Pulsed Discharge Plasma Treatment of Phenol in Sub-critical and Supercritical Fluids for Polymer Synthesis

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In this work, reactions of phenol were carried out in supercritical argon (critical temperature, Tc: 150.7 K, critical pressure, Pc: 4.8 MPa) with pulsed discharge plasma to understand reaction characteristics and to evaluate possibility that this technique will be applicable for a new "green" polymerization technique of functional polymeric materials. Experiments in subcritical water or in supercritical argon were conducted through the operation of a specially-designed SUS316 batch-type reactor (inner volume: 900 mL) at 373-523 K and 1-25 MPa, or at 303–373 K and 5 – 15 MPa, respectively. The electrode configuration consisted of a point (negative electrode) and a planar surface (positive electrode), which were made of tungsten and stainless steel, respectively. The distance between the two electrodes was fixed at 1 mm. Two kinds of power supply devices (BPFN and MPC) were employed. As results using a BPFN, it was found that reaction behavior in subcritical water at 373-523 K, 1- 25 MPa with less than 4000 times pulsed discharges basically similar to that in supercritical argon, but polymerized products of phenol could be obtained under larger pulsed discharge times like 5000 times at identical conditions. In contrast, phenol could be converted into hydroquinone but no polymerized product could be confirmed in supercritical argon. On the surface of the electrode used, it was found that phenol could be converted into amorphous graphite oxide with pulsed discharge plasma treatment in supercritical argon. This finding will be expected as a new method for the carbon-based functional materials in supercritical argon.

Key words: Subcritical water, Supercritical argon, Pulsed discharged plasma, Phenol, Polymerization

INTRODUCTION

Recently, green chemistry has been focused on from the viewpoint of environmental improvement. Reactions without toxic solvents and catalysts are important for green chemical processes. Supercritical fluids are widely used as novel processing media on various industrial fields because of the unique properties like high solubility, high diffusivity and low viscosity. The authors believe that water at the subcritical state (Tc = 647.2 K, Pc = 22.1 MPa) has high potential to take place chemical reactions under the introduction of pulsed discharge plasmas because of larger ion product (around 10-11) and relative high dielectric constant (about 30-40) in subcritical state. Generating plasma discharge in sub-critical water causes the formation of active species (H radical, OH radical, ions, free electrons, etc.) and probably the production of phenolic oligo- and polymers. In our previous work, the basic discharge property in ambient and subcritical water could be investigated experimentally [1].

In this work, argon at the supercritical state (Tc = 395 K, Pc = 4.8 MPa) was focused on as another candidate of solvents for chemical synthesis of aromatic compounds with pulsed discharge plasma. Argon is probably the chemical element studied most often. Like carbon dioxide, argon has easily obtainable critical points and it is also non-polluting [2]. Argon is also inexpensive and its optical transparency is superior to that of carbon dioxide since it is monatomic. Lock et al. initiated pulsed corona discharge under supercritical conditions, and reported that the breakdown voltage for a wire-in-cylinder configuration is three times lower than estimates based on Paschen's law due to the large in-homogeneties in the density of the supercritical fluid near the critical point [3]. Recently, the discharge plasma in supercritical fluids is an underdeveloped field, and the pre-breakdown phenomena are not well understood. Therefore, in this present study, argon was selected as the medium for plasma production to synthesis the aromatic compounds. The breakdown voltages were applied a negative DC voltage in order to characterize the electric discharges in supercritical argon. Finally, this research is expected to generate discharge plasmas in sufficiently large volumes that they can be used in various industrial applications, and to design a reactor with discharge plasmas in supercritical fluids.

In this work, reactions of phenol were investigated in sub-critical water and supercritical argon with pulsed discharged plasma in order to understand reaction characteristics of phenol under these conditions and to evaluate possibility that this technique is applicable for a new "green" and "unique" synthetic method for conducting polymers.

