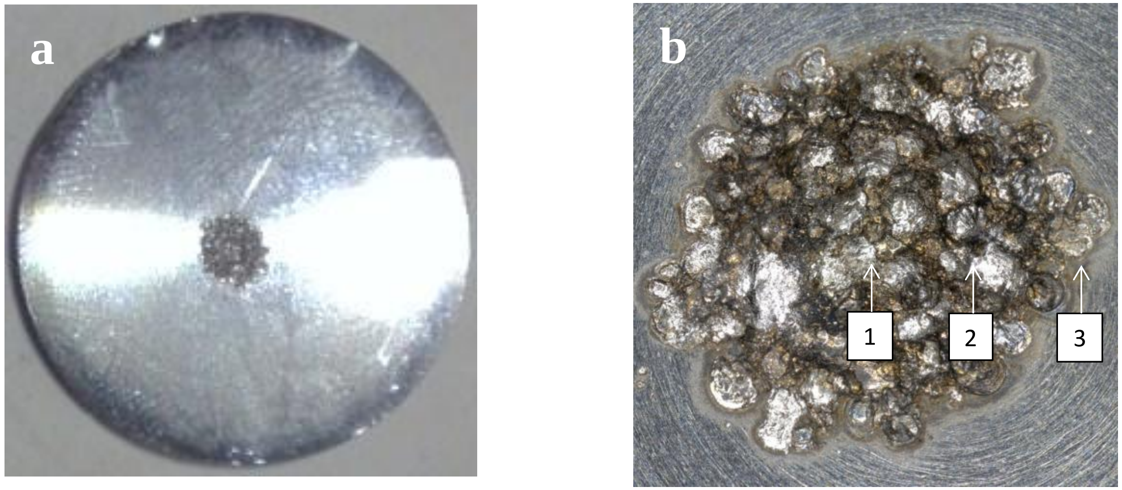


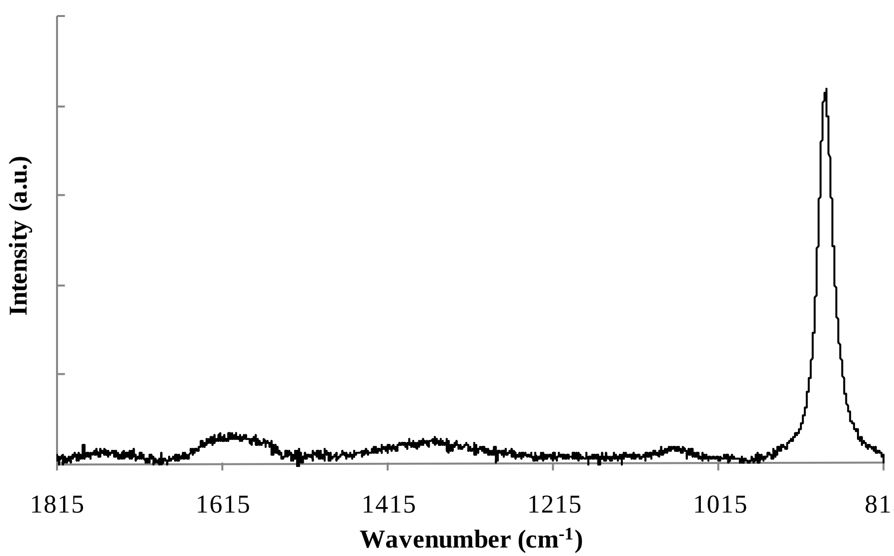






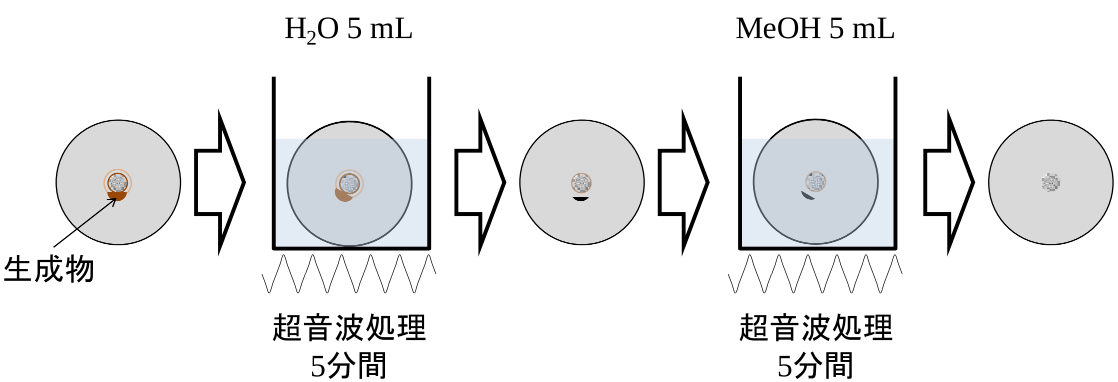
回収電極(亜臨界水プラズマ実験)

