Permanently heated micro-wire electrodes for electrochemistry above the boiling point

Zhihua Chang

University at Albany, State University of New York, changrpi@yahoo.com

The University at Albany community has made this article openly available. Please share how this access benefits you.

Follow this and additional works at: https://scholarsarchive.library.albany.edu/legacy-etd

Part of the Analytical Chemistry Commons

Recommended Citation
https://scholarsarchive.library.albany.edu/legacy-etd/2245

This Master's Thesis is brought to you for free and open access by the The Graduate School at Scholars Archive. It has been accepted for inclusion in Legacy Theses & Dissertations (2009 - 2024) by an authorized administrator of Scholars Archive. Please see Terms of Use. For more information, please contact scholarsarchive@albany.edu.
Permanently Heated Micro-wire Electrodes for
Electrochemistry above the Boiling Point

by

Zhihua Chang

A Thesis
Submitted to the University at Albany, State University of New York
In Partial Fulfillment of
the Requirements for the Degree of
Master of Science

College of Arts & Sciences
Department of Chemistry
2019
ABSTRACT

Heated micro-wire electrodes offer lots of advantages, such as, accurate temperature control, enhanced diffusion and accelerated reaction kinetics through micro-stirring effect, easy cleaning, and low cost, etc. Its application in high temperature electrochemistry has gained lots of interests since its debut in the mid-1990s. A maximum of 250 °C has been reported using heating pulses in duration of 5 ms. For various applications, permanently heating would be more useful. In this study, two types of micro-wire electrodes were successfully developed for electrochemistry above the boiling point with acetaminophen as model compound and a continuous heating time of at least 2 mins. Thermoelectrochemical behavior of acetaminophen in neutral pH = 7.4 at directly heated fork-type gold micro-wire electrodes (1 – 115 °C and atmosphere pressure) revealed two linear regions of activation energy corresponding to diffusion control with 14.5 kJ/mol at high temperatures and rate control with 33 kJ/mol at very low temperatures, while the two regions were not very distinctive in acidic condition of pH = 1 with activation energies of 16 kJ/mol at high temperatures and 22 kJ/mol at very low temperatures. The results using directly heated flow-cell-type gold micro-wire electrodes (24 – 136 °C and 50 bar) in neutral pH = 7.4 confirmed the similar two linear regions of activation energy with 14 kJ/mol at high temperature as a result of diffusion control and 59 kJ/mol in a very narrow low temperature range due to reaction rate control. Both types of micro-wire electrodes showed a very good precision of temperature control. Consistent calibrations have been achieved with both open-circuit potentiometry and resistivity thermometer methods for the flow-cell-type electrodes at 50 bar, 0.5 mL/min and up to 160 °C. The ultimate goal of the pressurized flow cell approach is to reach supercritical conditions and enable a calibration-free analysis of trace metals.
I would like to extend my gratitude to my thesis advisor Dr. Flechsig for giving me the opportunity to do research in hot-wire electrochemistry and providing tremendous helps and advice. My gratitude is also due to Dr. Scholes for introducing the EPR application in lipid field to me, which will be definitely useful in my future research plan. I was also honored to achieve the top grade in his Advanced Physical Chemistry class and P-chem has become my favorite chemistry course since then. Special thanks for Brian Smith in Machine Shop who provided invaluable advices for our flow cell design and also fabricated it. Finally I would like to thank my family and friends for their never-ending support and encouragement.
# TABLE OF CONTENTS

ABSTRACT .................................................................................................................. ii

ACKNOWLEDGMENT ................................................................................................... iii

LIST OF FIGURES ........................................................................................................ vi

1. Introduction .............................................................................................................. 1

2. Background ............................................................................................................. 3
   2.1 Development of hot-wire electrochemistry ......................................................... 3
   2.2 Comparison of high temperature techniques .......................................................... 4
   2.3 Electrochemical reaction mechanism of acetaminophen ...................................... 7

3. Experimental methods ............................................................................................ 9
   3.1 Fabrication of micro-wire electrodes ..................................................................... 9
   3.2 Temperature calibration methods ........................................................................ 10
   3.3 Experimental setup ............................................................................................. 10
   3.4 Reagents and electrochemical measurements .................................................... 12

4. Fork-type gold micro-wire electrodes .................................................................... 14
   4.1 Insulation materials for fork-type gold wire electrodes ......................................... 15
   4.2 Temperature calibrations for fork-type gold wire electrodes ................................. 17
   4.3 Temperature study on Linear Sweep Voltammetric (LSV) of acetaminophen .......... 20
   4.4 Preliminary concentration study on LSV of acetaminophen ................................. 24
   4.5 Summary ............................................................................................................ 25

5. Flow-cell-type gold micro-wire electrodes ............................................................. 26
   5.1 Design of a high pressure flow cell with directly heated gold wire electrodes ....... 26
   5.2 Temperature calibrations for flow-cell-typed gold wire electrodes ....................... 28
5.3 Temperature study on LSV of acetaminophen in a pressurized flow cell………………32
5.4 Chronoamperometry detection of acetaminophen in a pressurized flow cell…………35
5.5 Summary……………………………………………………………………………………..38
6. Conclusions……………………………………………………………………………………40
7. References……………………………………………………………………………………41
LIST OF FIGURES

Figure 2.1 SEM micrographs of gold wire electrodes.................................................................6
Figure 2.2 EC-reaction mechanisms of acetaminophen............................................................7
Figure 3.1 Fork-type Au wire electrodes...................................................................................9
Figure 3.2 Experimental setup with a fork-type Au wire electrode.........................................11
Figure 3.3 High-pressure flow cell setup..................................................................................12
Figure 4.1 Wax-sealed solder joint end of fork-type Au wire electrode.................................14
Figure 4.2 laminated solder joint end of fork-type Au wire electrode.......................................15
Figure 4.3 Burnt fork-type Au wire electrode with excessive wax insulation.........................16
Figure 4.4 Temperature calibration for 5 mm fork-type Au wire electrode T_{bulk}=21°C.........17
Figure 4.5 Temperature calibration for 30 mm fork-type Au wire electrode T_{bulk}=21°C.....17
Figure 4.6 Temperature calibrations for 30 mm fork-type Au wire electrodes T_{bulk}=1°C......18
Figure 4.7 Temperature overall calibration for 30 mm fork-type Au wire electrodes T_{bulk}=1°C…20
Figure 4.8 LSV temperature study of acetaminophen for a wax-sealed Au wire...............21
Figure 4.9 LSV temperature study of acetaminophen for a laminated Au wire.....................23
Figure 4.10 LSV concentration study of acetaminophen for a wax-sealed Au wire..............24
Figure 5.1 Laminated solder joint end of flow-cell-type Au wire electrode............................27
Figure 5.2 Preliminary temperature calibrations of flow-cell-type Au wire electrodes..........28
Figure 5.3 Temperature calibrations for flow-cell-type Au wire electrode............................31
Figure 5.4 LSV temperature study of acetaminophen for flow-cell-type Au wire electrode.....33
Figure 5.5 Additional electrochemical measurements for flow-cell-type Au wire electrode...34
Figure 5.6 Chronoamperometry detection of acetaminophen at different temperatures......36
Figure 5.7 LOD of acetaminophen detection at different temperatures.................................37
1. Introduction