MATERIALS AND METHODS

Materials

HPLC-graded phenol and methanol were purchased by Wako Pure Chemical Industries Inc. (Tokyo, Japan) with purities of 99.0 %, respectively. This compound was completely soluble in water and methanol at room temperature. 0.1 mol/L of phenol aqueous solution was prepared with distilled water and used in this study. Argon gas (purity: >99.9999 %) which was supplied from Uchimura Sanso Co., Ltd. (Kumamoto, Japan) was used as a solvent. 2,5-Dihydroxybenzoic acid (DHB), which was used as a matrix for MALDI-TOF/MS analysis, was purchased from Wako Pure Chemicals Industries Ltd. and had purities more than 99.0%. The analytical reagents (HPLC grade) used were methanol from Wako Pure Chemicals Industries Ltd. and all chemicals were used without further purification.

Experimental apparatus and procedure

Fig. 1 shows a schematic diagram for plasma production in supercritical argon. There are two inspection windows in this reactor to monitor the performance of plasma production. The reactor is made of stainless steel (SUS316) with volume of 900 mL. The maximum of temperature and pressure are 573 K and 30 MPa, respectively. A power lead was introduced through the center of a long bushing made of peak resin, and the annular space was sealed with double o-rings placed around its outer surface to prevent gas leakage. Water (or argon from a cylinder) was loaded directly into the reactor and controlled using a back-pressure regulator. A thermocouple and a backpressure regulator were user to control the temperature and the pressure of the reactor, respectively. After the temperature and pressure were achieved at desired operating values, the pulse power was applied to produce electric discharges.

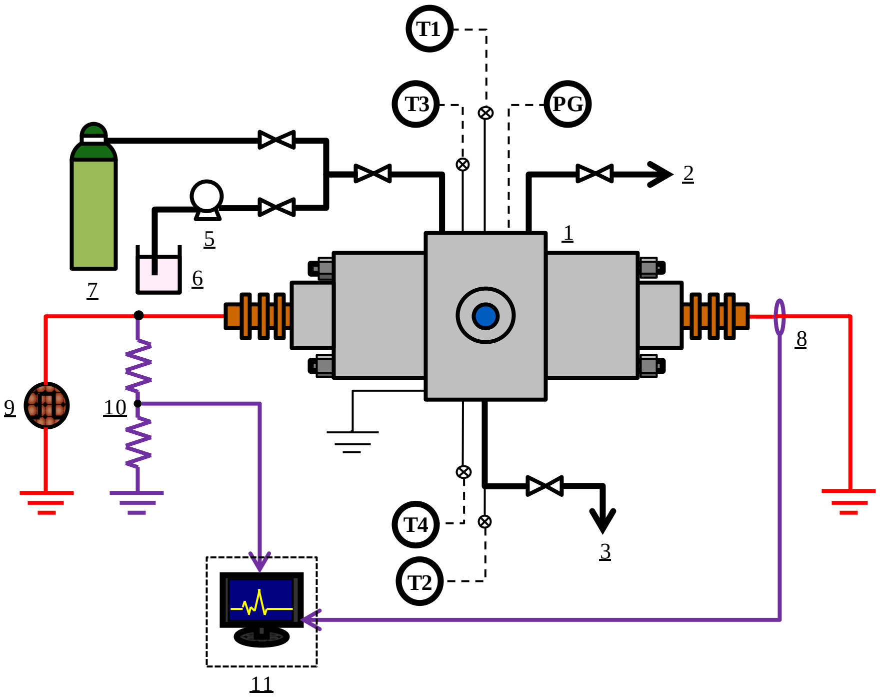


Fig. 1. Experimental setup for synthesis reaction of aromatic compounds in supercritical argon discharged plasma. 1, reaction cell; 2, gas outlet; 3, solution outlet; 4, gas inlet; 5, pump; 6, supply vessel; 7, Argon container; 8, current transformer; 9, Power supply device for high voltages; 10, high voltage probe; 11. digital oscilloscope. Red line: Plasma generation circuit; Purple line: Voltage-current measurement circuit.