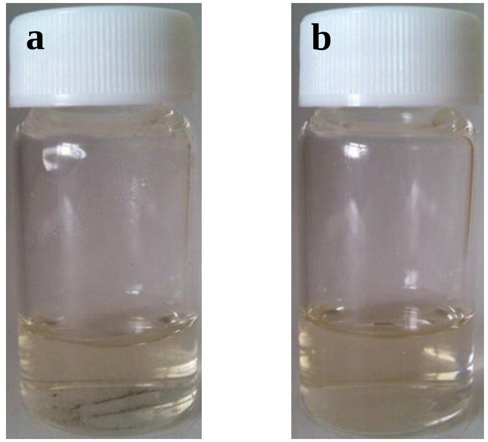




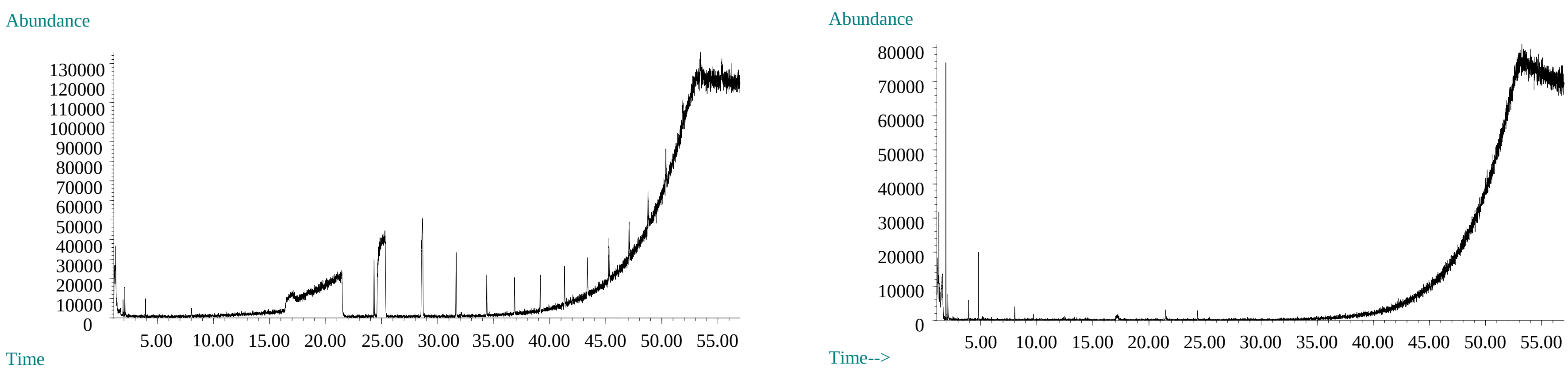
ラマンスペクトル

電極上生成物（超臨界Arプラズマ実験）



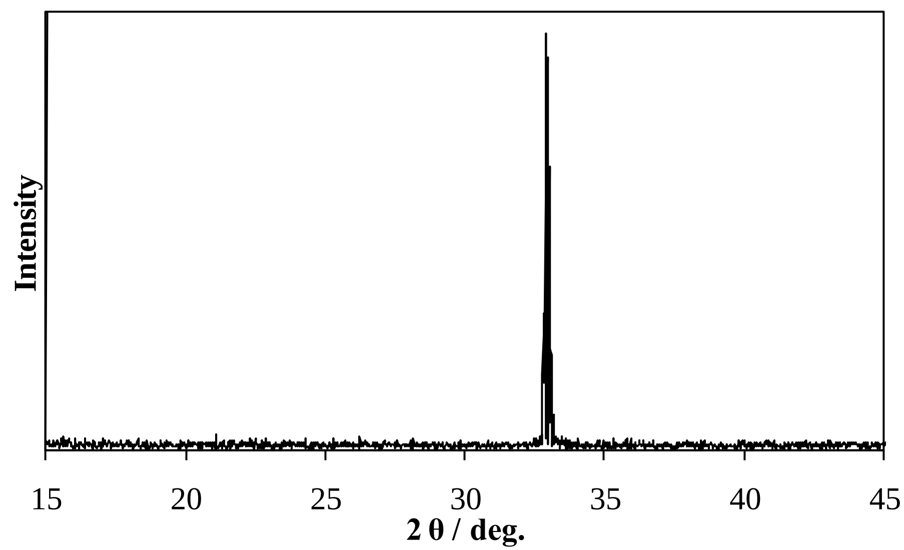


H_2O洗浄液　メタノール洗浄液



H_2O洗浄液（GC/MS分析）　メタノール洗浄液（GC/MS分析）

