Electrodecomposition in Subcritical Water Using *o*-Xylene as a Model for Benzene, Toluene, Ethylbenzene, and Xylene Pollutants

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Received: January 11, 2008; Revised Manuscript Received: May 2, 2008

The possibility of the combination of electrolysis and subcritical water as a novel electrolyte was investigated. A stainless steel reactor was used as an undivided electrochemical cell containing platinum as the anode and a stainless steel reactor as the cathode. At first, the effect of temperature on the electrolysis current as the main parameter was studied in a cell containing only pure water and a supporting electrolyte. It was realized that the electrolysis current (and, consequently, the electrolysis efficiency) increased linearly with temperature because of the change in viscosity and other physicochemical properties of subcritical water. As a result, at 553 K the electrolysis efficiency was over 14-fold higher than that under ambient conditions. The possibility of the applicability of the above combined techniques for the decomposition of *o*-xylene was also followed as a model for benzene, toluene, ethylbenzene, and xylene (BTEX) compounds. The effect of experimental conditions such as the electrolysis duration, the electrolysis voltage, and the temperature of subcritical water was investigated. Several decomposed products were identified. *o*-Xylene was directly electro-oxidized to 2-methylbenzyl alcohol and consecutively to the other oxidation products. Also, hydroxide ions were oxidized to oxygen molecules, where hydrogen was generated on the cathodic surface. The final oxidation product of the electro-oxidation reaction was identified as carbon dioxide. The results indicate that more than 95% of *o*-xylene can be decomposed under optimum conditions.

1. Introduction

Subcritical water (sub-CW) with a green ideology has generated considerable interest as a unique reaction medium. The advantages of such a medium are related to (1) the low viscosity, (2) the low dielectric constant (i.e., from 80 at 298 K to 2 at 673 K), (3) the ionic product that reaches a maximum value at around 523 K, (4) the high diffusivity,[1–3] and so on, which increase the ability of sub-CW to dissolve many water-insoluble organic compounds.[4,5] For example, when the temperature of water increases from 293 to 473 K, the solubility of chlorothalonil increases 130 000-fold.[6]

Because molecular oxygen is also highly soluble in sub-CW, molecular oxygen has been widely used as an oxidation agent for the chemical oxidation of a variety of organic compounds, particularly organic pollutants.[7]

Electrochemical methods for the oxidation of organic compounds, including organic pollutants from wastewater, have attracted a great deal of attention recently. Traditional destruction methods pose problems of corrosion and, more seriously, of emission if the treatment conditions are not perfectly controlled. Contrary to chemical methods, in the electrochemical reactions there is no tendency to produce secondary pollution. Electrochemistry offers promising approaches for the prevention of pollution problems in the processing industry. The inherent advantage is its environmental compatibility, which is due to the fact that it uses a clean reagent: the electron. To minimize the amount of energy consumed, it is desirable to operate the electrochemical reactions in the most efficient manner. One of the important aspects of electrochemical reactions is the electrolyte type with a high migration of electroactive species. Sub-CW can provide such a medium.

There are many advantages of electrochemical reactions under sub-CW conditions.[8,9] For instance, sub-CW has lower viscosity and lower surface tension than those of water under ambient conditions; the conductivity of sub-CW increases by a factor of about 120 (from 298 to 523 K). Because certain materials that are insoluble in water are completely soluble in sub-CW, the thermodynamics and kinetics of many reactions are more favorable under sub-CW conditions. In electrochemical studies, the changes in the dielectric constant, the viscosity, and the density with pressure and temperature are particularly significant. However, in electrochemical reactions in sub-CW, very few studies have been carried out, probably because the apparatus design and the experiment itself are difficult.

Some previous reports concern the corrosion studies or the electrolytic decomposition of water.[10] Most of the research concerning the anodic evolution of oxygen and the cathodic evolution of hydrogen has been carried out under sub-CW conditions to elucidate the kinetics of the reactions.[10] Serikawa et al.[11] have reported the wet electrolytic oxidation and the mineralization of organic compounds in wastewater at 523 K and pressures of 7 MPa. They improved the electrolytic oxidation reaction by adding molecular oxygen from an external source. Nonaka et al.[12] have reported the application of hot water (in the range of 364−523 K) for the satisfactory oxidation of carbon monoxide, methanol, formic acid, ethanol, and acetic acid on a platinum electrode. Sasaki et al.[13] have fundamentally studied the electrolysis behavior of glucose in water at 523 K and pressurized CO_2 as an alternative electrolyte.

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10.1021/jp800452s CCC: $40.75

In the present work, we selected the decomposition of *o*-xylene as a model of the BTEX compounds. Xylenes are one of the top 30 chemicals produced in the United States in terms of volume, and in Japan, more than 4 900 000 t of xylenes are produced annually, of which about 3.5% is emitted to the environment.[14]

In xylenes, *o*-xylene is the only naturally occurring form, and the other two are synthetic. It is one of the most difficult-to-degrade environmental pollutants. Generally, xylenes have been studied for a long time as possible risks to human health. Bioremediation is apparently the most desirable cleanup technique for groundwater contaminated by xylenes.[15] The solubility of *o*-xylene in water has been studied by many researchers. At 298 K and atmospheric pressure, McAuliffe,[16] Sutton and Calder,[17] and Price[18] have separately measured and reported the solubility of *o*-xylene in water, and they are in excellent agreement; the average solubility of *o*-xylene is about 18 mg in 100 g of water.

o-Xylene (and, generally, BTEX compounds) is almost water-insoluble. Therefore the oxidation reactions of *o*-xylene have been carried out mostly chemically in nonaqueous or gas phases.[19,20] Many oxidation methods of *o*-xylene (and generally, BTEX compounds) have also been reported. For example, electrochemical methods have offered efficient and clean processes for the oxidation of these compounds; however, as mentioned above, most of them were carried out in organic solvents and in the presence of different kinds of catalysts.[21,22] There is no available report on the electro-oxidation of *o*-xylene compounds and other BTEX compounds under sub-CW.