Direct electric heating in electrochemistry, or so-called hot wire electrochemistry, has drawn lots of attention since its breakthrough in the 1990s. After the AC distortion problem was solved with a symmetric electrode arrangement and a symmetric inductor bridge, this micro-wire joule heating technology became more popular because of the advantages, such as low cost, instantaneous heating of the electrode and its nearest surroundings to the desired temperature without changing the temperature of the bulk solution, easy cleaning of micro-wire electrodes by glowing in air, etc. Although this technique offers electrochemical measurements at far above the boiling point, this has been done through pulse heating. A maximum 250 °C with 5 ms heating pulses has been reported (Gründler and Degenring 2001). For various applications, continuous heating above the boiling point would be more useful. Our goal of this work is to develop new techniques for such purposes.

We improved our fork-type wire electrode fabrication method and made it more environmentally friendly by using recycled pen barrels and printed circuit board (PCB) bits (4x12x1.6 mm, less copper to be disposed and more flexible to make micro-wire electrodes with any length). With an ice bath to keep the bulk solution at 1 °C, reproducible temperatures above the boiling point (up to 120 °C) have been achieved for wax-sealed, laminated, and epoxy-sealed fork-type gold wire electrodes. Such a very wide temperature range provides a simpler way to find reaction kinetic data of various processes in a much shorter time compared to the applications of rotating disk electrodes. Particularly, both diffusion control and reaction rate control regions can be visible in Arrhenius plots within this wide temperature range. The normal temperature range for
polyethylene-paraffin wax mixture insulation was up to 70 °C and for lamination film it was up to 80 °C in the literature.

To push the limit further, we designed a high-pressure flow cell with directly heated gold wire electrodes for continuous electrochemical measurements at temperatures far above the boiling point. Both open-circuit potentiometry and resistivity thermometer methods confirmed this new approach has a very good precision of temperature control at 50 bar and up to 160 °C. The results of voltammetric experiments at 50 bar and working electrode temperatures up to 136 °C with acetaminophen as model compound revealed the similar two linear ranges in Arrhenius plots as those experiments with fork-type micro-wire electrodes (1 – 115 °C and atmosphere pressure). This thermal behavior indicates a diffusion control at higher temperatures and a reaction rate control at lower temperatures.

Our ultimate goal is to reach supercritical conditions in the electrolyte surrounding the highly heated working electrode, where a combination of complete deposition without sample preparation and subsequently coulometric stripping would create a new calibration-free analysis of trace metals. This will be our future work.
2. Background

2.1 Development of hot-wire electrochemistry

Direct electric heating of working electrodes for electrochemical investigations, or so-called hot wire electrochemistry, has become popular since the invention of high frequency AC direct heating with a symmetric electrode arrangement for simultaneous DC electrochemical measurements in the 1990s (Gründler et al. 1995 and 1999). Later, the development of a symmetric inductor bridge completely solved the AC distortion problem without the use of symmetric electrode configuration and made this method more convenient and practical for electrochemical studies (Wachholz et al. 2007). One of characteristic features of this technique is the instantaneous heating of the electrode and its nearest surroundings to the desired temperature with the bulk solution remained at ambient temperature. Other features, such as low cost, strong thermal convection near the heated electrode – so-called micro-stirring effect, and self-cleaning, etc., have made this method gain significant attentions over the past 20 years (Gründler et al. 2006, 2009 and 2015, Flechsig et al. 2012 and 2018).

Early applications of this method were focused on using heated noble metal micro-wire electrodes, e.g., gold and platinum wires, for electrochemical detection. Heated platinum wire electrodes were used to detect trace oxygen (Zerihun et al. 1996a), lead (Zerihun et al. 1996b), as well as some organic analytes (Zerihun et al. 1998). Heated gold wire electrodes were applied for detection of arsenic (V) (Gründler et al. 1998), mercury (Wang et al. 1999), and arsenic (III) and copper traces (Flechsig et al. 2001), etc. Also DNA hybridization could be detected at heated gold wire electrodes (Flechsig et al. 2005, Peter et al. 2007, and Walter et al. 2016). Moreover,

Most common high frequency AC being used for directly heated electrodes is in the range of 50 to 100 kHz. Baranski group (Baranski et al. 2002 and 2012, Boika and Baranski 2008) introduced a technique applying much higher frequency AC (0.1 – 2 GHz) between a micro-disk electrode and a counter electrode to create a hot spot at close vicinity of the micro-disk electrode, where highest temperature is achieved in the hot spot in solution due to much higher resistance than the micro-disk electrode itself. They reported a high temperature of 225 °C for at least 15 minutes. Gründler developed a technique of temperature pulse voltammetry known as TPV (Gründler et al. 1996 and 2000), which uses temperature pulses in the order of milliseconds to heat the electrodes at far above the boiling point of the solution while keeping the bulk solution at ambient temperature. A maximum 250 °C with 5 ms heating pulses has been reported (Gründler and Degenring 2001).

2.2 Comparison of high temperature techniques

In recent years, high-temperature electrochemistry, as well as high-pressure electrochemistry, have drawn growing interest due to the advantages such as greatly enhanced mass transport, significantly increased current signals, and therefore lowered detection limits, etc (Wildgoose et al. 2004, Giovanelli et al. 2004). Lots of technical difficulties are involved when working under high temperature and pressure conditions. Advances have been made over recent years to solve some of problems, however, the main issue still needs to be addressed, which is how to heat the system to reach the desired high temperature. Currently, heating is implemented through two
different approaches, either isothermal or non-isothermal ones. The most well developed
isothermal strategy is the use of autoclave cells. However, technical issues, such as safety under
high temperature and pressure, contamination caused by dissolution of wall/lining materials,
corrosion/cracking concerns, etc., make this approach remain a significant challenge (Wildgoose
et al. 2004, Flechsig et al. 2012). On the other hand, direct electric heating of working electrodes
as a non-isothermal method could be a good solution when it is coupled into a HPLC system
(Asghari et al. 2008) to achieve high pressure.

Directly heated electrodes offer numerous novel and unique advantages: temperature control in
addition to potential and current; quick switch to desired temperature on/off in a few seconds;
micro-stirring effect due to thermal convection; enhanced diffusion / accelerated reaction
kinetics; selectivity through thermal discrimination; thermal regeneration of biosensors; and
thermal cleaning of sensors, etc (Flechsig et al. 2012 and 2018). The applications of this
technique do not limit to just gold and platinum wires – the classic so-called hot wires. Heated
carbon paste electrodes for detection of DNA hybridization (Wang et al. 2000b and 2004),
heated bismuth film electrode for trace metal detection (Flechsig et al. 2002), heated screen-
printed carbon electrode/mercury film electrode for stripping analysis of trace metals (Jasinski et
al. 2001), as well as directly heated pencil electrodes (Sun et al. 2007, Wu et al. 2007 and 2013)
have been studied in recent years.

