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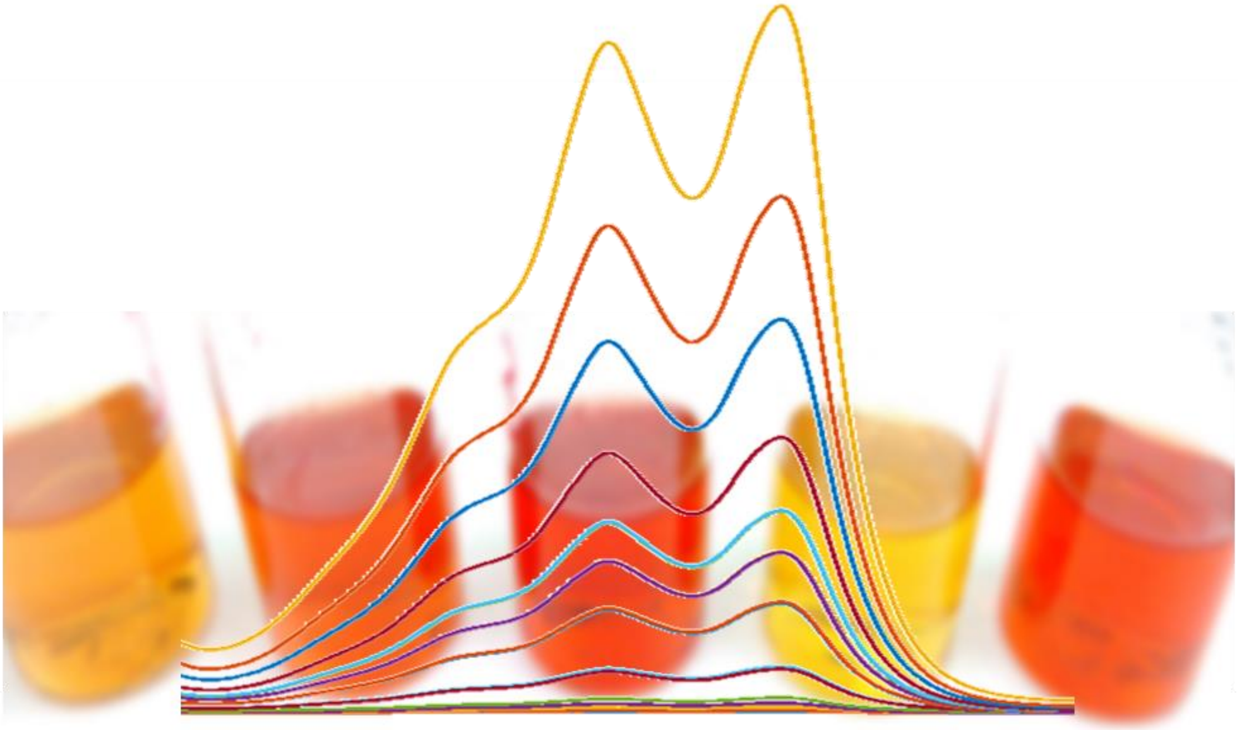

Electrochemical Oxidation of Chlorination Byproducts in Swimming Pool Applications

Master’s thesis in Erasmus Mundus Master of Science in Nanoscience and Nanotechnology

I-WEN HSU

Supervisor: Prof. Björn Wickman
Examiner: Prof. Anders Hellman
Co-promoter: Prof. Philippe Vereecken

Department of Physics
CHALMERS UNIVERSITY OF TECHNOLOGY
Gothenburg, Sweden 2016

Education and Culture
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Cover: urea and chlorine calibration showing spectra and colors at different concentrations

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ABSTRACT

Potential health risks related to disinfection byproducts (DBPs) in swimming pools have lately raised public concern and stringent legislation. This thesis presents a novel route to degrade DBPs with the use of electrochemical methods. A number of electrodes with nanoscale thin film materials have been investigated for this aim. Cyclic voltammetry results suggest that the byproducts from urea-chlorine reaction vary with initial chlorine concentrations. Having a higher amount of free chlorine induces transformation of monochloramine, dichloramine, and chlorourea into volatile trichloramine, nitrogen, and nitrate. In this work, free chlorine has been successfully regenerated from chlorination byproducts via pulse electrolysis. The process can be either direct or indirect oxidation of urea and DBP. Direct oxidation is the direct electron transfer from urea or chloramines to electrode. Indirect oxidation is mainly the electron transfer from chloride and chloramines to electrode, forming free chlorine, which is then used to oxidize urea and chloramines. Continuous electrolysis is suspected to convert hypochlorite to chlorate, decreasing the free chlorine concentration. A reaction mechanism for electrochemical oxidation of DBPs has been proposed. These findings clarify the role of free chlorine concentration in byproducts generation and open up new possibilities for DBP removal for water treatment applications.

