SUBTASK 1.6 – ENHANCED ELECTROCHEMICAL PROCESSES IN SUBCRITICAL WATER

Final Report

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TABLE OF CONTENTS

LIST OF FIGURES	ii
LIST OF TABLES	ii
EXECUTIVE SUMMARY	iii
INTRODUCTION	1
OBJECTIVES	2
STATEMENT OF WORK	2
Specific Deliverables	3
ACCOMPLISHMENTS	3
Cell Design	3
Media and Electrode Materials for Hydrogen Production	5
Dechlorination Studies	10
Electrical Conductivity	10
REFERENCES	10

LIST OF FIGURES

1	Flow-through micro cell designed to study electrochemical reactions under subcritical water conditions	4
2	Cyclic voltammograms recorded with Pt electrodes in 0.2 M Na ₂ SO ₄ (pH 1.4) supporting electrolyte at temperatures ranging from 25° to 250°C	6
3	Cyclic voltammograms recorded with Pt electrodes in 0.2 M Na ₂ HPO ₄ (pH 7) supporting electrolyte at temperatures ranging from 25° to 250°C	7
4	Cyclic voltammograms recorded with Pt electrodes in 0.4 M KOH (pH 11.5) supporting electrolyte at temperatures ranging from 25° to 250°C	8
5	Cyclic voltammograms recorded with Ni electrodes 0.4 M KOH (pH 11.5) supporting electrolyte at temperatures ranging from 25° to 250°C	9
6	Summary of the steady-state cell potentials the three media and two electrodes studied	11

LIST OF TABLES

1	Effect of Subcritical Water Temperature on Electrical Conductivity of Pure Water	12
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SUBTASK 1.6 – ENHANCING ELECTROCHEMICAL PROCESSES IN SUBCRITICAL WATER

EXECUTIVE SUMMARY

This project involved designing and performing preliminary electrochemical experiments in subcritical water. An electrochemical cell with substantially better performance characteristics than presently available was designed, built, and tested successfully. The electrochemical conductivity of subcritical water increased substantially with temperature, e.g., conductivities increased by a factor of 120 when the temperature was increased from 25° to 250°C. Cyclic voltammograms obtained with platinum and nickel demonstrated that the voltage required to produce hydrogen and oxygen from water can be dropped by a factor of three in subcritical water compared to the voltages required at ambient temperatures. However, no enhancement in the degradation of 1,2-dichlorobenzene and the polychlorinated biphenyl 3,3',4,4'-tetrachlorobiphenyl was observed with applied potential in subcritical water.

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INTRODUCTION

Many electrochemical processes related to energy production are potentially valuable, but these are presently limited by poor economics. The basic problems for processes such as hydrogen and oxygen production from water, fuel cells, and electrochemical decomposition of organic wastes include:

- The thermodynamics are sufficient (the reaction will work) at reasonable voltages, but the rates (e.g., mass transfer, electrode dynamics) are too slow for the process to be economically favorable.
- Increased rates require higher voltages (overpotential), which increases the cost and lowers efficiencies.
- Solubilities of many organics (e.g., polychlorinated biphenyls [PCBs]) are too low in water for electrochemical methods to be applied.

Recent studies have demonstrated that heating water above its boiling point under enough pressure to maintain the liquid state (so-called “subcritical” water) causes physicochemical changes in water that should be useful in reducing the rate problems discussed above, as well as increasing the solubilities of organics in water. The important properties that change when water is heated from ambient to the subcritical condition (typically 100° to 250°C, but always less than the critical temperature of 374°C) include:

1. Water’s dielectric constant (polarity) drops from 80 to about 20 [1]. Thus, water assumes solvent properties similar to those of organic solvents such as acetonitrile or methanol.
2. Water’s viscosity and surface tension both drop an order of magnitude [1].
3. The concentration of H^+ and OH^- increase by a factor of 20.