In this study, directly heated micro-wire electrodes are chosen over other types of heated
electrodes. Micro-wire electrodes have some unique features and simulations and experimental
studies have confirmed that they have the most uniform temperature distributions when heated in
solution due to their cylindrical shape (Beckmann et al. 2000, Mahnke et al. 2009, Duwensee et al. 2009, and Biala et al. 2015). Gold micro-wire is made of solid gold and can be easily cleaned by glowing in air for at least 5 s (before and after cleaning shown in Fig. 2.1).

Fig. 2.1 SEM micrographs of gold wire electrodes (25 µm in dia., Walter et al. 2016), A) gold micro-wire before glowing in air; B) gold micro-wire after glowing at ~ 800 °C in air.
2.3 Electrochemical reaction mechanism of acetaminophen

Acetaminophen (paracetamol) is an electroactive compound and a common drug. It can be electrochemically oxidized to N-acetyl-p-benzoquinone-imine (NAPQI), which will undergo different reaction pathways depending on pH conditions of the solution: hydrolysis in strong acidic conditions; dimerization in neutral pH conditions; and hydroxylation in strong basic conditions (Nematollahi et al. 2009). Figure 2.2 shows electrochemical reaction mechanisms of acetaminophen under acidic and neutral pH conditions, which involve several consecutive and parallel reaction steps that occur according to the chosen pH of the electrolyte. The oxidation product undergoes a consecutive reaction catalyzed by protons leading to an inactive product.

**Fig. 2.2 EC-reaction mechanisms of acetaminophen** (Nematollahi et al. 2009), [Left] dimerization in neutral conditions; [Right] hydrolysis in strong acidic conditions.

Acetaminophen (paracetamol) is an electroactive compound and a common drug. It can be electrochemically oxidized to N-acetyl-p-benzoquinone-imine (NAPQI), which will undergo different reaction pathways depending on pH conditions of the solution: hydrolysis in strong acidic conditions; dimerization in neutral pH conditions; and hydroxylation in strong basic conditions (Nematollahi et al. 2009). Figure 2.2 shows electrochemical reaction mechanisms of acetaminophen under acidic and neutral pH conditions, which involve several consecutive and parallel reaction steps that occur according to the chosen pH of the electrolyte. The oxidation product undergoes a consecutive reaction catalyzed by protons leading to an inactive product.
Therefore, at moderate scan rates, a reduction signal is visible at pH 7, but not in acidic solution (Nematollahi et al. 2009). Basically, under strong acidic conditions, the oxonium ions catalyze a quick consecutive hydrolysis of NAPQI, the electrochemical oxidation product of acetaminophen. The hydrolysis product of NAPQI is not electroactive, and thus, the cathodic (reverse) peak would be missing at moderate scan rates. Under neutral pH conditions, a dimerization occurs that has been used with good yield for electro-synthesis of the dimerized product (Nematollahi et al. 2009). Interestingly, this dimerization happens between the acetaminophen-oxidation product and another hydrolyzed acetaminophen molecule. That means it is a parallel - consecutive reaction at neutral pH. Based on these mechanisms, acetaminophen is a suitable model compound for electrochemical studies with our heated gold micro-wire electrodes.
3. Experimental methods

3.1 Fabrication of micro-wire electrodes

All gold micro-wire electrodes used in this study were prepared in the same length of 30 mm with a diameter of 25 µm purchased from Goodfellow. Fig. 3.1 shows the fork-type Au wire electrodes used in this project. Recycled pen barrels and printed circuit board (PCB) bits (4x12x1.6 mm) were assembled together with clear epoxy, and then Au wire electrode was soldered on two fork legs (PCB bits) and insulation materials were applied to seal the solder joints. Typical insulation materials include polyethylene-paraffin wax mixture, lamination film, and clear epoxy, etc. In the case of lamination film as insulation material, solder joints must be made extremely flat.

Fig. 3.1 Fork-type Au wire electrodes, Au 30 mm long, 25 µm in dia. Laminated/wax sealed.
3.2 Temperature calibration methods

Temperature calibration can be performed electrochemically with two methods:

1) Open-Circuit Potentiometry:

\[
T = \Delta E/(-1.6 \text{ mV/K}) + T_{\text{solution}}
\]  

2) Resistivity method:

\[
R = R_0 (1 + \alpha (T - T_0)), \text{ where } T_0 = 20 \degree \text{C}, \alpha = 0.0034 \text{ K}^{-1} \text{ for Au}
\]

In OCP method (interval 0.1 s), the electrode temperature can be determined via a potentiometric method with an EmStat 3 potentiostat, using an equimolar 5 mM ferro/ferri cyanide \((K_4[Fe(CN)_6], K_3[Fe(CN)_6])\) in 0.1 M KCl solution and the temperature coefficient of -1.6 mV/K (Gründler et al. 2006, Wachholz et al. 2007). In resistivity method, a 1-Ω resistor is included in the circuit and the electrode resistance can be calculated with the heating current measured by a Tektronix TBS 1032B oscilloscope on the resistor and the heating voltage drop measured by a Voltcraft VC960 multimeter across the wire electrode.

3.3 Experimental setup

In our electrochemical experiments, Autolab Model PGSTAT 204 Potentiostat/Galvanostat was used to conduct the voltammetric measurements. The gold micro-wire electrode (25 µm diameter, 30 mm length) was soldered on printed circuit board/bits, isolated with insulation materials, and was directly heated using 50 kHz AC current provided by a ThermaLab power generator (Gensoric GmbH, Rostock, Germany). The heated wire as a working electrode was connected to the potentiostat through a symmetric inductor filtering bridge (Wachholz et al. 2007). This way, AC distortion can be effectively blocked and the wire electrode can be simultaneously heated and used in voltammetric measurements. Potentiometric temperature
calibration (OCP method) was performed by connecting the ThermaLab and an EmStat3 potentiostat (Palmsens BV, The Netherlands) to the heated electrode with the symmetric inductor setup. The gold micro-wire electrode was cleaned by DC current with a power supply unit to red-glowing temperature in air for at least 5 seconds.

Fig. 3.2 Experimental setup with a fork-type Au wire electrode (Flechsig et al. 2005), [Left] Heated electrode design; [Right] Measurement arrangement: an electrochemical cell with working, reference, and counter electrodes (from left to right).