In this study, our objectives were the design, the development, and the application of an electrochemical cell operating under sub-CW conditions to learn about electrolysis under sub-CW condition. Also, the oxidation of *o*-xylene as an example of a water-insoluble compound was investigated over a range of temperature in an electrochemical cell.

2. Experimental Section

2.1. Chemical Reagents. Ethyl acetate (99.8%), *o*-methoxy phenol (99.0%), 2-methylbenzoic acid (95.0%), 1-phenylethanone (98.5%), NaCl (99.5%), and 2-methylbenzonitrile (95.0%) were from Wako Pure Chemical; 2-methylbenzyl alcohol (98.0%) and 2-methylbenzaldehyde (97.0%) were from Aldrich; KH_2PO_4 (99.0%) and KNO_3 (99.0%) were from Ishizu Seiyaku LTD; 3H-isobenzofuran-1-one was from Tokyo Kasei Kogyo Co. LTD; and *o*-xylene (99.0%) was purchased from Kishida Chemicals.

2.2. Undivided Electrochemical Batch Cell. All reactions were conducted by using a batch-type reactor, shown in Figure 1, in which a stainless steel tube (SS316 with an inner diameter of 16.5 mm and a total volume of 36.5 cm^3) and Swagelok fittings (ready-made, from Swagelok AG) were used. Platinum metal with a rectangular plate shape (with a diameter of 6.0 × 130.0 mm) and a stainless steel reactor were used as a anode and a cathode, respectively. The head cap of the reactor was drilled and tapped to accept an anode electrode feedthrough. The anode was electrically insulated from the reactor body by means of a Teflon bushing. To collect the gaseous products, a stainless steel high-pressure valve (from Swagelok AG, Switzerland) was utilized at the other end.

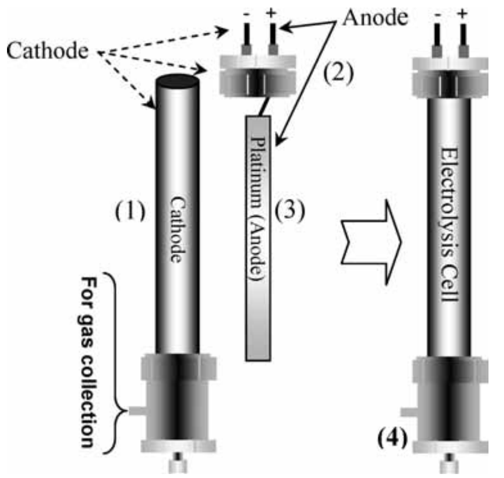


Figure 1. Schematic diagram of high-temperature, high-pressure undivided electrochemical batch cell: (1) body, (2) head cap with integrated electrode feedthrough, (3) platinum electrode, and (4) bottom cap containing a high-pressure valve.

2.3. Procedure. The electrolysis of pure water containing KNO_3 (0.1 M) was conducted over a wide range of temperature (from 298 to 553 K). A constant 3.0 V potential was applied (GPM 355 regulated dc power supply, Takasago Seisakusho, Ltd., Japan) between the two electrodes from 0 to 600 s. Table 1 summarizes the general experimental conditions. The electrolysis current data were obtained by an ammeter to evaluate the electrolysis efficiency as a function of electrolyte temperature.

For the electrodecomposition of *o*-xylene, in a typical reaction about 36 mg of *o*-xylene (as a reactant) and 24 g of water containing 0.1 M of KNO_3 (as a supporting electrolytes) were loaded into the reactor. Argon gas was used as a purging gas to force air out of the reactor, and then it was tightly capped and vigorously shaken and immersed in a salt or oil bath (Thomas Kagaku Co., Ltd. Japan) that was preheated to the desired temperature in the range of 313−553 K. A constant potential was applied by a power supply between the two electrodes to carry out the electrochemical reactions in the cell. For a comparison, a sub-CW treatment without electric potential was performed under the same operating conditions. Table 1summarizes the experimental conditions under which the decomposition of *o*-xylene was carried out. The reactor during the electrolysis was mechanically vibrating at about 680 Hz to decrease the diffusion layer and to remove the produced hydrogen, oxygen, and any other gaseous products from electrode surfaces. At the end of the reaction, the power supply was turned off, and the reactor was removed from the salt bath and was quickly quenched by immersion into a water bath at room temperature. All experiments were repeated in triplicate.

In this research, we studied electrodecomposition reactions under saturated sub-CW conditions and estimated the pressure inside the reactor from a steam table.[23]

2.4. Analysis. The reactor's contents were transferred to a 50 mL test tube containing 8.0 g NaCl as a salting agent and 2 mL of phosphate buffer (2 M, pH 7). Then, the inside of the reactor was rinsed four times with 5 mL of ethyl acetate, and the rinsed solutions (total volume of 20 mL) were added to the above test tube. The test tube was shaken at 90 rpm on a rotary shaker (Iwashiya−Sanki, Osaka, Japan) at 293 K for 10 h or longer to extract compounds from the aqueous phase into the ethyl acetate phase.

The internal standard solution (100 μL of *o*-methoxy phenol, 24 g/L) was added to 10 mL of the organic (ethyl acetate) phase and was then analyzed for remaining *o*-xylene and products by a GC-FID (gas chromatograph GC17A, Shimadzu, Japan) with a DB-FFAP column (30 m, i.d. 0.32, and film thickness of 0.25 μm).