Keywords: cyclic voltammetry, pulse electrolysis, electrochemical oxidation, chlorine, urea, trichloramine, DBP

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Last but not least, my family have always been giving me so much support and they are always by my side. I will never be able to finish all this work without them. Love you all!

This is not the end now. The new journey is just about to begin!

I-Wen Hsu

MC2, Chalmers, Gothenburg, Sweden

June, 2016

CONTENTS

List of Abbreviations

CE	Counter electrode
CV	Cyclic voltammetry
DBP	Disinfection byproducts
DPD	N,N-diethyl-p-phenylenediamine
FTO	Fluorine-doped tin oxide
NH_2Cl	Monochloramine
$NHCl_2$	Dichloramine
NCl_3	Trichloramine
REF	Reference electrode
RHE	Reversible reference electrode
WE	Working electrode

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Introduction

1.1 Swimming Pool Disinfection Methods

Swimming pool water without proper treatment will leave a variety of organic materials from swimmers, such as urine, sweat, skin, hair, and cosmetics. Among them, urea is one of the most abundant components in the pool water, as shown in Table 1.1. On average, 700 mg of sweat and urine is released by each swimmer [1]. The growth of microbiological infectants such as bacteria, virus, and fungi are promoted by the presence of organic nutrients and pose serious hazards to swimmers' health. Their infecting capability is dependent on pathogen's ability to pass the cell wall of microorganisms, which is then determined by surface charge and extent of hydration. Diseases like cholera, fever, gastroenteritis and schistosomiasis can develop by drinking infectious water. These contagious agents are eliminated through disinfection. Typical disinfecting methods include the usage of chlorine, hypochlorite, chlorine dioxide, bromine, ozone, ultraviolet (UV) light and electrochemical approaches [2]. Despite choices of several methods, disinfection by chlorine still remains the most common choice in swimming pools. The major oxidizing mechanism of free chlorine (Cl_2, OCl^- and HOCl) is believed to be chlorine substitution into proteins and nucleic acids of cells. Destroyed infectants are turned into inactivated forms. For example, formation of intracellular metabolites may be released into air by chlorination of algae in the swimming pools [2].

In addition, regular monitoring and feeding of fresh chlorine is essential for keeping the desirable disinfecting capacity. In swimming pools, the free chlorine is maintained at certain level (usually 0.5-2 mg/L) so that it can achieve the desired disinfection effect. The need for continuous feeding is because the stability of sodium hypochlorite solution is not infinite, but strongly dependent on concentration, temperature, pH, impurities, UV light, water circulation, and also the number of swimmers etc [3]. Gradual decomposition of sodium hypochlorite in improper conditions will produce sodium chloride, sodium chlorate and oxygen [4]. Understanding the chlorine chemistry is important for achieving a safe swimming environment.

Nitrogen sources (mg/L)	Urea	Ammonia	Amino Acids	Creatinine	Others	Total nitrogen
Sweat	680	180	45	7	80	992
Urine	10240	560	280	640	500	12220

Table 1.1: Sources of nitrogen-containing compounds in swimming pools. Data is expressed in mean values from A. Florentin et al [1]. Numbers can vary by more than 50% in different pools.

1.2 Health Risks from DBP

Even though harmful bacteria and other infectants are removed by disinfection chemicals, there are usually disinfection-by-products (DBP) left. The health risks of these DBPs are growing as a public concern in most chlorine treated water.

The type of by-products formed are determined by the disinfection conditions, including pH, temperature, types of infectants in the swimming pool, type of reactions, chemical concentration and disinfection methods, and so forth. For chlorination, i.e. disinfection with chlorine, hypochlorite, or monochloramine, the DBPs are trihalomethanes, haloacetic acids, chloramines, haloacetonitriles, chloral hydrate, chlorate, aldehydes and many more. Most of the comprehensive formation pathways are not clear yet. These compounds have been discussed by Chowdhury and Florentin in recent researches [1, 5] and some of them are summarized in Table 1.2. The sum of NH_2Cl, $NHCl_2$, and NCl_3 is known as combined chlorine. Sum of combined chlorine and free chlorine is total chlorine [2].