The important implications of these changes for electrochemical processes are that mass transfer will increase, ionic conductivity should increase because of increased diffusion coefficients, the solubilities of organics (e.g., PCBs) should increase, and hydrolysis (and possibly other reactions) of organics will be enhanced. Although only a very few research papers describe work in subcritical water, these important implications are supported by studies showing that the solubilities of hydrophobic organic pollutants increase by 4 to 6 orders of magnitude in subcritical water [2–4], the degradation of several pesticides and explosives (including HMX, RDX, and TNT) has been demonstrated using only pure water in the subcritical state, and the dechlorination of several types of organic pollutants has been demonstrated [5, 6]. Initial electrochemical

measurements in subcritical water demonstrated that the diffusion coefficient of Cu^{2+} increases by 100-fold in subcritical water, thus proving that enhanced mass transfer is achieved [7]. Finally, the electrolysis of water to H_2 and O_2 in subcritical water was demonstrated (using 50% KOH with Ni electrodes), demonstrating the potential for subcritical water to reduce the overpotential required for hydrogen production [8].

OBJECTIVES

The major objective of this initial study was to obtain the fundamental information needed to determine the potential usefulness of subcritical water for enhancing the electrochemical processes described above. On the basis of these results, initial investigations into enhancing electrochemical hydrogen and oxygen production, and electrochemical decomposition of PCBs will be performed.

Individual objectives include:

1. To determine the effect of water temperature on width and location of the “electrochemical window” (the voltage range within which the water is not hydrolyzed). This is important because a smaller window means lower voltages are required to produce hydrogen and oxygen (at faster rates with less overpotential). In contrast, a larger electrochemical window yields a larger voltage range over which water can be used as a solvent for organic (or inorganic) electrochemical reactions. (Note that understanding these parameters addresses hydrogen and oxygen production as well as fuel cell enhancement, since both are reversible reactions at electrode surfaces.)
2. To determine the effect of selected electrolytes and electrode materials on the electrochemical window.
3. To perform initial experiments determining the effects of subcritical water conditions on the hydrolysis of water to molecular hydrogen and oxygen.
4. To perform initial experiments determining the effect of subcritical water conditions on the electrochemical decomposition of PCBs (or a similar chlorinated organic).

STATEMENT OF WORK

Electrochemical cells will be fabricated and tested for electrochemical stability under subcritical water conditions. Although corrosion in subcritical water is not significant from a safety standpoint, materials such as stainless steel cannot be used for electrochemical studies, because even very low production of metal ions cannot be tolerated. Likely materials for cell fabrications are millable ceramics (alumina) and/or titanium [9, 10]. A micro cell for fundamental studies will be built first. Attempts based on the success of the first cell will be made to fabricate a

larger cell to allow gas separations (e.g., for hydrogen production studies). Both static and flowing systems will be considered.

Once a useful cell is built, the effect of subcritical water temperature, electrolytes, and electrode material on the electrochemical window of subcritical water will be determined. These results will then be used to design and perform initial studies on enhancing the hydrolysis of water to produce hydrogen and oxygen, and to enhance the dechlorination of PCBs (or other selected chlorinated organics).

Specific Deliverables

1. (0–6 months) The electrochemical cell(s) will be fabricated, and design, abilities, and limitations will be reported.
2. (4–10 months) The effect of subcritical water temperature on the electrochemical window (including three electrolytes and two electrode materials) will be determined and reported.
3. (5–12 months) The results of initial studies on the effect of water temperature on hydrogen and oxygen production (using conditions selected from Deliverable 2) will be reported.
4. (7–12 months) The potential to use subcritical water under the electrochemical conditions determined above to dechlorinate PCBs (or a similar chlorinated organic) will be reported.

ACCOMPLISHMENTS

Cell Design

Substantial advances were made in electrochemical cell design for subcritical water studies. A novel low-volume (<1-mL), isothermal, flow-through electrochemical cell was found to provide better reliability and performance than any previous cell used for subcritical water studies. While bomb-type cells can be placed entirely within an oven and reliably equilibrated to a specified temperature, these static cells do not allow solution exchange to remove accumulated electrolysis products or electrode-fouling species. By contrast, zone-heated cells provide a simple configuration for solution flow because normal high-pressure fittings can be used in cooler regions. However, these cells are inherently non-isothermal, with only one electrode (the working electrode) present within the heated zone. This configuration is prone to inaccurate temperature estimates even when a thermocouple is placed within the electrolyte. It is also impractical for certain water-splitting studies because temperature slows the electrolysis kinetics at the colder counter electrode.