Meanwhile, a GC-MS (GC-17A and GCMS-QP5050, Shimadzu) with a Stabilwax DA column (30 m, i.d. 0.25, and film

TABLE 1: Experimental Conditions for the Electrolysis and the Electrodecompositon of Pure (Subcritical) Water and *o*-Xylene, Respectively

Electrolysis of Pure (Subcritical) Water Containing only 0.1 M KNO_3 as Supporting Electrolyte[a]

reactor temp. (K)	reactor pressure (MPa)	electrolysis time (s)
298	0.00327	0−600
313	0.007619	0−600
333	0.020582	0−600
353	0.048929	0−600
373	0.101418	0−600
393	0.19867	0−600
413	0.36153	0−600
433	0.61823	0−600
453	1.00281	0−600
473	1.5549	0−600
493	2.3196	0−600
513	3.3470	0−600
533	4.6923	0−600
553	6.4166	0−600

Electrodecomposition of *o*-Xylene under Sub-CW Containing 0.1 M KNO_3 as Supporting Electrolyte

run 1				run 2				run 3			
reactor temp. (K)	reactor pressure (MPa)	applied voltage	electrolysis time (min)	applied voltage (V)	reactor temp. (K)	reactor pressure (MPa)	electrolysis time (min)	electrolysis time (min)	applied voltage	reactor temp. (K)	reactor pressure (MPa)
453	1.00281	3.0	10	1	513	3.3470	10	5	3.0	513	3.3470
473	1.5549	3.0	10	1.5	513	3.3470	10	10	3.0	513	3.3470
493	2.3196	3.0	10	2	513	3.3470	10	15	3.0	513	3.3470
513	3.3470	3.0	10	2.5	513	3.3470	10	20	3.0	513	3.3470
533	4.6923	3.0	10	3	513	3.3470	10	25	3.0	513	3.3470
553	6.4166	3.0	10	3.5	513	3.3470	10	30	3.0	513	3.3470
				4.0	513	3.3470	10				
				4.5	513	3.3470	10				

[a] Applied voltage of 3.0 V.

thickness of 0.25 μm) was used to identify the decomposition products (in the ethyl acetate phase) by electrolysis in sub-CW. A CSPAK narrow-bore column C18 (2.1 × 100 mm^2) in a high-performance liquid chromatography (HPLC) apparatus using two Varian ProStar 210 solvent delivery modules coupled with ES and APC ionization mass spectrometry (Varian 1200 Quadrupole MS/MS) and with a photodiode array (PDA) detector (Varian PDA 330 detector) for the identification of compounds in the aqueous phase was also used.

The amount of gaseous products was recorded by means of the equipment shown in Figure 2. The gaseous products were quantitatively analyzed by a GC coupled to a TCD detector (Varian CP-3800) with a Carbowaxen 1010 plot column (30 m, film thickness of 0.53 μm, Supelco Co.).

3. Results and Discussion

3.1. Electrolysis of Sub-CW. The electrolysis of water containing 0.1 M of KNO_3 as a supporting electrolyte was performed over a wide range of temperature from room temperature to 553 K. Obviously, pure water under either ambient or sub-CW conditions is a poor conductor of electricity; therefore, it is necessary to add a supporting electrolyte to produce a significant current flow.

Figure 3 shows the time course of the electrolysis current at different sub-CW temperatures. At 298 K, the electrolysis current through the electrode surface was approximately 0.05 A. When the electrolysis cell (i.e., sub-CW reactor) was heated in the salt bath or oil bath, the electric current of electrolysis increased with temperature until it leveled off to steady values. The time needed to reach the current is correlated to the heating time of the water inside the reactor. The difference in heating times depends on the initial temperature, the final temperature set point, the reactor size, the mechanical vibrational frequency of the reactor, and so on.

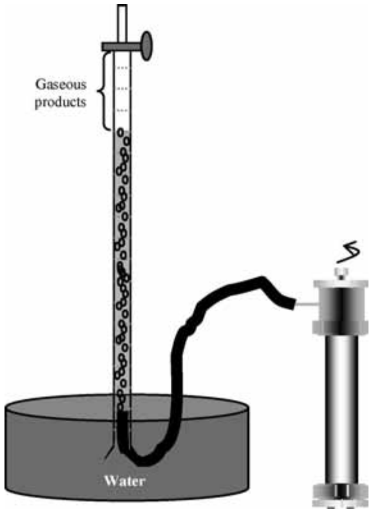


Figure 2. Schematic diagram of the gas product collection system.

Figure 4 shows the relationship between the steady-state electrolysis currents and the temperature. The electrolysis current increased up to 14-fold as the temperature of water was raised from 298 to 553 K. It is obvious that this intensification can be optimized by modifying the cell structure, the geometric parameters of the cell, the particular materials of working electrodes, and other related parameters. This interesting finding

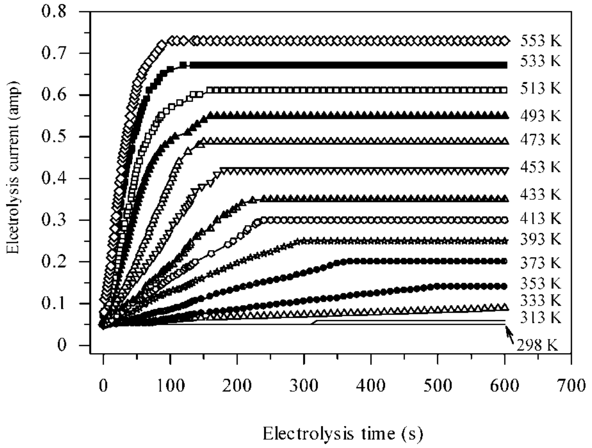


Figure 3. Time course of current in the electrolysis of sub-CW (containing 0.1 M KNO_3) at different temperatures ranging from 298 to 553 K; applied voltage 3.0 V.