DBPs generally exist in a relatively small amount as to original infectants concentration, but their health risks cannot be ignored. One of the most harmful and well-studied compound is trichloramine, or the so-called nitrogen trichloride. It is formed from reaction between chlorine and amine-related compounds, including ammonia and urea. Its formation pathways are described in the section 2.3. Typical concentration of trichloramine in water is very low because of its low solubility in water and high volatility. In fact, it accounts for the most abundant DBP in air, approximately 0.56 mg/m^3 [5]. Good ventilation of indoor pools can effectively decrease concentration of trichloramine in the air. Outdoor swimming pools usually have less problems with trichloramine thanks to the open air environment.

Chowdhury and Florentin also discussed several health risks and syndromes that have been linked to DBPs, such as cytotoxicidity, cancer, asthma, coughing, itchy eyes, red eyes, runny nose, voice loss, cold, diarrhea, skin inflammation/rash (contact dermatitis), atopy, rhinitis, upper respiratory syndromes and other airway inflammation. These syndromes happen especially often on children, frequent swimmers and indoor swimming pool attendants. While trihalomethanes are the most abundant DBP in pool water, they are not a significant cause of all these diseases, unless at very high concentration. Trihalomethanes are easily metabolized by livers in humans and thus pose much less harm. Haloacetic acids are also rapidly metabolized or excreted. Other less abundant DBPs have taken up less concerns and have not been fully studied in literature. Trichloramine is regarded as one of the major causes for most diseases.

Chemicals in pools water	Concentrations
Free chlorine (mg/L)	1.28±0.43
Monochloramine NH_2Cl (mg/L)	0.29±0.11
Dichloramine $NHCl_2$ (mg/L)	0.38±0.14
Trichloramine NCl_3 (mg/L)	<0.10
Chloroform $CHCl_3$ (μg/L)	15.4±3.5*
Total trihalomethane CHX_3 (μg/L)	49.6±10.6

Table 1.2: Concentrations of common DBPs in swimming pool water [6]. *Chloroform having concentration more than 1 mg/L was also recorded.

1.3 Removal of DBPs

Chlorine can react with organic compounds either by direct oxidation (accepting electrons), or by substitution of elements (e.g. hydrogen) in organics. Most of the chlorine goes through the first route and leaves chloride ions in the solution, which can be oxidized again during electrolysis to form chlorine [2]. Some of the chlorine forms DBPs such as chloramines and then undergo further reactions.

The accurate control of amount of free chlorine is crucial for minimizing DBP production. While maintaining free chlorine in pool is indispensable, it is equally important to avoid too high concentration reacting with skin of swimmers and minimize the formation of undesirable DBPs. It can be understand by the concentration relation between ammonia and chlorine shown in Figure 1.1. This curve is commonly known as “breakpoint curve” where the chlorine concentration starts to decrease at a bit higher input and then increases again, as discussed in J. Hrubec’s book [7]. In zone 1, zone 2 and zone 3, most of the total chlorine exists as NH_2Cl, $NHCl_2$, and Cl_2, respectively. When adding too much Cl_2, NH_2Cl will be converted to $NHCl_2$ as well as many other DBPs until most of NH_2Cl has been consumed. It is sometimes recommended to conduct “superchlorination”, a sudden increase of free chlorine, to react with most bacteria and also reduce combined chlorine. Typical decomposition rate of urea is very slow (about 1% per hour) in a regular swimming pool containing an average concentration of 18 μM of urea and 1.7 mg/L of free chlorine [8]. The residual urea in water acts as a slow source of ammonia, which forms chloramines easily with free chlorine. To decrease chloramines we can try to increase the degradation rate of urea or remove chloramines directly. Activated carbon has also been applied in removing chloramines and other DBPs [9]. The disadvantage of this method is the simultaneous removal of free chlorine by activated carbon. Extra free chlorine is required to replenish the loss. Therefore, the proposed method –oxidation of urea and DBPs through electrochemical approach– has been investigated in this study.