In a typical experimental setup with a fork-type Au wire electrode shown in Fig. 3.2, a glass cell, Ag/AgCl reference electrode (Metrohm, in 3 M KCl) and a glassy carbon counter electrode were used during electrochemical measurements. The fork-type gold micro-wire electrode was placed in a voltammetry cell (Metrohm-Autolab) filled with electrolyte and cooled on ice to maintain 1°C bulk solution temperature. The electrode temperature was calibrated in this cell using the potentiometric (OCP) method with an EmStat 3 potentiostat and an equimolar 5 mM
ferro/ferricyanide in 0.1 M KCl solution and the temperature coefficient of -1.6 mV/K (Gründler et al. 2006, Wachholz et al. 2007).

Fig. 3.3 High-pressure flow cell setup (Chang et al. 2019). A) flow-cell (red frame) coupled HPLC; B) Flow cell components: body halves (PEEK), rubber gaskets (black), printed circuit board with gold wire (25 µm in dia., 30 mm length, green frame), solder joints, copper lead wires, and lamination film insulation; C) Part of the flow cell that contains the Ag-pseudo-reference electrode (blue frame).

A preliminary high-pressure flow cell was manufactured in our machine shop using PEEK (polyether ether ketone). Fig. 3.3 illustrates our experimental setup with a flow-cell-type gold wire electrode: a HPLC system coupled with preliminary high-pressure flow cell. The stainless steel connection (nut) was used as auxiliary/counter electrode. The cell was tested up to 225 bar and 200 °C electrode temp.

3.4 Reagents and electrochemical measurements

All reagents were purchased from Sigma-Aldrich and the solutions were prepared using distilled water. Britton Robinson buffer was prepared by using solutions of acetic acid (0.04 M), phosphoric acid (0.04 M) & solid boric acid and then the pH was adjusted to 7.4 using 1 M sodium hydroxide. 0.05 M sulfuric acid (pH 1) was prepared from 0.5 M sulfuric acid stock
solution. A 5,000 ppm acetaminophen stock solution was prepared by weighing 1 g and dissolving in 200 mL of distilled water (some crystals of acetaminophen would be formed if 10,000 ppm stock solution is prepared and kept at 4 °C).

Same parameter settings were used in all electrochemical measurements for both fork-type and flow-cell-type gold wire electrodes. In Linear Sweep Voltammetry (LSV) measurements at an acetaminophen concentration of 200 ppm, the potential scan range for neutral pH was between 0 and 1 V and for H$_2$SO$_4$ the potential range was between 0.2 V and 1.2 V using the same scan rate of 10 mV/s with a step potential of -0.00244 V. In the experiments with fork-type gold wire electrodes, voltammetric signals were smoothened by Savitzky Golay Mode (Level 2) using NOVA 2.1 software, while no smoothing was needed for flow cell-type gold wire electrodes. Cyclic Voltammetry (CV) measurements were mainly performed in neutral pH with a scan rate of 100 mV/s and a range of -0.2 V to 0.8 V. Chronopotentiometry with a setting of total 1200 seconds and an interval time of 0.5 s was also carried out to check if both type wire electrodes had a leakage on solder joint or not. Concentration study of acetaminophen with flow-cell-type gold wire electrodes was performed via chronoamperometry at 800 mV for totally 300 s and an interval of 0.1 s, where the flow cell gold wire electrode worked as a detector to monitor the current change when a 100-µL sample was injected into the HPLC. All the experiments were done in triplicate.
4. Fork-type gold micro-wire electrodes

The goal of this project is to reach supercritical conditions and then implement an absolute analysis of trace metals based on complete deposition followed by coulometric stripping, which requires that gold wire electrodes should have relatively significant amount of resistance for accurate measurement of heating voltage/current (0.552V/0.346A - 30mm wire at 30°C). Typical fork-type gold wire electrodes used in our lab were 5 mm long and about 0.4 Ω (Biala et al. 2015 and Walter et al. 2016). We designed the flow-cell-type gold wire electrodes with a length of 30mm and about 1.6 Ω and did tests with the same length fork-type gold wire electrodes.

Fig. 4.1 Wax-sealed solder joint end of fork-type Au wire electrode. Formation of cavity on solder joint ends of Au wire (25 µm in dia., 30 mm long, wax sealed).
4.1 Insulation materials for fork-type gold wire electrodes

30 mm long fork-type gold wire electrodes were fabricated with different insulation materials on both solder joint ends. The normal temperature range for polyethylene-paraffin wax mixture insulation was up to 70 °C and for lamination film (5 mil/0.127mm from Staples) it was up to 80 °C. Beyond these ranges, the insulation materials start to melt and some cavities are formed. Fig. 4.1 shows that melt wax sprouted after some heating cycles greater than 70 °C, which led to a small hole formed at one solder joint end.

![Image of insulation materials for fork-type gold wire electrodes]

**Fig. 4.2 laminated solder joint end of fork-type Au wire electrode.** Formation of cavity on solder joint ends of Au wire (25 µm in dia., 30 mm long, laminated).
Lamination glue has the same behavior as wax when temperature goes over 80 °C (shown in Fig. 4.2). Once some cavities are formed, they can trap some air and bring some noise during an electrochemical measurement, and also affect the reproducibility of temperature calibration of Au wire electrodes. These cavities can be refilled carefully under a microscope. The electrodes should be inspected under a microscope after a high temperature heating cycle. This will prevent a possible leakage when a formed cavity causes the solder joint exposed to the electrolyte solution. Excessive insulation materials can cause Au wire burn out. Fig. 4.3 illustrates that melt wax crepted along a 5mm long gold wire electrode and eventually caused the gold micro-wire burned out.

![Fig. 4.3 Burnt fork-type Au wire electrode with excessive wax insulation. Melt wax crepted along Au wire and caused the burnt-out of Au wire (25 µm in dia., 5 mm long, wax sealed).](image-url)
4.2 Temperature calibrations for fork-type gold wire electrodes

![Temperature calibration graphs](image)

Fig. 4.4 Temperature calibration for 5 mm fork-type Au wire electrode $T_{\text{bulk}}=21^\circ\text{C}$. [Left]

Potentiometry of 5 mM $K_3/K_4[\text{Fe(CN)}_6]$ in 0.1 M KCl cell while applying heating pulses of increasing power, [Right] the according temperature calibration plot with power steps (a.u.).

![Temperature calibration graphs](image)

Fig. 4.5 Temperature calibration for 30 mm fork-type Au wire electrode $T_{\text{bulk}}=21^\circ\text{C}$. [Left]

Potentiometry of 5 mM $K_3/K_4[\text{Fe(CN)}_6]$ in 0.1 M KCl while applying heating pulses of increasing power, [Right] the according temperature calibration plot with power steps (a.u.).
All temperature calibration experiments with fork-type gold wire electrodes were done in a glass cell using an equimolar 5 mM ferro/ferri cyanide in 0.1 M KCl solution and the Open-Circuit Potentiometry (OCP method) was applied for temperature calculations with the temperature coefficient of -1.6 mV/K.

Fig. 4.6 Temperature calibrations for 30 mm fork-type Au wire electrodes $T_{\text{bulk}}=1^\circ$C.