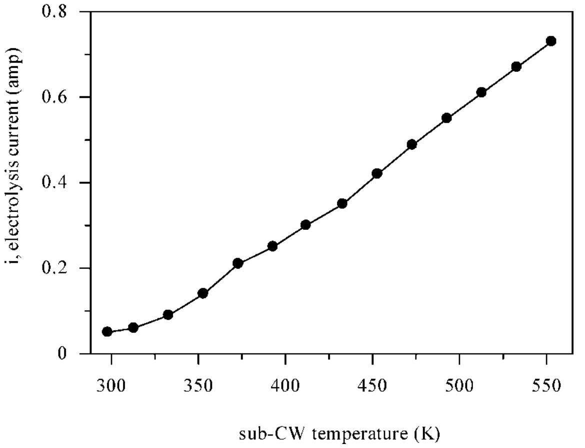


Figure 4. Effect of sub-CW temperature (containing 0.1 M KNO_3) on the steady-state electrolysis current; applied voltage was a constant 3.0 V.

shows the significance of the changes of many physicochemical properties of water when its temperature increases toward the critical point.

The increase in the electrolysis current is caused by an increase in the number of electroactive species that arrive at the surface of the electrode. In sub-CW, the dissociation constant of water increases by increasing the sub-CW temperature, reaching a maximum at about 513 K. The important implication of electrolysis current improvement under sub-CW conditions is the enhancement of mass transfer (and number) of the electroactive species (owing to the dropping off of viscosity and the increasing dissociation constant of water with temperature) and of the ionic conductivity (due to an increase in the diffusion coefficient). It has already been reported that the electrochemical conductivity of sub-CW increased substantially with temperature; that is, it increased by a factor of 120 when the temperature was increased from 298 to 523 K.[8] In another report,[10] it was demonstrated that the diffusion coefficient of Cu^{2+} increases by 100-fold in sub-CW; thus, it can be concluded that enhanced mass transfer can be achieved under sub-CW conditions.

3.1.1. Comparison of "Electrolysis Efficiency" under Ambient and Sub-CW Conditions. The amount of the electrochemical reaction that occurs at an electrode surface is proportional to the quantity of electric charge (*Q*, Coulomb's law) passing through the cell, which is defined as

$$Q_{\mathrm{amb}} = \int i_{\mathrm{amb}}\,\mathrm{d}t \qquad (1)$$

and

$$Q_{\mathrm{sub}} = \int i_{\mathrm{sub}}\,\mathrm{d}t \qquad (2)$$

under ambient and sub-CW conditions, respectively. Assuming a constant electrolysis current, eqs 1 and 2 simplify to

$$Q_{\mathrm{amb}} = i_{\mathrm{amb}}t \qquad (3)$$

and

$$Q_{\mathrm{sub}} = i_{\mathrm{sub}}t \qquad (4)$$

Generally, the electrolysis efficiency (η) is defined as

$$\eta = \frac{\text{output energy}}{\text{input energy}} \qquad (5)$$

and then the ratio of η for electrolysis under sub-CW conditions and under ambient conditions is

$$\frac{\eta_{\mathrm{sub}}}{\eta_{\mathrm{amb}}} = \frac{\text{output energy}_{\mathrm{sub}}}{\text{output energy}_{\mathrm{amb}}} \qquad (6)$$

or

$$\frac{\eta_{\mathrm{sub}}}{\eta_{\mathrm{amb}}} = \frac{Q_{\mathrm{sub}}}{Q_{\mathrm{amb}}} = \frac{i_{\mathrm{sub}}t}{i_{\mathrm{amb}}t} \qquad (7)$$

From Figure 4, it is apparent that at 298 and 553 K

$$i_{\mathrm{sub}} \approx 14(i_{\mathrm{amb}}) \qquad (8)$$

Then,

$$\frac{\eta_{\mathrm{sub}}}{\eta_{\mathrm{amb}}} \approx 14 \qquad (9)$$

Therefore, it can be concluded that under these experimental conditions the electrolysis efficiency (η) increases 14-fold when the temperature rises from 298 to 553 K. This is attributed to the change in the physicochemical properties of water at its critical point.

This finding has a promising application of sub-CW instead of conventional water for electrolysis reactions.

3.2. Electrochemical Decomposition of *o*-Xylene under Sub-CW Conditions. It has been known that an increase in water temperature increases the solubilities of organic compounds.[6] Miller et al.[24] have studied the solubility of polycyclic aromatic hydrocarbons in sub-CW. They found that increasing temperature up to 498 K increased the solubilities by 5 orders of magnitude. Taniguchi et al.[25] have reported that an increase in pressure at ambient temperature increases the solubilities of *o*-, *m*-, and *p*-xylenes. Thus, sub-CW possesses excellent properties for dissolving a variety of organic compounds that cannot be dissolved in water under ambient conditions. Consequently, combinations of electrolysis and sub-CW hold promise for the decomposition of many organic compounds.

Preliminary experiments were carried out for the decomposition of *o*-xylene by only (a) hydrolysis under sub-CW conditions up to 553 K, (b) electrolysis under ambient conditions, and (c) electrolysis under sub-CW conditions.