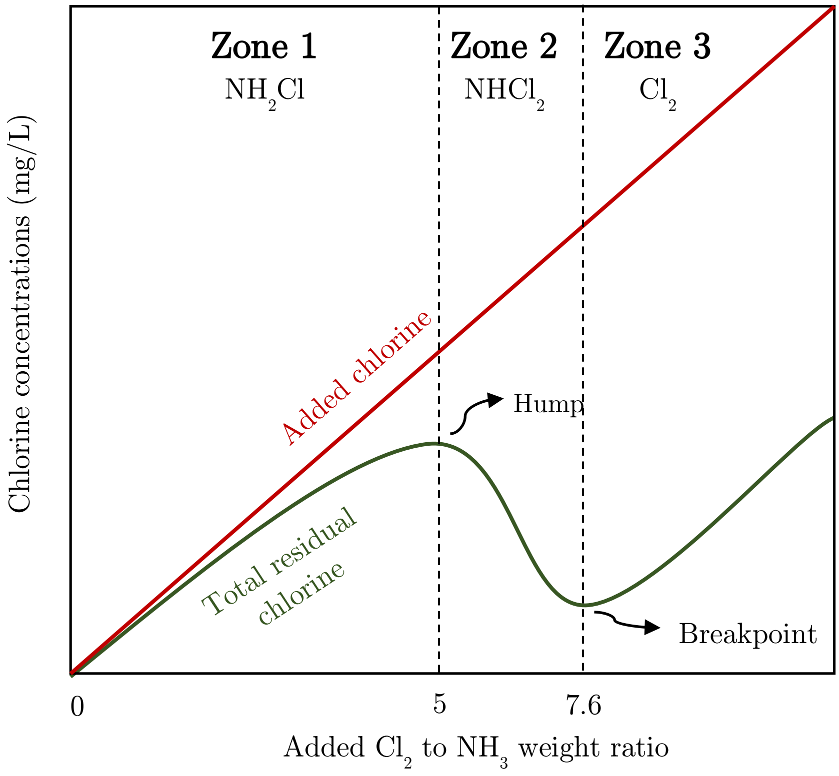

Figure 1.1: Breakpoint curve of ammonia chlorination.

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Background and Theory

2.1 Analytical Methods

To analyze and monitor concentration variation in solution during electrochemical treatment, one needs to build up relevant tools first. There are mainly two components that are of interest. One is urea and the other is chlorine. The chlorine includes both total and free chlorine. The difference between total and free is combined chlorine [2].

2.1.1 Urea Concentration

There are a few established methods for determination of urea concentration. Some of them are only suitable when working at concentrations higher than 0.1 M (mole/L). For example, in Fourier transform infrared spectroscopy (FTIR), CO and CN absorbance peak at 1560 and 1460 cm^{-1} respectively, which are proportional to urea concentration [10]. Other methods such as colorimetric, UV absorbance, chemiluminescence, potentiometry and fluorescence have also been reported [11].

Direct measurement of the whole solution, such as urine for dialysis, by UV-vis spectrometry is possible but ineffective due to interferences from other chemicals that also absorb UV lights (<300 nm), and also from shift in absorption wavelength after urea reaction with other chemicals [12]. Direct measurement under controlled chemistry with only two to three compounds is more likely to work. Similar situation of direct measurement is also true for chlorine and chloramines.

The approach used in this work is based on colorimetric measurement by having color reagents reacting in acids with urea as described in the experimental methods in Chapter 3. It is first invented by Prescott et al. in 1969 [13] and recently modified by Cozzi in 2004 [14]. The reaction mechanism has been proposed by Paul S. Francis et al [11]. In the reaction, diacetyl monoxime is first hydrolyzed in acid to diacetyl (also known as butanedione), and followed by nitrogen substitution to form chromogen, as in Figure 2.1(d). The chromogen absorbs light at peak wavelength around 510 to 512 nm in experiment. Addition of thiosemicarbazide and ferric chloride can enhance the color formation and stabilization. The accuracy of this method is affected by salinity, degradation of color reagents, cooling condition, etc. The peak can increase by more than 30% under high salt concentration due change of refractive index, change of ionic strength, and side reaction of diacetyl monoxime with salt [14]. More importantly, this method is unable to distinguish between urea and chloroureas [15]. Other drawbacks are the use of toxic chemical and acids, long process time, high temperature for the reaction, and absorption variation by manual measurement. The variation of color absorption can be minimized by fully automatized measurement in a commercial instrument.