The electrode configuration consisted of a point (positive electrode) and a planar surface (negative electrode). They were made of tungsten and stainless steel, respectively. This configuration produces a non-uniform electric field. The electrode gap was < 1 mm. A voltage was applied to the positive electrode using MPC (MPC2000S, Suematsu Electronics Co. Ltd., Japan) or BPFN that was charged by a high-voltage stabilization DC power supply. Fig. 2 shows the profiles of repetition rates of these power supplies. The breakdown voltage and the current were respectively measured using a high-voltage probe (EP100K, Pulse Electronic Engineering Co. Ltd., Japan) and a current transformer (4997, Pearson Electronics, Inc., USA) that were connected to a digital oscilloscope. After the reaction time had elapsed, the electric current was cut off and the autoclave was opened.

ANALYTICAL SECTION

After each experiment, the water-soluble portion was analyzed its organic carbon content by using a TOC analyzer (TOC-5000A, Shimadzu Co., Japan) and by HPLC with a JASCO MD-2010 Plus. The methanol-soluble portion which could be collected after quenching the reactor down to 363 K was analyzed by GC/MS (HP model 6890 series GC system and 5973 mass selective detector) and MALDI-TOF/MS to identify products and by GC-FID. The conversion of phenol was calculated on the basis of the change in concentrations before and after treatments through the HPLC analysis of the collected samples.

RESULTS

Reactions in sub-critical water **[4]**

Prior to experiments, waveforms at each operating condition were obtained in order to understand what kind of discharge did it occur. Fig. 2 shows the typical waveforms in sub-critical water. The pulse voltage increased rapidly to about 50 kV within 20 - 30 ns and suddenly dropped down to zero when the discharge took place. At 40 ns, the current rapidly jumped up to about 7 kA. This phenomenon clearly indicates the occurrence of arc discharge in sub-critical water.

In all the experimental conditions with a BPFN power supply, the conversions of phenol were in the range of 10-30 mol% in subcritical water at 373 and 523 K and 1 – 25 MPa although it increased slightly with the times of pulsed discharge. Only aqueous product solution could be obtained in most cases, but water-insoluble (methanol soluble) fraction could be recovered in the cases where the discharge time was more than 4000 at 523 K and 25 MPa. Fig. 3 shows the GC/MS chromatogram of methanol-soluble fraction obtained after the 4,000 times discharge treatment at 523 K and 25 MPa. From this figure, it was found that there were polymerized products of phenol (like dimer and trimer) as one of products. As for the trimer, phenoxy radical (Ph-O-) was found to be bonded at meta position of another phenol molecule. In general, this kind of bonding do not follow the principle of reaction chemistry, so the plasma discharge treatment in sub-critical water might have a unique reaction mechanism not following the principle of general organic chemistry.