The results of experiment (a) proved that *o*-xylene is almost stable in the hydrolysis reactions under sub-CW conditions; only a small amount of *o*-xylene was decomposed after 10 min at 553 K. Because of the immiscibility of *o*-xylene and water, obviously, no decomposition products were identified from the electrolysis of *o*-xylene in water under ambient conditions, even

TABLE 2: Total Identified Chemical Compounds from the Electrolysis of *o*-Xylene under Sub-CW Conditions at 513 K by applying a 3.0 V Potential in the Presence of 0.1 M KNO_3 as Supporting Electrolyte

	electro-oxidation of *o*-xylene	electrodecomposition of *o*-xylene	electrolysis of sub-CW
1	2-methylbenzaldehyde[a]	2-methylbenzonitrile[b,c]	oxygen (O_2)[a]
2	2-methylbenzyl alcohol[a]		hydrogen (H_2)[a]
3	2-methylbenzoic acid[a]		
4	3H-isobenzofuran-1-one[a]		
5	1-phenylethanone[b,c]		
6	carbon dioxide[a]		

[a] Major product. [b] Minor product. [c] Identified in this study.

after very long electrolysis times. However, in the case of using the sub-CW as an electrolysis medium, a variety of products were identified by the decomposition of *o*-xylene.

3.3. Identified Products from the Electrolysis of *o*-Xylene under Sub-CW. Several products were identified from the electrolysis of *o*-xylene under sub-CW conditions. It is clear that the oxidation reactions take place at the anode; namely, there are two species competing to yield their electrons at the anode surface: *o*-xylene and hydroxide (OH^-) from the ionization of sub-CW. The reaction at the cathode is supposed to be the only reduction in protons (H^+) of sub-CW. However, it is worth mentioning that it is possible to destroy the products of the oxidation of *o*-xylene or any other valuable compounds by unwanted processes at the counter electrode in the undivided electrochemical cell.

For typical reaction conditions (1500 ppm *o*-xylene, 3.0 V applied potential, and temperature of 513 K), a mixture of compounds were identified and listed in Table 2. The compounds are divided into three groups: (a) *o*-xylene and those results from the oxidation of *o*-xylene; (b) products from the decomposition (from unknown reaction pathways) of *o*-xylene; and (c) gaseous products from the electrolysis of sub-CW.

We propose the decomposition and oxidation pathways of *o*-xylene shown in Scheme 1. *o*-Xylene is directly converted to partially oxidized products such as 2-methylbenzyl alcohol, 3H-isobenzofuran-1-one, and 1-phenylethanone.[26,27] *o*-Methylbenzyl alcohol, then, can be electro-oxidized to 2-methylbenzaldehyde and subsequently to 2-methylbenzoic acid.[28–30] 3H-Isobenzofuran-1-one is an intermediate in the oxidation of *o*-xylene to benzene-1,2-dicarboxylic acid or its anhydrate;[31] however, we did not identify benzene-1,2-dicarboxylic acid in this research. One of the possible oxidation pathways of *o*-xylene to 1-phenylethanone could be as follows: the carbonyl oxygen of 2-methylbenzaldehyde (produced from the oxidation of *o*-xylene) can be protonated in an acidic medium to form an enol structure with a resulting positive charge on the ring carbon bonded to the methyl group. Then, the delocalization of an electron pair from the exocyclic double bond back into the ring, followed by the simultaneous migration of methyl to the carbonyl carbon and hydride to the ring forms 1-phenyl-1-propanol. It could then be further oxidized to 1-phenylethanone. Carbon dioxide was the final oxidation product of any carbon-containing organic compounds as well as *o*-xylene and byproduct. No carbon monoxide was identified. An interesting finding was the formation of 2-methylbenzonitrile in the presence of NO_3^- and the lack of 2-methylbenzonitrile observed in the absence of NO_3^-. In addition, mass chromatograms showed a few minor peaks, which could not be identified in this research.

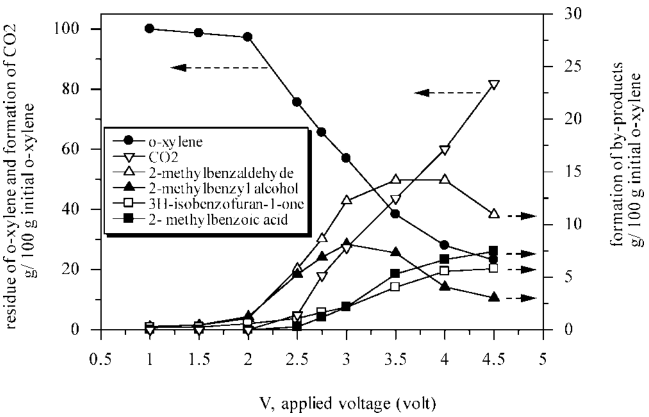
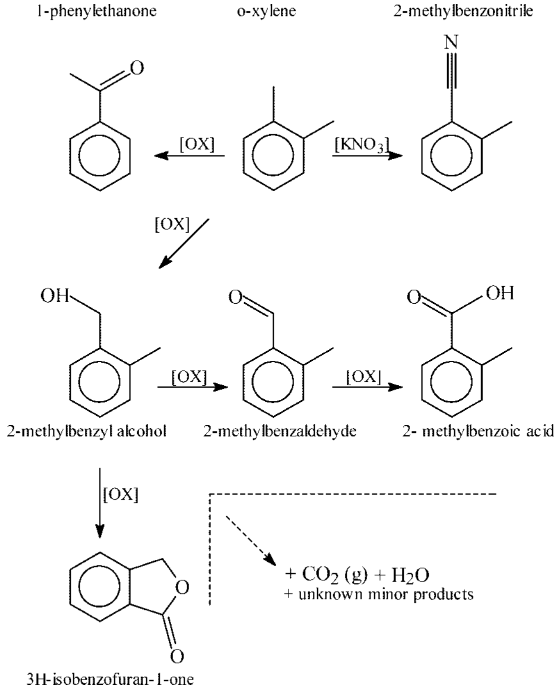


Figure 5. Effect of applied voltage on the decomposition of *o*-xylene and the formation of byproducts; sub-CW temperature 513 K, reaction time 10 min, supporting electrolyte 0.1 M KNO_3 .