Potentiometric temperature calibration plots with power steps (a.u.) ranging from 1 to 115 °C at atmospheric pressure. [Top row] different polynomial order fitting for wax-sealed electrode. [Bottom row] different polynomial order fitting for laminated electrode.

In our initial calibration tests, temperature profiles for 5 mm and 30 mm fork-type wax-sealed gold wire electrodes were investigated using a 1024-step ThermaLab AC generator, which has an
automatic calibration function with a built-in EmStat3 potentiostat. The surface temperatures on
gold wire electrodes were calculated by Equation 3.1 in Chapter 3. Temperature calibration
curves in Figures 4.4 and 4.5 (on the right) show that accurate temperature controls were
achieved where the bulk solutions were kept at room temperature of 21 °C: for 5 mm Au wire,
up to 57 °C; and for 30 mm Au wire, up to 61 °C. The potential plots with 20-second heating
pulses in Figures 4.4 and 4.5 (on the left) had very level baselines indicating that there was no
leakage and polyethylene-paraffin wax was a good insulation material for experiments below 70
°C.

Further wide range temperature calibrations (1 – 115 °C) were performed with two 30 mm fork-
type gold wire electrodes: one wax-sealed and the other laminated (three trials for each
electrode). To minimize the formation of air bubbles at temperatures above the boiling point, an
ice bath was used to keep the bulk solution at 1 °C. Since applying heating pulses manually was
easier during initial tests, a 64-step (0 to 63) ThermaLab AC generator was utilized thereafter for
all directly heated experiments. The calibration results are shown in Fig. 4.6: top graphs for wax-
sealed Au wire and bottom graphs for laminated Au wire. The best fit curves were polynomial
3rd order possibly due to the significant heat loss at higher temperatures. Figures 4.6 and 4.7
show that both electrodes had very similar temperature profiles when the bulk solution was kept
at 1 °C and they were basically identical, which indicates that: 1) our wire electrode fabrication
method is robust and the most important step is to keep the effective length as 30 mm for all
electrodes; and 2) polyethylene-paraffin wax and lamination glue exhibited similar properties
(e.g., melting behavior near the solder joint ends) with the temperature of the bulk solution kept
at 1 °C. An overall calibration curve including all of data for wax-sealed and laminated gold wire electrodes was plot on the right in Fig. 4.7.

![Graph showing calibration curve](image)

**Fig. 4.7 Temperature overall calibration for 30 mm fork-type Au wire electrodes T\textsubscript{bulk}=1°C.**

Potentiometric temperature calibration plots with power steps (a.u.) ranging from 1 to 115 °C at atmospheric pressure. [Left] wax-sealed electrode vs. laminated electrode. [Right] the overall temperature calibrations.

### 4.3 Temperature study on Linear Sweep Voltammetry (LSV) of acetaminophen

In the literature (Nematollahi et al. 2009), 1 mM acetaminophen (152 ppm) was used for most of voltammetric experiments. Thus, to ensure a good quality of electrochemical signals, 200 ppm acetaminophen was utilized in all our voltammetric measurements. LSV experiments using 200 ppm acetaminophen in bulk solutions ice-bathed at 1 °C were performed with heated fork-type gold micro-wire electrodes at a temperature range of 1 – 115 °C in both neutral (Britton Robinson buffer, pH = 7.4, scanned from 0 to 1 V at a rate of 10 mV/s) and acidic conditions (0.05 M H\textsubscript{2}SO\textsubscript{4}, pH = 1, scanned from 0.2 to 1.2 V at a rate of 10 mV/s).
Fig. 4.8 LSV temperature study of acetaminophen for a wax-sealed Au wire (Mathivanan et al. 2018). Effect of electrode temperature upon linear-sweep voltammetric response of 200 ppm acetaminophen at a heated wax-sealed gold micro-wire electrode in the temperature range between 1 and 115 °C, A, C) Britton-Robinson buffer at pH 7.4, and B, D) 0.05 M H₂SO₄ at pH 1; C, D) resulting Arrhenius plots based on limiting currents; scan rate 10 mV/s, bulk solution was kept at 1 °C. In the equation, “y” stands for ln(I/A), and “x” stands for 1/T.

The activation energy $E_a$ can be calculated by the following Arrhenius equation 4.1, where the slope of the Arrhenius plot of ln(I/A) vs. 1/T (K⁻¹) is the negative value of $E_a$ divided by the gas constant $R = 8.314$ Jmol⁻¹K⁻¹ assuming that the current I (reading at 800 mV under pH 7.4 or
reading at 900 mV under pH 1) represents validly the overall rate constant controlled by either chemical reaction rate or diffusion rate.

\[
\ln I = \ln A - \frac{E_a}{RT}
\] (4.1)

Fig. 4.8 shows the results of LSV temperature study of 200 ppm acetaminophen under pH 7.4 (Fig. 4.8 A and C) and under pH 1 (Fig. 4.8 B and D) and their corresponding Arrhenius plots for a fork-type wax-sealed gold micro-wire electrode. The difference between Fig. 4.8 A and B reflects the different reaction mechanisms found at pH 7.4 and pH 1. At pH 7.4, a dimerization involving both parallel and consecutive reaction to the electrochemical oxidation of acetaminophen has been reported (Nematollahi et al. 2009), while a simple consecutive hydrolysis occurs at pH 1. The Arrhenius plots (Fig. 4.8 C and D) show that two linear ranges existed corresponding to two different processes as rate-limiting steps. Under neutral conditions, distinctive activation energy values were assigned by slopes of -3984 and -1745 K in the Arrhenius plot (Fig. 4.8 C) using Arrhenius equation (4.1): 33.1 kJ/mol at low temperatures (1 – 30 °C) in reaction rate control region and 14.5 kJ/mol at high temperatures (30 – 115 °C) in diffusion control region. At pH 1, however, two regions were not very distinguishable with activation energies of 16.2 kJ/mol at high temperatures and 22.2 kJ/mol at very low temperatures. These findings are comparable with the results obtained by rotating disk electrodes (RDE) and a detailed comparison is available in the literature (Mathivanan et al. 2018). The very strong micro-stirring effect due to thermal convection allows directly heated micro-wire electrodes as an emerging technique to find very similar kinetic reaction data with considerably simpler apparatus in much shorter time.
Fig. 4.9 LSV temperature study of acetaminophen for a laminated Au wire. Effect of electrode temperature upon linear-sweep voltammetric response of 200 ppm acetaminophen at a heated laminated gold micro-wire electrode in the temperature range between 1 and 115 °C, A, C) Britton-Robinson buffer at pH 7.4, and B, D) 0.05 M H₂SO₄ at pH 1; C, D) resulting Arrhenius plots based on limiting currents; scan rate 10 mV/s, bulk solution was kept at 1 °C. In the equation, “y” stands for ln(I/A), and “x” stands for 1/T.