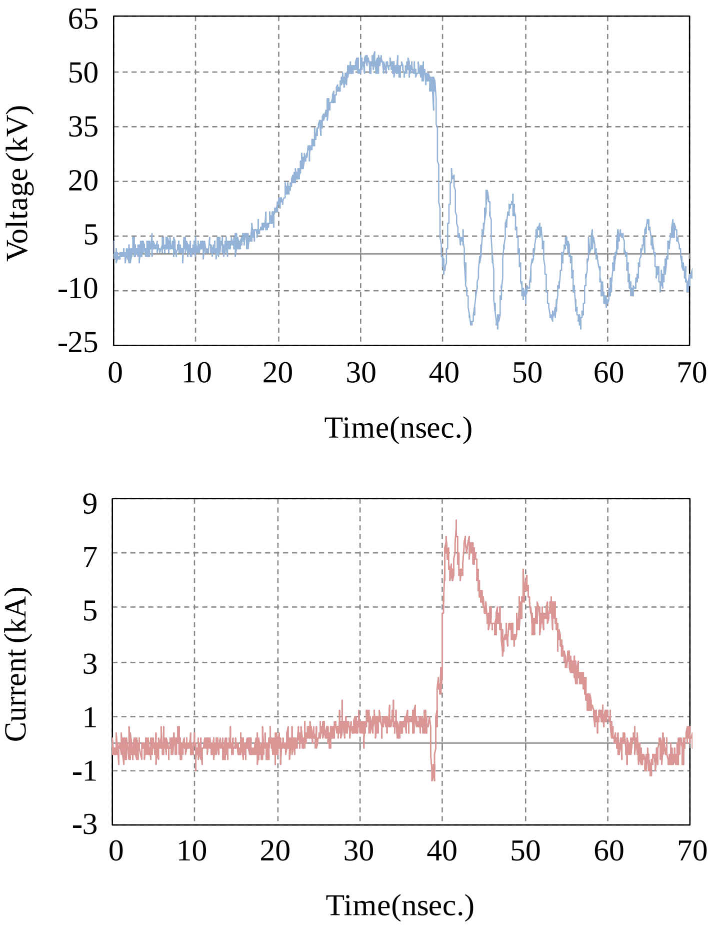


Fig. 2 Typical waveforms of pilsed voltage and current in sub-critical water. (at temperature of 523 K and pressure of 25 MPa)

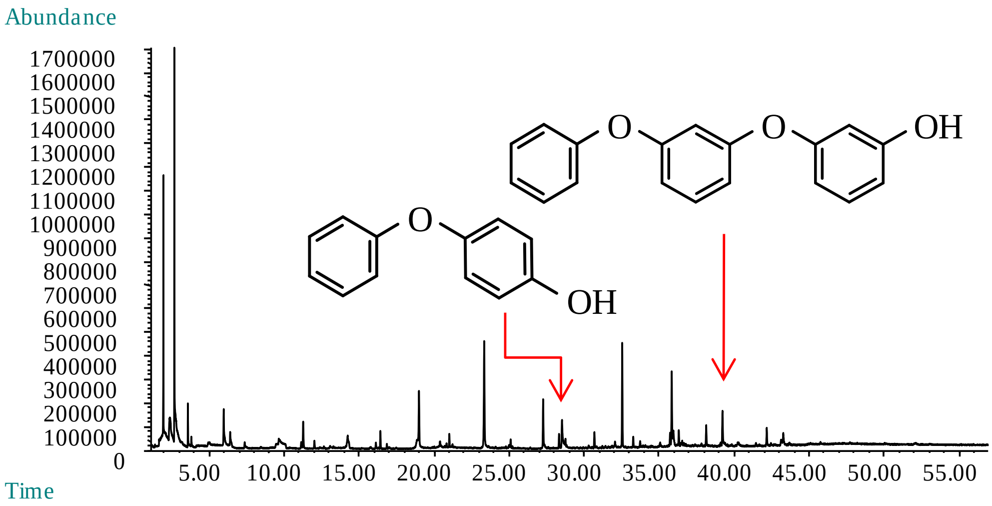


Fig. 3 GC/MS chromatograph of methanol-soluble fraction at 4,000 times discharged at 523 K and 25 MPa.

As the times of pulsed discharge were more than 4000 times (e.g. 5000 times), there were several peaks which were corresponded to phenol oligomers in methanol-soluble fraction as shown in Fig. 4. From these findings, it was suggested that hydroxyl radicals which generated from the decomposition of water activated phenol molecules to form phenoxy radicals, resulted in the production of higher degree of polymerization components under subcritical water atmosphere.