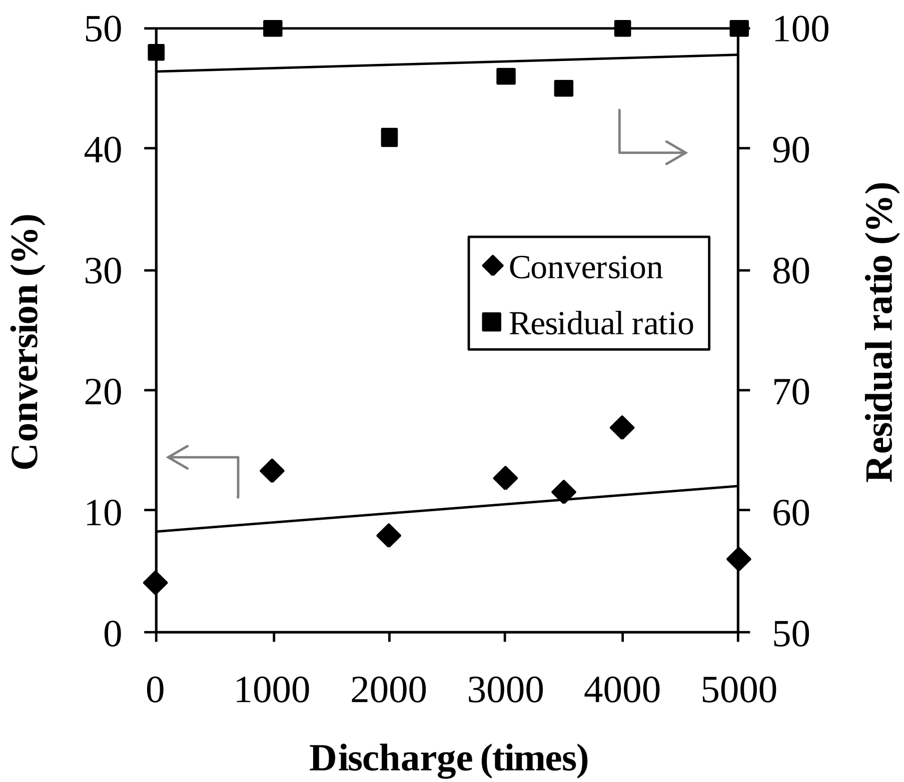
XRD分析結果



濃度が低く、基板として用いたシリコンのみが検出された

回収物

<u>フェノール転化率・残存率</u>



<u>フェノール転化率算出式</u>

$$Conversion\ (\%) = \left(1 - \frac{Recov\,erd\ (AREA)}{Initial\ \ Sample\ (AREA)}\right) \times 100$$