2.1.2 Chlorine Concentration

The analytical methods for free and total chlorine concentrations include DPD colorimetric, DPD titration, iodometric titration, amperometric titration, conductivity method, and so forth [16].

DPD (N,N-diethyl-p-phenylenediamine) colorimetric method is adopted in this study. The analysis is realized by oxidization of DBP color reagent by free chlorine, forming Wurster dye with magenta color. The absorption wavelength is 490 to 555 nm, and Figure 2.2 shows the dye's chemical structure [17]. The absorption spectra are measured by UV-vis spectrophotometer. Spectra are then calibrated by having different standard concentrations. The concentration of a sample solution can be determined from the calibrated standards. Note that the absorption is not linear with concentration, thus a careful calibration with a series of concentrations must be made. To obtain total chlorine concentration, iodide is also added into the solution along with DPD, reducing monochloramine and dichloramine into ammonia and releasing triiodide ion (I_3^-). Triiodide then react with DPD to form Wurster's dye.

There are a few things we need to notice when using the DPD method. First, the absorption suffers from interference in the presence of other oxidants such as dissolved oxygen, ozone, manganese oxides, so one should either avoid mixing them or try to compensate the absorbance. Second, the spectra of chlorine-DPD solution may keep changing with time. The change mainly comes from slow monochloramine reaction with DPD [17]. Therefore, it is critical that the free chlorine spectrum is measured shortly after the addition of DPD reagents. Third, if the chlorine concentration is too high, excess chlorine can further react with Wurster's dye and produce a colorless product. Fourth, the presence of organic nitrogen could interfere with the determination of free chlorine concentration.

In water treatment practices, there are two other confusing terms. One is available chlorine or active chlorine, which is a measure of oxidizing power for any forms of chlorine compared to that of chlorine gas (Cl_2). It is usually expressed in weight percent. The other is residual chlorine, which is the concentration of free/total chlorine after reactions in chlorinated water over a period time.

2.1.3 DBP Concentrations

Apart from urea and chlorine, there are some other chemicals that are possible to detect with more sophisticated devices. For example, membrane introduction mass spectrometry (MIMS) has been introduced to determine the concentration of chloramines in water [18]. Ion chromatography is able to tell the concentrations for nitrate, nitrite, chlorate, chloride, chlorite, and so on [19]. Gas chromatography can distinguish different kinds of gas components such as trichloramine, carbon dioxide, chloroform, etc. These techniques are beyond the scope of this work.

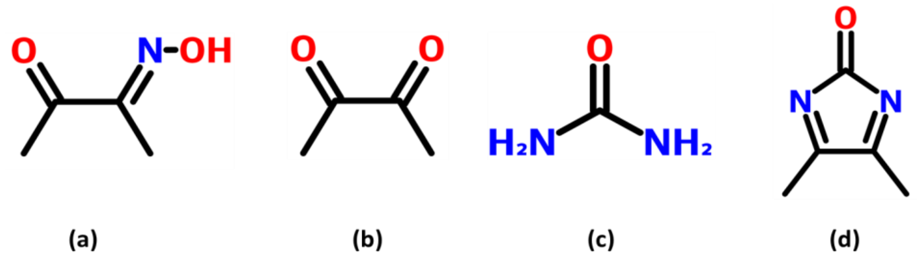

Figure 2.1: Structures of (a) diacetyl monoxime, (b) diacetyl, (c) urea and (d) one of the possible products of chromogen after reaction.

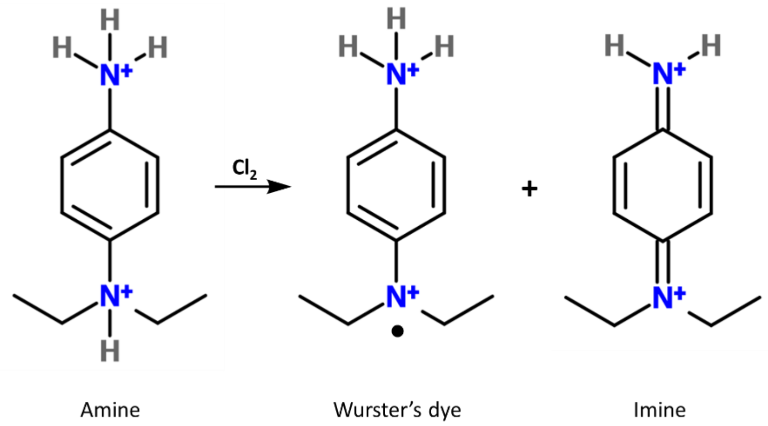

Figure 2.2: Reaction of DPD with free chlorine forming colored dye and colorless imine.