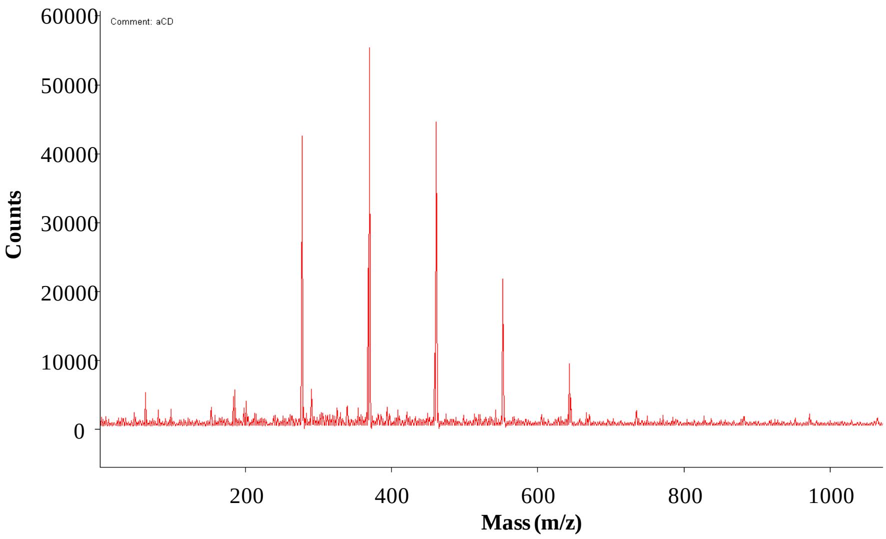
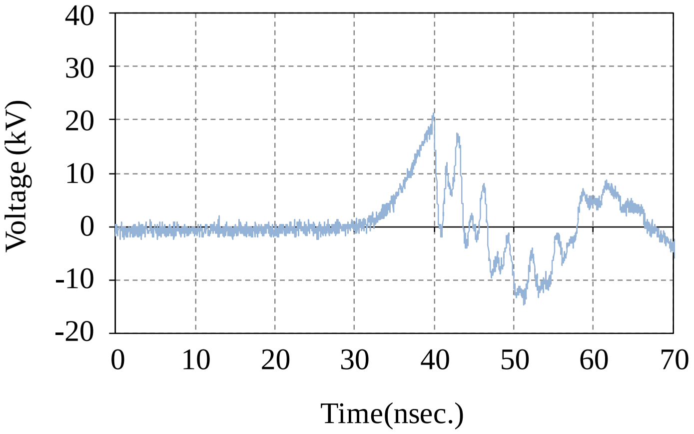


Fig. 4 MALDI-TOF/MS analysis of oily products at 5,000 times discharged at 523 K and 25 MPa.

Reactions in supercritical argon

In case of supercritical argon, the waveforms at each operating condition were also examined to understand what kind of discharge did it occur. Fig. 5 shows the typical waveforms in supercritical argon. The pulse voltage increased rapidly to 20 kV within 10 ns and then decreased to zero when the discharge took place. As soon as the pulse voltage reached 20 kV, the current increased to about 5 - 7 kA. This is found to be arc discharge, but it can be said that discharge can occur in supercritical argon much easier than in sub-critical water.



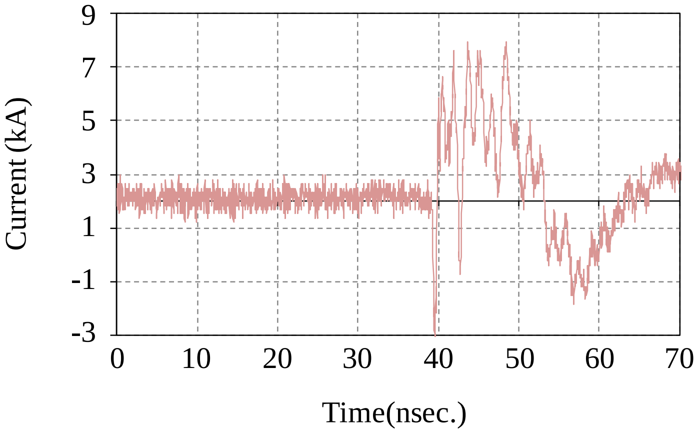


Fig. 5 Typical waveforms of nano-pulsed voltage (top) and current (bottom) in supercritical argon. (at temperature of 313 K and pressure of 5 MPa).