SCHEME 1: Pathways Leading to the Electrodecomposition of *o*-Xylene under Sub-CW Conditions



Hydrogen and oxygen gases as byproducts are produced by the dissociation of hydrogen and oxygen from water molecules by electrolysis under either ambient or sub-CW conditions. These two gaseous products were not quantified in this study.

No contamination of the solution by the electrolysis cell was identified during the experiment.

3.4. Effect of Experimental Parameters on the Decomposition of *o*-Xylene. ***3.4.1. Effect of Electrolysis Voltage.*** Figure 5 shows the effect of the electrolysis voltage on the decomposition of *o*-xylene and the formation of byproduct at 513 K after 10 min. Because of the ohmic drop (IR drop), theelectrochemical reactions did not occur up to ~2 V. When we increased the voltage, the decomposition rate of *o*-xylene and, consequently, the formation of byproduct increased. At higher potentials (i.e., >3.5 V) the decomposition curve of *o*-xylene tends to level off somewhat; it seems that the electro-oxidation of *o*-xylene may be limited by mass transport at high potentials. The carbon dioxide concentration obviously increased almost linearly with potentials higher than 2.5 V. 2-Methylbenzyl alcohol and 2-methylbenzaldehyde showed wide peaks at potentials between 3.0 and 4.0 V; at higher potentials, the

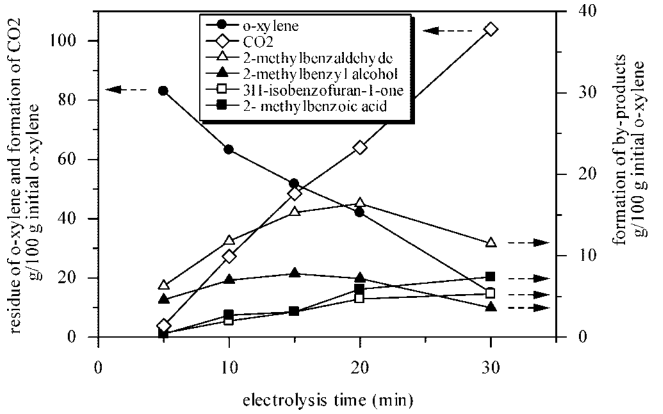


Figure 6. Time course of the decomposition of *o*-xylene and the formation of byproducts; sub-CW temperature 513 K, applied voltage 3.0 V, supporting electrolyte 0.1 M KNO_3.

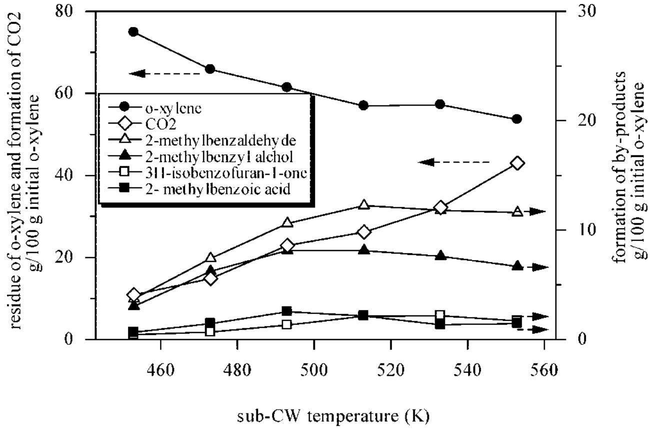


Figure 7. Effect of sub-CW temperature on the decomposition of *o*-xylene and the formation of byproducts; reaction time 10 min, applied voltage 3.0 V, supporting electrolyte 0.1 M KNO_3.

amount of these compounds decreased because of the further decomposition to other byproducts. The amounts of 3H-isobenzofuran-1-one and 2-methylbenzoic acid increased almost linearly with an increasing applied voltage.

3.4.2. Effect of Electrolysis Time. Figure 6 shows the time course of the decomposition of *o*-xylene and the formation of byproducts at 513 K. By increasing the electrolysis time, the amount of *o*-xylene decreased, and, consequently, the amount of carbon dioxide increased almost linearly. 2-Methylbenzyl alcohol and 2-methylbenzaldehyde showed wide peaks between 15 and 20 min. 2-Methylbenzoic acid and 3H-isobenzofuran-1-one showed little increase in concentration with the increase in electrolysis time.

3.4.3. Effect of Sub-CW Temperature. Figure 7 shows the effect of sub-CW temperature on the decomposition rate of *o*-xylene and on the formation of byproducts. When we raised the temperature, the decomposition rate of *o*-xylene and the formation of byproducts increased somewhat. Despite the fact that temperature showed a great effect on the current efficiency of pure sub-CW electrolysis, temperature variation did not show a strong effect on the electrodecomposition of *o*-xylene (compared to the two other investigated parameters, i.e., electrolysis time and applied voltage).

This series of experiments showed the possibility of the decomposition of *o*-xylene by electrodecomposition under sub-CW conditions; at typical operation conditions (i.e., applied voltage of 4.5 V, water temperature higher than 513 K, and electrolysis times longer than 30 min), the amount of decomposed *o*-xylene was up to 95%.