2.2 Electrochemistry

Electrochemistry the study of chemical reactions accompanying charge transfer occurring on electrode surfaces [20]. The current flows as a result of charge transfer, which also induces redox (reduction and oxidation) reactions. There is usually a conductive ion matrix called electrolyte to assist the flow of current. The current can be either supplied externally by a power source or produced from chemical reactions. There are several techniques and applications of electrochemistry including electrophoresis, electrodeposition, electrolysis, corrosion, batter, etc. The two particular electrochemical techniques used in this work are cyclic voltammetry and pulse electrolysis.

2.2.1 Reference Electrode

Reference electrode is an electrode having a constant redox potential at equilibrium. In a simple two-electrode setup, the measured voltage is between working and counter electrodes, and the potential on working electrode is unknown. Therefore, a reference electrode is inserted to comprise three-electrode configuration. It serves as a stable reference of potential so that accurate control of potential on working electrode can be achieved. There are a few commonly used reference electrodes in electrochemistry. Each provides different potential from reduction-oxidation reaction. The standard redox potentials against normal hydrogen electrode (NHE) are 0.242 V for saturated calomel electrode (SCE), 0.197 V for silver-silver chloride (Ag/AgCl) and 0.64 V for mercury-mercurous sulfate (Hg/Hg_2SO_4) [20]. For example, Hg/Hg_2SO_4 has the following equilibrium:

$$\mathrm{Hg_2SO_4 + 2\,e^- \rightleftharpoons 2\,Hg_{(l)} + SO_4^{2-}} \quad \mathrm{E^0 = 0.64\,V} \tag{2.1}$$

For convenience of comparison between electrolytes having different pH values, the conversion to reversible hydrogen electrode (RHE) is made. It has the following equilibrium:

$$\mathrm{H_3O^+ + 2\,e^- \rightleftharpoons H_2 + 2\,H_2O} \quad \mathrm{E^0 = 0 - 0.059 * pH} \tag{2.2}$$

Therefore, the conversion from Hg/Hg_2SO_4 to RHE is calculated by

$$\mathrm{E(RHE) = E(Hg_2SO_4) + 0.059 * pH = 0.64 + 0.059 * pH} \tag{2.3}$$

The pH for a normal swimming pool is about 6.5 to 7.5. In this thesis, it is about 8 to 9 due to weak base of urea and hypochlorite. In later experimental results, all the voltages have been converted from Hg/Hg_2SO_4 reference electrode to RHE by adding 1.1 V to original voltages, except the case in H_2SO_4.

2.2.2 Cyclic Voltammetry

Cyclic voltammetry (CV) is a type of linear scan voltammetry that sweeps back and forth continuously between two predefined voltages and measures the corresponding current [20]. An ideal case with reversible reactions is depicted in Figure 2.3. The unique current at a specific voltage is the required flow of electrons necessary to support the electrochemical process at the working electrode. If the potential on the working electrode is much lower than the standard electrode potential of half-cell reaction, no current flows, i.e. no reaction happens. If the potential is much higher than required, the reactions on electrode surface would be very fast and the concentration of reactants near electrode surface would be depleted. By varying the scan speed, analyte species, concentration, electrode area, and voltage range, one can tell the voltage that the analyte starts to oxidize/reduce and the species that are oxidizing/reducing.

In this work, the voltage scan rate was chosen at 100 mV/s. Different scan rates did not give much shift in peaks.

2.2.3 Pulse Voltammetry

A pulse means a potential step, or a sudden change of potential in other words. If this step of potential largely exceeds the standard electrode potential of a reaction, a lot of reactants are instantly depleted at electrode surface in a very short time. A lot of charge is rapidly passed to the electrode, and since the diffusivity is not infinite, this creates a very high concentration gradient as well. The consequence is a sharp peak of current. The continuous diffusion of reactants will then gradually reach electrode surface and the depletion region grows accordingly. The diffusion rate decreases over time, so does the current. If at any moment the voltage is turned off, the build-up of products from previous reaction near electrode surface will quickly undergo reverse reaction. A reverse current spike is created. This reverse current is also gradually decreases with time due to depletion. Reversing the polarity instead of turning off would give even large current spike. It is schematically sketched in Figure 2.4. This method was applied in this work to continuously reestablish concentration gradient and regenerate current.