In case of reactions of phenol in supercritical argon were carried out with two kinds of power supplies (BPFN and MPC). At 313 K and 5 MPa, phenol was treated in supercritical argon by using a BPFN. As a result, no product could be detected after the reaction even though 5000 times discharges have been done. On the contrary, when the MPC power supply was employed on the reaction of phenol and experimented at the same temperature and pressure. Fig. 5 shows the GC/MS chromatogram of the compound produced through the synthesis reaction of phenol in supercritical argon at 313 K and 5 MPa with pulsed discharged plasma (100,000 times discharge by MPC). From this figure, it was found that hydroquinone could be obtained as a main product and small amount of unidentified polymerized compounds could be also detected. These experimental results can be explained as follows: In this system, phenol radicals underwent alkyl rearrangement and re-polymerized to form heavier cross-linked phenolic materials which contain oxygen functional groups such as hydroxyl, carboxyl, carbonyl groups, ether and ester bonds with meta and para types. At this condition, mehta and para types compounds were probably derived from ortho types compounds. It could be considered that they were produced via C-O bonds cleavage from phenol molecule. Initial reaction responsible for the decomposition of phenol is most likely to be the scission of an O-H bond, resulting in the formation of a hydroxyl-substituted phenoxy radical and H atom. Then the H atom generated can react with phenol, displacing an OH with H. At the same time, the association of phenoxy radicals occurred to form the higher molecular weight compounds. Another possibility that polymeric compounds cannot be obtained in this system is that the pulsed power generator loaded current and power too much than required ones for polymerization. At present situation, oligomeric intermediates which might form during the treatment at once would degrade into phenol or other minor components due to the high energy loading to the system.

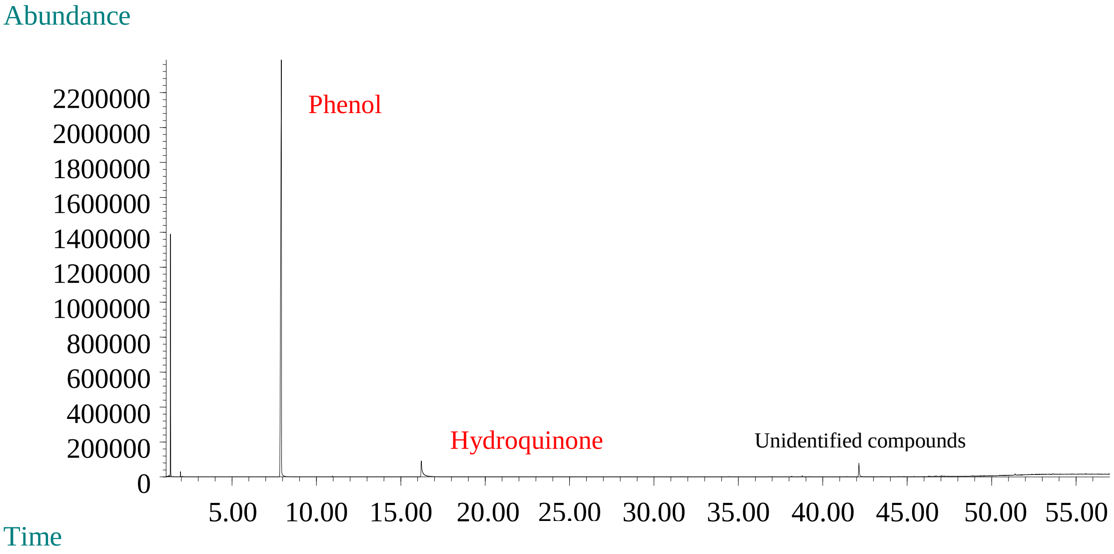


Fig. 6 GC/MS chromatograms of methanol-soluble fraction obtained after pulsed discharge plasma treatment in supercritical argon at 313 K, 5 MPa and 100,000 times discharges (with MPC power supply)..