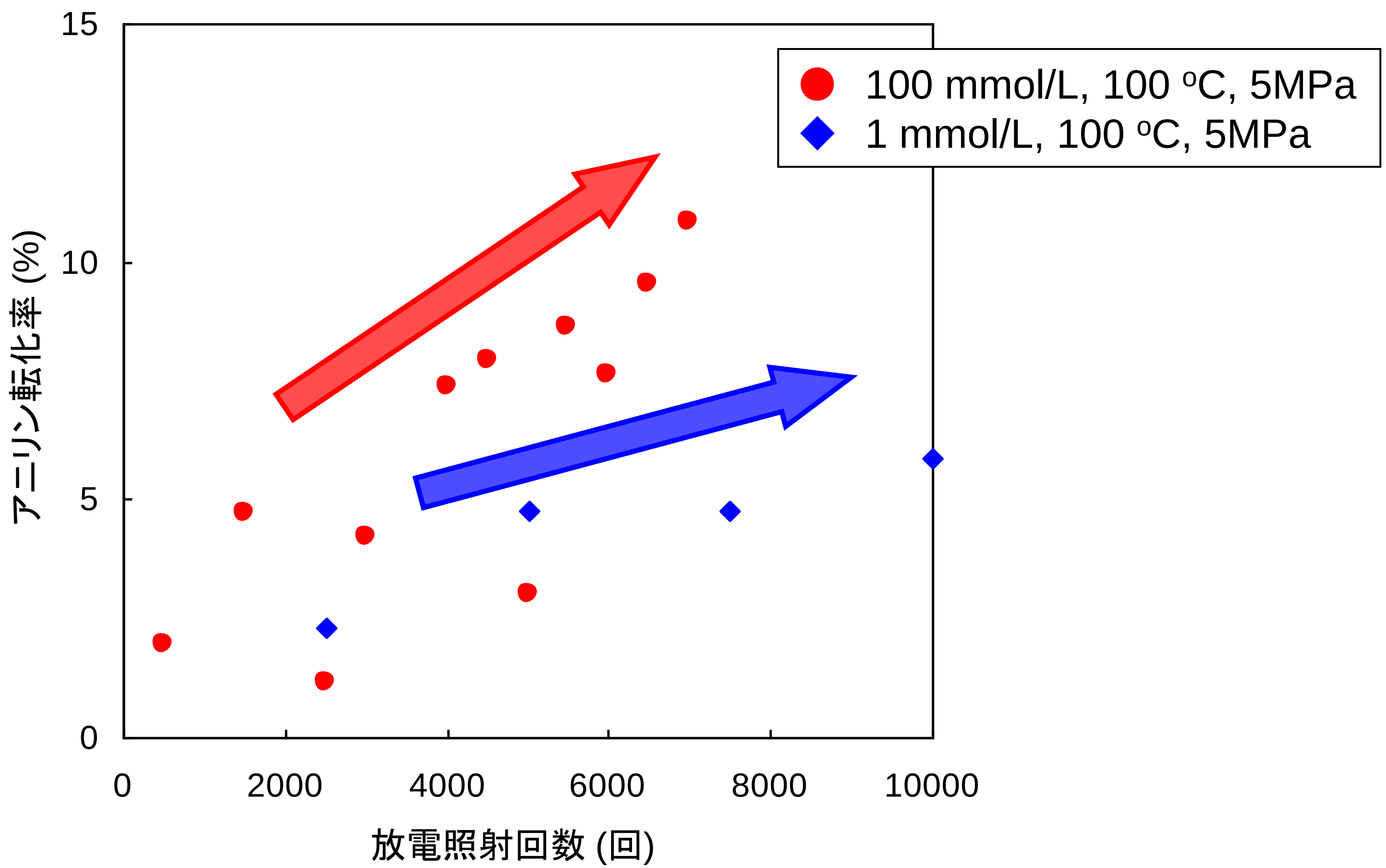
<u>残存率算出式</u>

$$Residual\ \ ratio\ (\%) = \left(\frac{Recov\,erd\ (ppm)}{Initial\ \ Sample\ (ppm)}\right) \times 100$$