2.2.4 Electrolysis

Electrolysis is the continuous flow of direct electrical current on electrodes to generate continuous chemical reactions in the electrolyte. Electrolysis can be used to drive a non-spontaneous reaction and to modify the components in solution. The electrolysis process can be controlled by fixing the potential or by fixing the current. Having a high electrode area to electrolyte volume (A/V) ratio can facilitate the process.

In this research, electrolysis was combined with pulse voltammetry where the voltages were not fixed but varied with time in a periodic manner. It is termed **pulse electrolysis** in this study.

Note that if the controlled voltages are higher than the oxidation potential of water (1.23 V vs. RHE in theory), the irreversible generation of oxygen will begin and an exponential increase in current will take place.

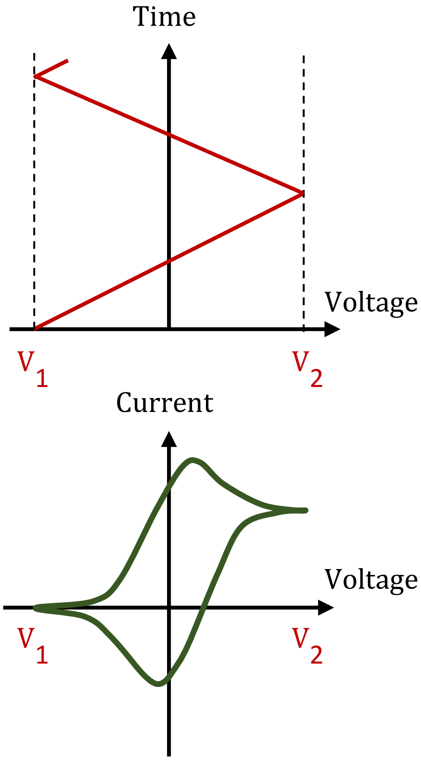

Figure 2.3: Cyclic voltammetry (CV) with triangular wave of voltage as a function of time (top) and the response current as a function of voltage (bottom).

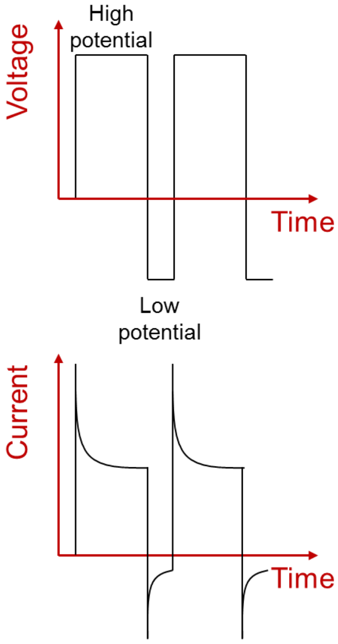

Figure 2.4: Schematic representation of pulse electrolysis method.

2.3 Chlorination principles

Hypochlorite

Hypochlorite is the strongest oxidizing agent among chlorine species with standard redox potential of 0.89 V, compared to chlorite (0.78 V), chlorate (0.63 V) and perchlorate (0.56 V) in both neutral and basic solutions [21]. The dissociation of hypochlorous acid depends on pH. The pKa of hypochlorous acid is about 7.5, so in a more acidic solution, more HOCl than OCl^- will exist and vice versa [2]. In most swimming pools, the pH ranges from 6.5 to 7.5, so about half of chlorine is in the form of HOCl.

OCl^- ion is also in equilibrium with Cl_2 and Cl^-. The latter might naturally exist in stock solutions as a result of this equilibrium but also from manufacturing process.

$$2\ H^+ + OCl^- + Cl^- \rightleftharpoons Cl_2 + H_2O \tag{2.4}$$

OCl^- is not very stable and can undergo disproportionation into chloride, oxygen and chlorate under heating.

$$2\ OCl^- \rightarrow 2\ Cl^- + O_2 \tag{2.5}$$

$$3\ OCl^- \rightarrow 2\ Cl^- + ClO_3^- \tag{2.6}$$

OCl^- is also slowly self-decomposing in water and releasing hydroxyl radicals.