MALDI-TOF/MS analysis of the methanol-soluble fractions was also carried out to evaluate whether polymerization of phenol would take place or not at this condition. As a result, MALDI-TOF/MS spectrum revealed that main massed peaks distributed from 30 to 800 amu and that the formation of low molecular weight compounds (less than 100 amu) could be confirmed as main products. This is probably due to the scission of O-H bond in a phenol molecule. At the same time, higher molecular weight compounds (more than 200 amu) were slightly formed by the association reaction of phenol and its derived compounds. These results provide evidence that functional groups react with other phenolic structures to form higher molecular weight compounds. Judging from these results, the synthesis reaction of phenol in supercritical argon discharged plasma probably progressed in through the scission and association, which leads to the formation of lower or higher molecular weight compounds.

Reaction pathways

Considered from the experimental results obtained, the reaction pathway for phenol in sub-critical or supercritical argon can be proposed as shown in Fig. 7. In sub-critical water, water can be degraded into OH radical and H radical easily and H radical might attack to phenol molecule to form phenoxy radicals ($C_6H_5O\cdot$). Phenoxy radicals can generate dimeric or oligomeric species to connect each other, resulted in the formation of phenolic oligomers with pulsed discharge plasma in sub-critical water. On the contrary, phenoxy radicals can generate through the pulsed discharge treatment in supercritical argon but they might be deactivated by attacking exited argon species to form phenol or benzene plus OH radical. During the reaction, the OH radicals might connect with phenol to generate hydroquinone or pyrocatechol under this condition.

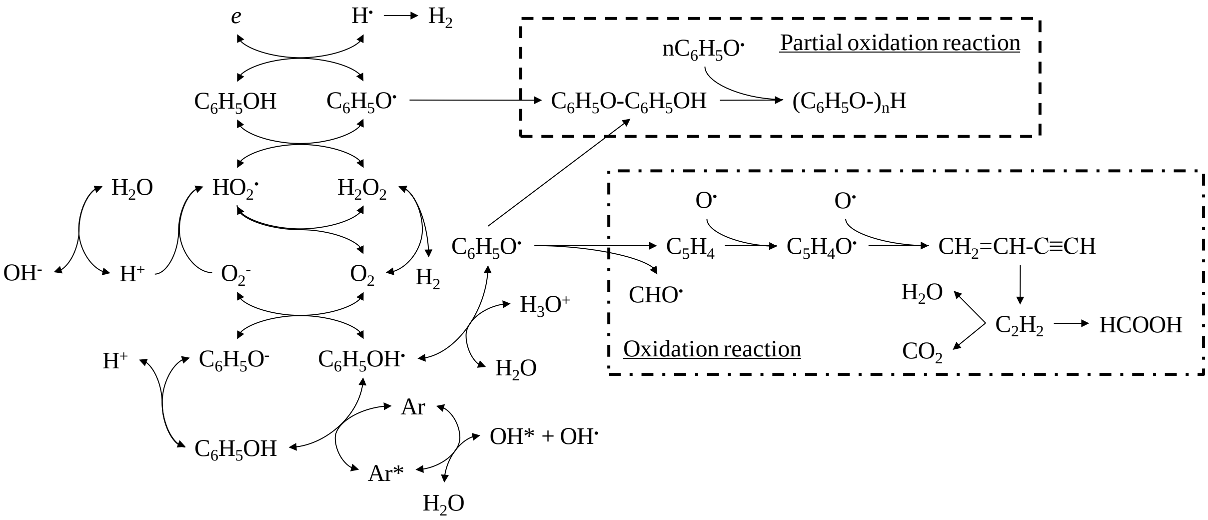


Fig. 7 Possible reaction pathway in sub-critical water and supercritical argon.

It was confirmed that a film material was generated as shown in Fig. 8 and that the material was consisted of carbon and oxygen element subjects. Fig. 9 shows the analytical result of Raman spectroscopy of the electrode which was collected after pulsed discharge treatment. There were two peaks, about 1590 cm^{-1} and 1350 - 1400 cm^{-1} on the Raman spectra, which can be considered as G band peak (sp^3 bonding) and D band peak (sp2 bonding), respectively. From this analysis, it could be understood that this amorphous carbon film was the carbide having sp^3 and sp^2 bond linkages. The characteristic of the film obtained was strongly similar to that of the hard, amorphous carbon film which prepared by conventional methods such as the RF plasma CVD method operated at 200 - 300 °C.