Table 3 shows the carbon balance for three different experimental conditions. The overall carbon balance did not account for the initial amount of carbon and showed a deficit of between 0 and 30% depending on the reaction conditions. This amount was attributed to the formation of gaseous (other than CO_2) products and other undetected compounds. Precision expressed as the relative standard deviation was calculated from three replicate experiments.

3.5. Direct or Indirect Decomposition of *o*-Xylene. Electrochemical destruction can be attempted by both direct and indirect oxidation; that is, *o*-xylene can be oxidized by either direct oxidation on the anode surface or by oxidation with molecular oxygen produced from the hydrolysis of water. In fact, both sub- and supercritical water has been widely investigated as media for the total wet oxidation reactions of organic species.[28] The advantage is that both sub- and supercritical water act as solvents for oxygen and organic substrates, providing a single-phase oxidation that overcomes the mass-transfer limitations.[32]

To see the effect of the produced oxygen on the decomposition of *o*-xylene, a series of experiments was carried out by the modification of the electrochemical cell (see Figure 8). The injection valve along with the HPLC pump allowed the injection of the reagents while the cell was in operation inside the salt bath at any time interval from 0 to the end of the reaction.

(a) In the first experiment, immediately after immersing the reactor containing only a supporting electrolyte into the salt bath, *o*-xylene was fed, and the power supply was turned on. After 10 min, the power supply was turned off, and the reactor was quenched. (b) In the second experiment, the reactor containing only a supporting electrolyte was immersed in the salt bath, and then 3.0 V of potential was applied for 10 min to generate oxygen molecules inside the reactor. Then, the electric power was turned off, and *o*-xylene was fed immediately into the reactor. The reactor was kept inside the salt bath for the next 10 min, and finally it was quenched. (c) The third experiment was conducted as a control reaction, that is, in absence of electrolysis and oxygen molecules. After the reactor containing only a supporting electrolyte was immersed in the salt bath, *o*-xylene was fed into the reactor. Electric power was not applied; after 10 min, the reaction was quenched.

Figure 9 shows the results of the *o*-xylene treatment in the set of the above experiments. In experiment a, by the direct oxidation of *o*-xylene on the anode surface, about 45% of the reactant was decomposed. However, it is worth noticing that the decomposition of *o*-xylene can be increased up to 95% by increasing the electrolysis time. Experiment b was carried out to test the possibility of the indirect (not directly on the anode surface) oxidation of *o*-xylene by the electrochemical generation of molecular oxygen. Although sub-CW is able to dissolve a significant amount of molecular oxygen, only about 14% of the reactant decomposed under this condition. It can be concluded that the oxidation of *o*-xylene by molecular oxygen does not seem to be a major reaction pathway. Experiment c was carried out as a control reaction to compare with the two above experiments. The results showed that under sub-CW conditions, because of the higher stability of *o*-xylene, there is no noticeable decomposition reaction; less than 3% of *o*-xylene was decomposed.

These results support the hypothesis that the oxidation on the anode surface is involved in the major oxidation pathways. Molecular oxygen also has the ability to decompose *o*-xylene (a partial amount); almost the same byproducts were obtained from the electro-oxidation and the oxidation by oxygen molecules.

TABLE 3: Carbon Balace of the Electrodecomposition Reaction of *o*-Xylene as a Function of Applied Potential, Electrolysis Time, and Sub-CW Temperature

	carbon balance (%)												
	remained *o*-xylene	%RSD (±)	2-methylbenzaldehyde	%RSD (±)	2-methylbenzyl alcohol	%RSD (±)	3H-isobenzofuran-1-one	%RSD (±)	2- methylbenzoic acid	%RSD (±)	CO_2	%RSD (±)	unknown
Carbon Balance as a Function of Applied Potential[a]													
applied potential (V)													
1.0	100.0	0.7	0.3	0.5	0.3	0.1	0.2	0.2	0.0	0.0	0.0	0.0	−0.7
1.5	98.6	0.3	0.4	0.9	0.4	0.2	0.2	0.1	0.0	0.0	0.0	0.0	0.4
2.0	97.2	0.4	1.0	0.1	1.1	0.7	0.5	0.2	0.0	0.0	0.0	0.0	0.3
2.5	75.6	0.8	5.1	0.1	4.6	0.6	0.9	0.0	0.2	0.0	1.5	0.7	12.2
3.0	65.6	0.5	7.6	0.9	6.0	0.2	1.3	0.4	0.9	0.3	5.4	1.7	13.2
3.5	56.9	0.1	10.8	0.4	7.1	0.1	1.7	0.7	1.7	0.1	8.2	1.7	13.6
4.0	38.4	0.4	12.6	0.4	6.3	0.0	3.2	0.1	4.1	0.0	13.1	2.1	22.3
4.5	28.0	0.6	12.6	0.1	3.5	0.5	4.4	0.0	5.2	0.5	18.1	1.6	28.2
Carbon Balance as a Function of Electrolysis Time[a]													
electrolysis time (s)													
5	83.0	0.9	5.6	0.0	4.0	0.3	0.4	0.2	0.3	0.0	1.2	0.6	5.6
10	59.0	0.5	10.4	0.5	6.1	0.4	1.6	0.6	2.1	0.7	8.2	0.4	12.6
15	51.7	1.2	13.5	0.3	6.8	0.5	2.5	0.8	2.4	0.5	14.6	0.0	8.5
20	42.0	0.6	14.5	1.0	6.3	0.0	3.7	0.7	4.6	0.5	19.3	1.4	9.7
30	15.1	0.7	10.2	0.4	3.1	0.8	4.2	0.1	5.8	0.1	31.3	1.8	30.3
Carbon Balance as a Function of Sub-CW Temperature[a]													
sub-CW temperature (K)													
453	74.9	1.1	3.3	0.9	2.6	0.3	0.3	0.0	0.5	0.3	3.3	1.1	15.1
473	65.8	0.6	6.5	0.3	5.4	0.9	0.5	0.1	1.1	0.1	4.5	0.9	16.1
493	61.4	0.9	9.4	0.2	7.1	0.4	1.0	0.1	2.0	0.7	6.9	0.6	12.3
513	56.9	0.4	10.8	0.1	7.1	0.0	1.7	0.7	1.7	0.3	7.9	1.0	13.9
533	57.2	0.2	10.4	0.6	6.6	0.6	1.7	0.6	1.1	0.5	9.7	1.2	13.3
553	53.6	0.8	10.2	0.1	5.8	0.4	1.4	0.1	1.1	0.1	12.9	0.4	14.9