The final version of the micro cell is shown in Figure 1. With this design, the entire micro cell was placed in a normal gas chromatograph oven, brought to pressure by Valve A, and equilibrated up to 250°C within 30 minutes. It was also possible to flush up to 5 mL of electrolyte solution from the Keystone isolation vessel through the cell by opening Valve B. The two Ti crosses separately housed the working and counter electrodes. They were joined by a 1.5-in. × 0.125-in. outside diameter ceramic tube that provided better electrical isolation than the previously reported Ti tube. This ceramic tube also allowed the counter electrode to be extended into the working electrode compartment. This modification significantly decreased the interelectrode separation. A second ceramic tube at the inlet of the working electrode cross was also found to provide better electrical isolation from the pump.

Ferrules of 15% graphite in Vespel were used for all of the cell fittings. While this material provided adequate electrical isolation and excellent sealing qualities, it was found to chemically degrade in all electrolyte solutions, especially in basic media. To slow the degradation, all exposed ferrules were covered with Teflon tape. For the more exposed ferrules that secured electrodes, it was more effective to face the ferrules with a machined plug of Teflon.

A manuscript describing this cell, its capabilities for studying electrochemical reaction under subcritical water conditions, and its potential application as a detector for subcritical water chromatography is being prepared for submission as a Technical Note to *Analytical Chemistry*.

Figure 1. Flow-through micro cell designed to study electrochemical reactions under subcritical water conditions.

Media and Electrode Materials for Hydrogen Production

Three electrolytes having widely different pH values (NaHSO_4 , Na_2HPO_4 , and KOH) and two electrode materials (Pt and Ni) were individually investigated under subcritical water conditions ($P = 100$ bar, $T = 25^\circ\text{--}250^\circ\text{C}$). Figures 2–4 show rapid polarization sweeps (cyclic voltammetry at 1 Vs^{-1}) across the passive electrochemical widow for each medium using platinum-wire electrodes. Figure 5 shows similar data for nickel electrodes. However, because dissolution of nickel electrode becomes significant below pH 8, only the data for KOH were obtained.

The potential scales at all temperatures in Figures 2–4 (Pt electrodes) were assigned a reference of 0 V where the hydrogen evolution current density was about 4 mA cm^{-2} . This point occurred at the negative (cathodic) window limit of each scan. The opposite (anodic) widow limit caused by oxygen evolution was then adjusted until a similar (but negative) current density of -4 mA cm^{-2} was obtained. The peaks observed in the center of the window corresponded to surface redox processes occurring with the platinum electrode. The reference point for the Ni electrode in KOH (Figure 5) was assigned 0 V where the hydrogen evolution current density was about 4 mA cm^{-2} at 25°C . The peaks observed near the positive window in this figure corresponded to surface redox processes occurring with the nickel electrode.

All three media and electrode materials showed significant decreases in their voltage window as temperature was raised to 250°C . These decreases were indicative of normal rate limitations in the hydrogen and oxygen evolution reactions that controlled the negative and positive voltage window limits, respectively. As temperature was increased, both reactions became faster and required a lower voltage to produce the same level of current. The most significant consequence of a lower voltage window is that less power is required to produce the same amount of hydrogen fuel.

Basic media promoted the greatest window contraction, as indicated by the polarization data in Figures 3–5. The window for Pt in sodium phosphate buffer (pH about 7, Figure 3) was 200 mV wider at 25°C than in either sodium sulfate (pH 1.4, Figure 2) or KOH (pH 11.5, Figure 4). However, the window for this medium contracted by nearly 800 mV to nearly 1.3 V at 250°C . In KOH , the window for Pt demonstrated an even more dramatic contraction above 200°C , with the voltage span supporting 4 mA cm^{-2} requiring only about 600 mV. The Ni electrodes also showed a significant contraction in KOH medium. While this major contraction occurred at a lower temperature than for Pt (150°C versus 200°C), the window for Ni reached only about 1.2 V at 250°C .