The same experiments with a laminated gold micro-wire electrode confirmed the above findings with similar parameters and a bit more noise: under neutral conditions of pH 7.4 (Fig. 4.9 A and C), two linear regions of activation energy revealed diffusion control with 14.2 kJ/mol at high
temperatures (30 – 115 °C) and reaction rate control with 36.2 kJ/mol at very low temperatures (1 – 30 °C), while two indistinct linear ranges in acidic conditions of pH 1 gave activation energies of 14.6 kJ/mol at high temperatures and 19.5 kJ/mol at very low temperatures. All these results have shown that directly heated micro-wire electrodes can be used to disclose behavior and parameters of kinetic reactions that are hard to study by traditional stationary electrodes in thermostated bulk solutions using jacketed cells.

4.4 Preliminary concentration study on LSV of acetaminophen

Fig. 4.10 LSV concentration study of acetaminophen for a wax-sealed Au wire. Linear sweep voltammetric response observed on fork-type gold micro-wire electrode at A) 24 °C and B) 60 °C. Measured in Britton-Robinson-buffer (pH 7.4) with increasing acetaminophen concentration at a scan rate of 10 mV/s.

Fig. 4.10 illustrates the effect of acetaminophen concentration upon voltammetric response at two different electrode surface temperatures (Fig. 4.10 A at 23 °C and B at 60 °C) in neutral pH 7.4 with a scan rate of 10 mV/s. Temperature increase from 23 to 60 °C resulted in rising
sensitivity due to increased diffusion rate. Further detailed experiments using differential pulse voltammetry (DPV) would provide more insights.

4.5 Summary

The experimental results have indicated that our wire electrode fabrication method is very robust and the most important step to achieve a good reproducibility is to keep the effective length as 30 mm for all electrodes while periodically checking and fixing the formation of cavities at solder joint ends is also necessary. At directly heated micro-wire electrodes, two temperature regions were found due to different rate control processes: from 30 to 115 °C, a diffusion control was suggested by low activation energies. Between 1 and 30 °C, much higher activation energies indicated a chemical reaction rate control. Directly heated micro-wire electrodes can reach a surface temperature above the boiling point (e.g., 115 °C), if the bulk solution is kept at 1 °C. By using such a very wide temperature range, various processes may show multiple control regions including the rate-limiting one and be visible in Arrhenius plots due to their different linear ranges.
5. Flow-cell-type gold micro-wire electrodes

In Chapter 4, our results showed that permanent heating up to 115 °C for at least 2 minutes was achieved with fork-type gold micro-wire electrodes in ice-bathed bulk solutions at 1 °C in an open cell under atmospheric pressure. To reach higher temperatures, a pressurized system is a must to minimize the formation of air bubbles and improve the accuracy and precision of this directly permanent heating. A HPLC system provides a perfect platform for this purpose. The development of a high pressure flow cell housing directly heated gold wire electrodes and preliminary experimental data are presented in this chapter.

5.1 Design of a high pressure flow cell with directly heated gold wire electrodes

The design of a finely machined PEEK (polyether ether ketone) flow cell body with integrated REF (Ag-pseudo-reference) and AUX (stainless steel) electrodes is shown in Fig. 3.3. The flow cell carries a printed circuit board (PCB) with the micro-wire soldered onto it. A channel in dimension of 5 x 5 x 30 mm inside the flow cell assembly was made to hold enough bulk solution at ambient temperature. Copper foils on the PCB at both ends of the channel were kept as solder joints, which also establishes a major heat sink, under high-pressure conditions. Simulations have revealed a cool area at both ends of the heated wire electrode (Mahnke et al. 2009, Biala et al. 2015), which will be used to provide protection against overheating of the short wire parts inside the insulation. The PEEK flow cell has been tested up to 225 bar and 200 °C electrode temperature.

Initially, lamination films were the only insulation material applied onto the solder joints. Further heating tests (up to 110 °C), however, revealed the formation of cavity at both ends of the solder
joints (Fig. 5.1). This issue was addressed by adopting two approaches: 1) applying multilayer of different insulation materials, e.g., epoxy glue + lamination glue; 2) making solder joints as close to the edges of the channel as possible. Using epoxy glue as insulation material significantly minimized the formation of cavity at the solder joint ends. A further discussion is presented in the following temperature calibration section.

![Image of laminated solder joint end of flow-cell-type Au wire electrode](image)

**Fig. 5.1 Laminated solder joint end of flow-cell-type Au wire electrode.** Formation of cavity on solder joint ends of flow-cell Au wire (25 µm in dia., 30 mm long, laminated).
5.2 Temperature calibrations for flow-cell-typed gold wire electrodes

Fig. 5.2 Preliminary temperature calibrations of flow-cell-type Au wire electrodes. A), B) and C) Potentiometry of 5 mM K$_3$/K$_4$[Fe(CN)$_6$] in 0.1 M KCl using the flow cell (Fig. 3.3) while applying heating pulses of increasing power: A) up to 36 power steps (a.u.), flow+1-Ω resistor vs. flow+no resistor vs. 1-Ω resistor+no flow; B) with 1-Ω resistor up to 63 power steps (a.u.); C) no resistor vs. 1-Ω resistor; D) the temperature calibration plots B) with power steps (a.u.).

Temperature calibration experiments for flow-cell-type gold wire electrodes were performed in the flow-cell coupled HPLC system (Fig. 3.3) using an equimolar 5 mM ferro/ferri cyanide in 0.1 M KCl solution as HPLC mobile phase under operating conditions of 50 bar and 0.5 mL/min. Directly heating was provided via a 64-step ThermaLab AC power unit generating 30-second
heating pulses followed by 150 s in waiting time/interval. Surface temperatures at the flow-cell-type gold wire electrodes were calculated by both Open-Circuit Potentiometry (OCP) and resistivity methods, where OCP used the temperature coefficient of -1.6 mV/K for calculations and the latter one included a 1-Ω resistor in the circuit and determined electrode resistances by measuring heating current on the resistor and the heating voltage drop across the wire electrode. The flow-cell-type gold micro-wire electrodes were insulated by both epoxy and lamination glues.