According to recent reports, it is well known that the amorphous carbon films prepared by RF plasma CVD does not have a D band peak (around 1340 cm-1) and the intensity of the D band peak remarkably increased by annealing at 500 - 600 °C. Considered from this knowledge, it can be thought that the amorphous carbon film could be produced from phenol with the nano-pulsed electrical discharge plasma.

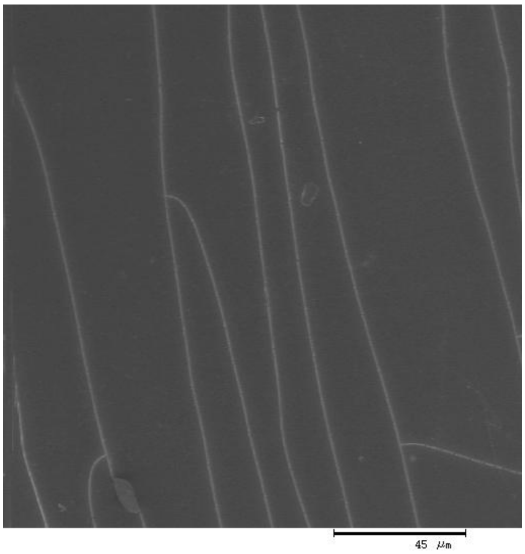


Fig. 8 SEM image of the surface of the electrode collected after the nano-pulsed discharge plasma treatment of phenol in supercritical argon.

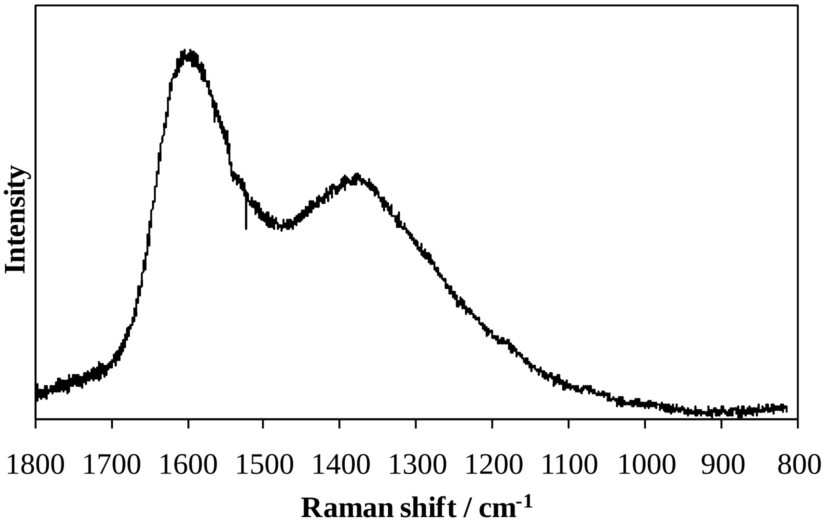


Fig. 9 Raman spectroscopy of the surface treated with pulsed discharge plasma in supercritical argon.

CONCLUSIONS

Reactions of phenol were experimentally investigated by applying pulsed high-voltage discharge plasmas in sub-critical water and supercritical argon. As the result, it was found that phenol could be polymerized and obtained phenol oligomers at specific operating conditions in subcritical water. In supercritical argon, in contrast, addition reaction of hydroxyl group into phenol molecules could be confirmed at 313 K and 5 MPa, but no polymerization products could be obtained. The difference in the product distributions was probably because of the difference in reaction mechanisms and pulsed energy loaded during the reaction. Detailed analysis of the reaction mechanism will be reported in the near future. In contrast, it was found that phenol could be converted into amorphous graphite oxide with pulsed discharge plasma treatment in supercritical argon. This finding will be expected as a new method for the carbon-based functional materials in supercritical fluids.

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