These findings are significant because the windows for both Pt and Ni in basic media above 200°C were less than the thermoneutral potential of about 1.5 V. Here the unfavorable entropic (i.e., temperature-dependent) portion of the reaction free energy change for the cell becomes smaller than the overall reaction enthalpy change. At cell potentials below 1.5 V, electrical energy required to split water is less than the thermochemical energy of the reaction, and the entire cell process becomes endothermic. Under these conditions, water splitting can

Figure 2. Cyclic voltammograms recorded with Pt electrodes in 0.2 M Na₂SO₄ (pH 1.4) supporting electrolyte at temperatures ranging from 25° to 250°C.

Figure 3. Cyclic voltammograms recorded with Pt electrodes in 0.2 M Na₂HPO₄ (pH 7) supporting electrolyte at temperatures ranging from 25° to 250°C.

Figure 4. Cyclic voltammograms recorded with Pt electrodes in 0.4 M KOH (pH 11.5) supporting electrolyte at temperatures ranging from 25° to 250°C.

Figure 5. Cyclic voltammograms recorded with Ni electrodes 0.4 M KOH (pH 11.5) supporting electrolyte at temperatures ranging from 25° to 250°C.

become economically feasible if surplus heat can be supplied from a convenient source (e.g., solar).

The polarization data in Figures 2–5 represent electrochemical windows under dynamic conditions (i.e., potential sweeps of 1 V s^{-1}). To determine the potential windows required for long-term electrolysis, measurements were made by applying a constant current and monitoring the steady-state cell potential. In all cases, a current density of 1.1 mA cm^{-2} was applied and steady-state cell potential (within $\pm 5 \text{ mV}$) was reached in less than 1 min. The steady-state cell potentials for the three media and two electrodes are summarized in Figure 6. Under long-term measurements, the cell voltage for Pt in each medium reached the thermoneutral potential. However, more basic media required a lower temperature to reach this potential. While Pt in KOH showed the largest cell voltage drop at 250°C , yielding a power savings of 66% versus room temperature, both Ni and Pt reached the thermoneutral potential at about 150°C . This second finding suggests a cost preference of Ni electrodes if water splitting under subcritical conditions is considered at a large scale.

Dechlorination Studies

Dechlorination was first attempted for 0.02 mg/mL 1,2-dichlorobenzene in 0.2 M sodium carbonate media. Toluene was also present at the same concentration as an internal standard. A static tee-cell was used with a 1-mm-diameter glassy carbon rod acting as cathode opposed to a 0.5-mm-diameter Pt wire anode. Electrolysis was performed with a current of 1 mA for 20, 40, or 60 min with the cell equilibrated at 250°C . Results of these electrolytic studies showed no substantial degradation of the dichlorobenzene.

Dechlorination was also attempted for 0.5 mg/mL of 3,3',4,4'-tetrachlorobiphenyl in 0.2 M sodium carbonate medium with 0.5 mg/mL of anthracene present as an internal standard. These solid reagents were weighed and added directly to the tee-cell. Although electrolysis was attempted at various current levels and for various time periods with the cell equilibrated at 250°C , cell conductivity was too low to sustain the electrolysis, and no significant degradation occurred.

Electrical Conductivity

The effect of temperature on the electrical conductivity of pure water was determined using a simple conductivity cell consisting of a single “cross” fitting (instead of the two fittings shown in Figure 1), and constructed with platinum electrodes. The conductivity in subcritical water heated to 250°C was about 120 times higher than the conductivity at room temperature.

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Figure 6. Summary of the steady-state cell potentials the three media and two electrodes studied. Reference line is the thermoneutral potential 1.5 V.

TABLE 1

Effect of Subcritical Water Temperature on Electrical Conductivity of Pure Water

Water Temp., °C	Pressure, bar	Conductivity, μ Siemens ^a
25	1	5.5
25	15	4.6
25	75	4.3
50	75	10
100	75	30
150	75	84
200	75	200
250	75	520

^aOne Siemen is equal to one ohm⁻¹.

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