[a] Relative standard deviations were calculated from triplicate experimental results.

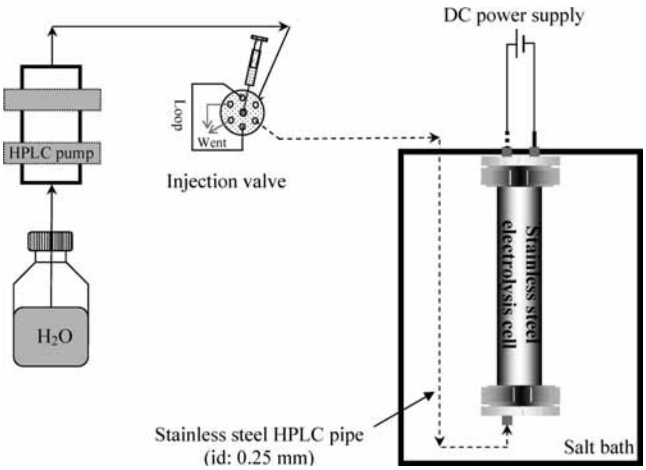


Figure 8. Schematic diagram of a batch electrolysis cell (sub-CW reactor) containing an online injection system. The volume of the injection loop was 40 μL.

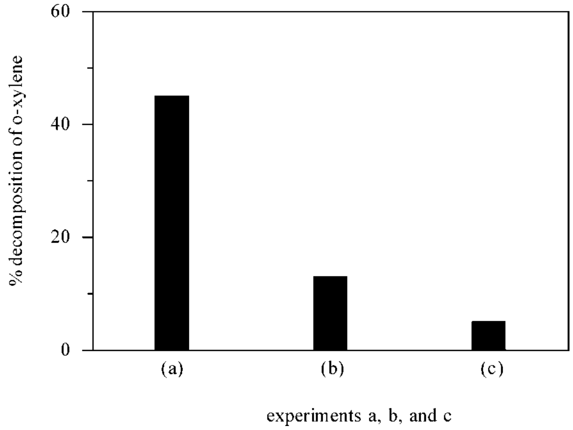


Figure 9. Comparison of *o*-xylene decomposition under different experimental conditions at 513 K for 10 min: (a) by electrolysis under sub-CW, (b) by using oxygen molecules as an oxidation agent produced by the electrolysis of sub-CW, and (c) by only sub-CW treatment (the control reaction).

More studies are necessary for us to fully understand the mechanism of the oxidation of *o*-xylene under sub-CW conditions.

4. Conclusions

This study proved that variations of the dielectric constant, viscosity, and some other properties of water with temperature provide a feasible means for both the dissolution of highly nonpolar compounds and electrolysis with higher efficiency. The "current efficiency" as a function of the reaction progress dramatically increased when the temperature of water increased toward its critical point, which definitely increased the economic feasibility of the electrochemical reactions. It has been shown that sub-CW as a reaction medium minimized the amount of energy consumed for electrolysis.

Usually, organic solvents have been used as electrolysis media for a number of water-insoluble compounds. This report suggests that sub-CW can be a possible replacement for these environmentally unaccepted organic solvents.

o-Xylene and, generally, BTEX compounds are almost thermally stable in sub-CW. Their complete solubility in sub-CW makes their electrodecomposition possible. We found that experimental parameters such as sub-CW conditions (i.e., temperature and, consequently, pressure) and electrolysis conditions as well as electrolysis time can be optimized to control the reaction pathways. The proposed method has a demonstrated ability to remove *o*-xylene from the initial concentration of 1500 ppm to less than 75 ppm. This method can be applicable to more water-insoluble compounds by the proposed method.

Taking into the account that the current efficiency of the electrolysis reactions under sub-CW is higher than that under ambient conditions, this combined method can also be used for a variety of electrooxidation reactions with economic feasibility, for example, the large-scale decomposition of the chemical contamination of soil and groundwater and the production of hydrogen gas as an important clean energy source for use in fuel cells. However, many parameters must still be investigated for these purposes.

Finally, to prevent unwanted processes at the counter electrode in the undivided electrochemical cell from destroying the products produced from the oxidation of the reactants or any other valuable compounds, a divided sub-CW cell needs to be designed and utilized. This is now the subject of an investigation.

Acknowledgment. We gratefully acknowledge the financial support of a part of this work provided by the ministry of Education, Culture, Sports, Science, and Technology of Japan in the form of the 21st Century COE program (E19, Science and Engineering for Water Assisted Evolution of Valuable Resources and Energy from Organic Wastes).

Nomenclature

A	ampere
i	electric current
K	kelvin
Q	coulombs
s	second
t	time
η	electrolysis efficiency

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JP800452S