HPLC分析ではフェノール以外のピークは確認できなかった

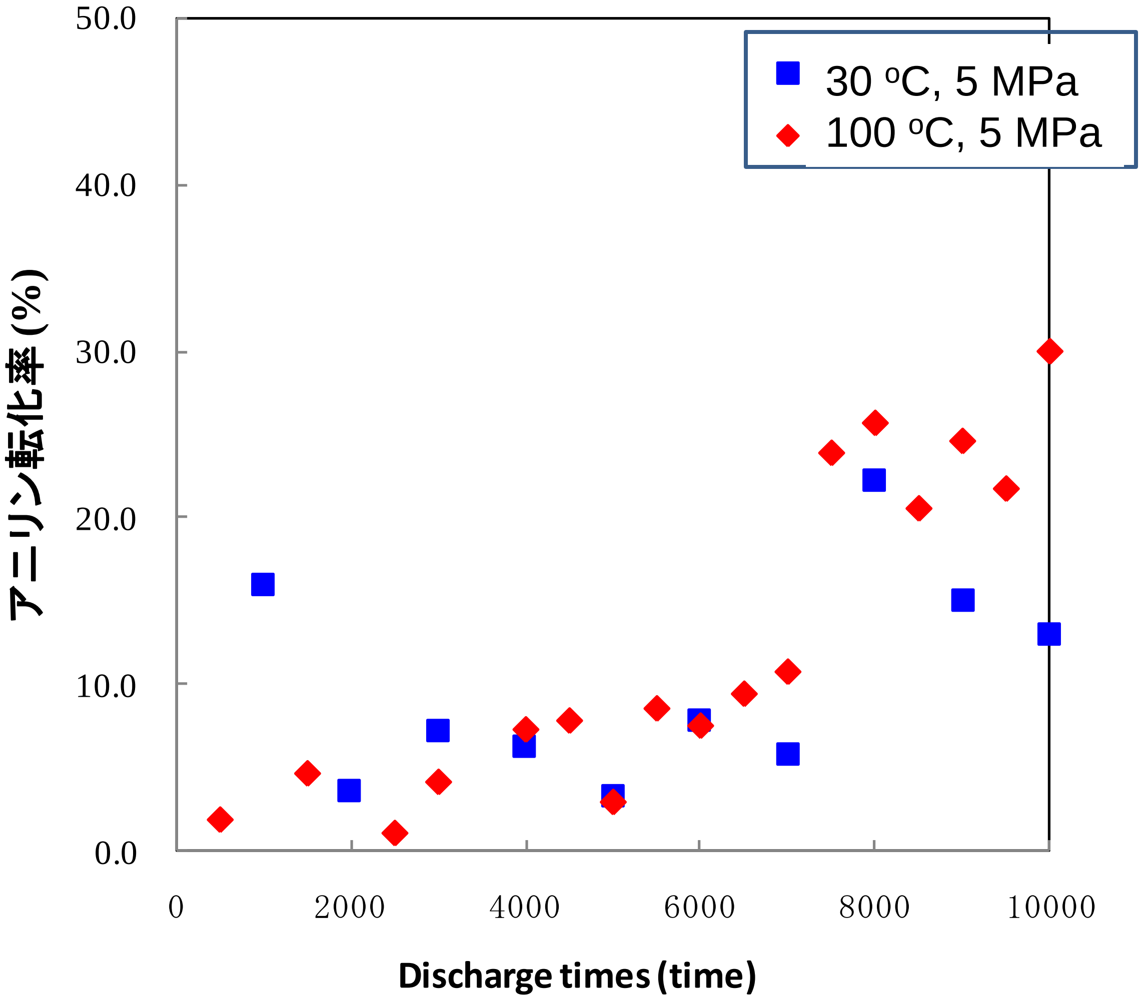
→ **<u>フェノールは水不溶性成分に転化した可能性が高い</u>**

アニリン転化率に与える初期濃度および放電回数の効果



- 放電回数が増加するに連れて、アニリン転化率は増加した。
- 高濃度で処理した場合の方が高い転化率が得られることが確認できた。

アニリン転化率に与える温度の効果



➢温度依存性はわずか。しかしながら, 放電回数の多い領域では高温ほど転化が増大(最大30 %)