Before doing full-range high temperature calibrations with the 64-step ThermaLab AC generator, possible highest temperatures at heated wire electrodes that could be achieved with the current AC generator were estimated through three trials under different conditions: 1) 1-Ω resistor + flow (50 bar, 0.5 mL/min; in Fig. 5.2 A labelled as “flow R”); 2) no resistor + flow (50 bar, 0.5 mL/min; in Fig. 5.2 A labelled as “flow no-R”); 3) 1-Ω resistor + no flow (0 bar/atmospheric pressure, 0 mL/min; in Fig. 5.2 A labelled as “no-flow R”). The recorded potential plots at 24 °C room temperature are shown in Fig. 5.2 A. The heating power steps were up to 36 for all three trials. Theoretically a 30-mm (effective length) gold wire electrode would have a resistance of 1.6 Ω at 20 °C, which means that it can only get approximately 62% (= 1.6/2.6) of the total supplied power if a 1-Ω resistor is included to form a series circuit. In Fig. 5.2 A, at the highest applied power step of 36 during the experiments, trial “flow R” reached 100 °C electrode temperature, while trials “flow no-R” and “no-flow R” achieved 136 and 110 °C electrode temperatures respectively. Assuming that for gold wire electrodes the absolute value of potential change ΔE (OCP method) would be proportional to the supplied power, estimated electrode temperatures at the maximum output of the current AC generator (power step = 63) would be: 1)
for trial “flow R”, \( T = (100 - 24) \times 63/36 + 24 = 157 \, ^\circ C \); 2) for trial “flow no-R”, \( T = (136 - 24) \times 63/36 + 24 = 220 \, ^\circ C \). These estimated temperatures depend on how accurately electrode temperatures at power step of 36 were determined and how well the electrode itself was built. The actual temperatures would be possibly lower than the estimated values due to substantial heat loss. The potential plots in Fig. 5.2 A also show that at 0.5 mL/min flow rate the potential baseline (no heating) was basically level (trials “flow R” and “flow no-R”), however a shutoff of flow led to a drifting-down baseline (trial “no-flow R”) suggesting that the bulk solution in the flow cell was heated up and not at room temperature any more. These results indicate that our flow cell is an efficient design suitable for studying high temperature electrochemistry at heated wire electrodes while keeping the bulk solution at ambient temperature. Figures 5.2 B and D illustrate a full-range (0 – 63 power steps) temperature calibration of a flow-cell-type gold microwire electrode in a series circuit with a 1-\( \Omega \) resistor. At the highest power step of 63, 1st trial reached an electrode temperature at 172 \( ^\circ C \), however, 2nd and 3rd trials only achieved electrode temperatures of 163 and 158 \( ^\circ C \), respectively. This may be caused by the overheating of the short portions of gold wire inside the insulation between the solder joints and the edges of the channel. Fig. 5.2 C shows that without 1-\( \Omega \) resistor electrode temperature reached 180 \( ^\circ C \) prior to a burnt-out at 207 \( ^\circ C \).
Fig. 5.3 Temperature calibrations for flow-cell-type Au wire electrode. A) Potentiometry of 5 mM $\text{K}_3\text{K}_4[\text{Fe(CN)}_6]$ in 0.1 M KCl using the flow cell (Fig. 3.3) while applying heating pulses of increasing power; C) the according temperature calibration plot with power steps (a.u.); B) and D) comparison of OCP and resistivity: B) with power steps (a.u.); D) with square of current

Based on the above findings, our new design of flow-cell-type gold micro-wire electrodes features solder joints being made as close to the edges of the channel as possible in addition to multilayer of epoxy and lamination insulation. The temperature calibration results of a newly improved wire electrode in the pressurized flow cell at 50 bar and up to 160 °C are shown in Fig. 5.3. A 1-Ω resistor was included in the series circuit so that both OCP and resistivity methods could be used to determine the electrode temperatures. Three repetitions demonstrate the great
precision: at the highest power step of 63, 1st trial achieved an electrode temperature of 156.3 °C using OCP method while the other two trials reached 158 and 159.6 °C, respectively. Figures 5.3 B and D illustrate that the resistivity method results show very good agreements with those OCP ones and both have a best fit of the square function of power steps as well as a best linear fit when temperature being correlated to the square of current. These results indicate that the current design and fabrication method for flow-cell-type gold micro-wire electrodes are very robust and reproducible, and also provide great accuracy and precision.

5.3 Temperature study on LSV of acetaminophen in a pressurized flow cell

In previous section 5.2, experimental results of electrode temperature calibrations demonstrated good performances of our pressurized flow cell and newly improved flow-cell-type gold micro-wire electrodes, indicating that they were desirable for high temperature electrochemical studies. As thermoelectrochemistry of acetaminophen was successfully studied with our fork-type gold micro-wire electrodes in a wide range from 1 to 115 °C using Linear Sweep Voltammetry (LSV) in Chapter 4, acetaminophen became a good model compound for investigations on high temperature electrochemistry. It has been reported that acetaminophen has a parallel-consecutive reaction mechanism under neutral pH conditions, where a consecutive dimerization is based on a reaction of the acetaminophen-oxidation product with the starting material acetaminophen (Nematollahi et al. 2009). LSV experiments with flow-cell-type gold micro-wire electrodes were very similar to those with fork-type ones (scan rate 10 mV/s). To prevent any potential damage to HPLC system (e.g., corrosion under acidic conditions), only LSV measurements with 200 ppm acetaminophen in Britton-Robinson buffer (pH = 7.4) as the mobile phase were studied at 50 bar up to 136 °C. Current readings at 800 mV were used for Arrhenius plots.
Fig. 5.4 LSV temperature study of acetaminophen for flow-cell-type Au wire electrode. A) Linear-sweep voltammograms of 200 ppm acetaminophen in Britton-Robinson-buffer (pH 7.4) using the flow cell (Fig. 3.3) at 0.5 mL/min, 50 bar; B) Arrhenius plots of currents at 0.8 V.

Figure 5.4 depicts voltammetric experiments with acetaminophen at various temperatures up to 136 °C for studying the kinetics of this parallel-consecutive reaction. The results revealed two distinct linear regions in the Arrhenius plot (Fig. 5.4 B) suggesting each temperature range had a different process acting as the corresponding rate control. Using Arrhenius equation (4.1), activation energies were found as 58.5 kJ/mol at low temperatures (24 – 32 °C) in reaction rate control region and 13.9 kJ/mol at high temperatures (32 – 136 °C) in diffusion control region from slopes of -7039 and -1669 in the Arrhenius plot (Fig. 5.4 B), respectively. These findings are very similar to those with fork-type gold micro-wire electrodes under neutral conditions (Fig. 4.8 C: 14.5 kJ/mol at higher temperatures in diffusion control region). The only significant difference is that the current study has a higher activation energy of 58.5 kJ/mol in reaction rate...
control region compared to a corresponding value of 33.1 kJ/mol in Chapter 4. This may be due to the fact that the current lower temperature range is very narrow at 24 – 32 °C and only had three data points including the room temperature one without heating. If only data points with heated electrode temperatures (27 and 32 °C) are being considered, the activation energy in this reaction rate limit range would be 36.2 kJ/mol and comparable to the value of 33.1 kJ/mol in Chapter 4. These findings support that our flow cell electrode assembly has a great precision of temperature control and can provide a quick and simple way for reaction kinetic studies.

Fig. 5.5 Additional electrochemical measurements for flow-cell-type Au wire electrode. Using the flow cell (Fig. 3.3) at 0.5 mL/min, 50 bar, A) Chronopotentiometry: interval 0.5 s; 5 mM \( \text{K}_3\text{K}_4[\text{Fe(CN)}_6] \) in 0.1 M KCl solution as mobile phase; B) Cyclic Voltammetry of 200 ppm acetaminophen in Britton Robinson pH7.4 buffer (mobile phase); scan rate 0.1V/s.

As the solder joints in the latest version of flow-cell-type gold micro-wire electrodes are very close to the edges of the channel, Chronopotentiometry measurements in the standard calibration solution (an equimolar 5 mM ferro/ferri cyanide in 0.1 M KCl solution) for a total 1200 s and an interval of 0.5 s were performed to check if there is a leakage on solder joints. Fig. 5.5 A shows
that the potential baselines were leveled eventually and there was no drifting-down indicating that the solder joints were well protected. In order to provide additional insights on different control processes in Arrhenius plots, Cyclic Voltammetry (CV) measurements were also carried out with 200 ppm acetaminophen in Britton-Robinson buffer (pH = 7.4) using a scan rate of 100 mV/s and a range of -0.2 V to 0.8 V. Fig. 5.5 B illustrates the temperature dependence of cyclic voltammograms in which the anodic peak at 0.75 V is the one for the two-electron reaction of acetaminophen oxidation and the other anodic peak at near 0.4 V could be possibly related to the other parallel reaction - one proton dissociation reaction of acetaminophen. At room temperature of 24 °C, the two peak currents were very close. As electrode temperature increased, the acetaminophen oxidation reaction became dominant and the two distinctive linear ranges in the Arrhenius plot in Fig. 5.4 B reflected this transition.

5.4 Chronoamperometry detection of acetaminophen in a pressurized flow cell

Directly heated gold micro-wire electrodes have been used as detectors in flow analysis (Wang et al. 2000a). Since our pressurized flow cell can be easily coupled to a HPLC system, testing if our flow cell can work well as a detector does not require extra preparations. Experiments for acetaminophen detection with flow-cell-type gold wire electrodes were performed via chronoamperometry at 800 mV for a total 300-s time window with 0.1 s interval. Britton-Robinson buffer (pH = 7.4) was used as the mobile phase and the flow-cell coupled HPLC was operated at 50 bar and 0.5 mL/min, where the flow-cell gold wire electrode worked as a detector to monitor the current change when a 100-µL sample of certain concentration of acetaminophen was injected into the HPLC.
Fig. 5.6 Chronoamperometry detection of acetaminophen at different temperatures. Using the flow cell (Fig. 3.3) at 0.5 mL/min, 50 bar, T<sub>room</sub> = 24°C, Britton Robinson pH7.4 buffer as mobile phase, injection volume 100 µL; Chronoamperometry: interval 0.1s, voltage 0.8V; Savitzky-Golay smoothed data at level 4 with blank subtracted.

Figure 5.6 illustrates preliminary amperometric experiments at different temperature for acetaminophen detection. All amperometric signals were smoothened by Savitzky Golay Mode (Level 4) using NOVA 2.1 software and then was treated with blank subtraction and baseline correction using Origin software.
Fig. 5.7 LOD of acetaminophen detection at different temperatures. Using the flow cell (Fig. 3.3) at 0.5 mL/min, 50 bar, \( T_{\text{room}} = 24^\circ \text{C} \), Britton Robinson pH7.4 buffer as mobile phase, injection volume 100 µL; X-axis: acetaminophen concentration; Y-axis: current peak height; Savitzky-Golay smoothed data at level 4 with blank subtracted

Our flow cell was not originally designed to work as a detector. Due to the relatively large volume of the channel in the flow cell (~750 µL for maintaining the bulk solution at ambient temperature), the analyte concentration is being diluted when the sample enters into the flow cell. This caused that peaks in amperograms were broadened and in the case of experiments at room temperature some peaks were even splitted/flattened. When the flow-cell wire electrode was
heated, amperometric signals were significantly enhanced: at 110 °C, the signals were increased by nearly a factor of 10 compared to those at room temperature 24 °C; signal intensity was almost doubled when electrode temperature was elevated from 110 to 136 °C. However, signal drifting also became more severely when increasing electrode temperature and that is why peaks in amperograms at 110 °C had the best shapes. Figure 5.7 shows that the best LOD of 2.41 ppm was achieved at 110 °C while LOD at 136 °C was 10.26 ppm and without directly heating LOD at room temperature was only 16.68 ppm.

5.5 Summary
Experimental findings have shown that our preliminary pressurized flow cell is a good design for high temperature electrochemistry and has been tested up to 225 bar and 200 °C. It can house highly heated gold micro-wire electrodes providing a great precision of temperature control up to 160 °C, which was supported by results with both OCP and resistivity thermometer methods. The flow-cell coupled HPLC system can work very well as a platform for reaction kinetic studies in the meantime as a detector for flow analysis. The voltammetric measurements using the pressurized flow cell at 50 bar and 24 – 136 °C with acetaminophen as the model compound confirmed the similar two linear regions in Arrhenius plots from our previous findings with fork-type gold micro-wire electrodes at 1 – 115 °C: a diffusion control at higher temperatures and a reaction rate control at lower temperatures. The activation energies for the former region matched very well, while the difference in activation energies for the latter one may be due to insufficient data points in an extremely narrow temperature range. To further improve our flow cell design, a shorter micro-wire electrode and a smaller channel in the flow cell may significantly enhance the performance of the pressurized flow cell as a detector. Moreover, the
current design of our pressurized flow cell can only provide an estimated highest temperature of 220 °C based on the analysis made with gold wire and the 64-step AC generator. A shorter gold wire would reach a higher temperature with the maximum power from the current AC generator. Using platinum wires would be our future direction to fulfill our goal of achieving supercritical conditions.
6. Conclusions

Directly heated gold micro-wire electrodes offer numerous novel and unique advantages, such as, accurate temperature control, kinetic acceleration, micro-stirring effect, enhanced selectivity, easy cleaning, and low cost, etc.

Our wire electrode fabrication methods for both fork and flow-cell types are robust with good reproducibility. Arrhenius plots of both type heated micro-wire electrodes in voltammetric measurements of acetaminophen oxidation revealed two linear regions under neutral pH conditions corresponding to diffusion control with 14 kJ/mol at high temperature and 33 kJ/mol at very low temperature. The latter range was very narrow and probably belongs to a transition region towards a kinetic activation energy.

Our flow cell is an efficient design offering high precision temperature control, which is supported by highly consistent OCP and resistivity results. The flow cell can also work as a detector for flow analysis and achieved a good LOD at 110 °C electrode temperature. An improved flow cell with a smaller channel and shorter gold micro-wire electrode, however, would serve this purpose better.

The ultimate goal of the pressurized flow cell approach is to achieve supercritical conditions in the electrolyte solution at closest surroundings of the highly heated working electrode. This is our future work and would enable a sample preparation-free analysis of trace metals when combing complete deposition with subsequent coulometric stripping.
7. References