$$OCl^- + H_2O \rightarrow Cl^- + 2\ HO\cdot \tag{2.7}$$

The addition of chlorine gas (Cl_2), hypochlorous acid (HOCl) and hypochlorite ion (OCl^-) in water will result in a chemical equilibrium:

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl \tag{2.8}$$

$$HOCl \rightleftharpoons H^+ + OCl^- \tag{2.9}$$

$$HOCl + OH^- \rightleftharpoons OCl^- + H_2O \tag{2.10}$$

The evolution of one chlorine species to another is called speciation. In a more basic environment, more hypochlorite ion will form than hypochlorous acid. In general, hypochlorous acid is a stronger oxidant and more reactive than hypochlorite ion. It can react with more species and also faster than chlorine gas. While addition of Cl_2 and HOCl would lead to decrease of pH, addition of NaOCl will increase the pH in the pool. In the experimental conditions, pH ranges approximately from 8 to 9, meaning that about 80% of hypochlorite will stay as OCl^- while about 20% will be HOCl [2].

Ammonia chlorination

Oxidation of ammonia is easily achieved by chlorination. The addition of chlorine will quickly consume all ammonia present in pool water. Nitrogen and chlorine containing intermediate compounds can form. The compounds then undergo deamination reaction to release monochloramine and a hydroxyl group. Monochloramine is then further oxidized by even more chlorine or acidified to form dichloramine and trichloramine. Hypochlorite and chloramines reactions are described in equation (2.11) to (2.13). The chloramines can react with each other, water, ammonia, chlorine, or oxygen to form nitrate, nitrogen gas, higher chlorinated chloramines, chloride, and other intermediates. A comprehensive reaction scheme was proposed by Javert [22].

$$\mathrm{OCl^- + NH_3 \rightleftharpoons NH_2Cl + OH^-} \tag{2.11}$$

$$\mathrm{OCl^- + NH_2Cl \rightleftharpoons NHCl_2 + OH^-} \tag{2.12}$$

$$\mathrm{OCl^- + NHCl_2 \rightleftharpoons NCl_3 + OH^-} \tag{2.13}$$

A loss of organic nitrogen has been observed by Randtke et al. at high chlorine concentration or high chlorine to nitrogen ratio due to the gaseous components after chlorination [2].

Urea chlorination

While chlorination of ammonia is relatively simple, chlorination of urea is a lot more complex due to structure containing C=O bond with nitrogen. All kinds of chloramines are expected to form from ammonia chlorination, but for urea chlorination NCl_3 is regarded as the major byproduct. NH_2Cl and $NHCl_2$ are mostly from NCl_3 hydrolysis. For example [15],

$$\mathrm{NH_2Cl + HOCl \rightleftharpoons NCl_3 + H_2O} \tag{2.14}$$

The chlorination mechanism, reversibility, and kinetics of urea are not well understood. The products and byproducts from urea are more diverse than those of ammonia. Besides, the chlorine reaction with urea is a lot slower (1.2×10^{-8}) than with ammonia. Urea is thus a slow yet efficient NCl_3 source. Some of the proposed reactions of urea with Cl_2 are [23]:

$$\mathrm{H_2NCON}H_2 + \mathrm{Cl_2 \rightleftharpoons H_2NCONHCl + HCl} \tag{2.15}$$

$$\mathrm{H_2NCON}H_2 + \mathrm{3\,Cl_2} + H_2\mathrm{O} \rightarrow \mathrm{CO_2} + N_2 + \mathrm{6\,HCl} \tag{2.16}$$

The reaction mechanism of hypochlorite and urea was proposed by Blatchley et al. in a recent study [15]. They suggest that urea undergoes sequential chlorination as chlorourea, dichlorourea, trichlorourea and tetrachlorourea in the presence of chlorine gas (Cl_2), followed by more chlorination and substitution as monochloramine, trichloramine, chloride and carbon dioxide. Monochloramine can further react with alkaline forming hydroxyl nitrogen and nitrate. The initial chlorination reactivity between free chlorine and urea is slow, the rate determining step, and it is expected to be higher at lower pH value due to higher proportion of Cl_2 in acid. The end products of chlorination depends on pH and Cl_2:N ratio. However, in normal swimming pools, most of free chlorine quickly evolves into other forms other than molecular chlorine (Cl_2), depending on the pH of swimming pool. The overall reactions by Blatchley are summarized in equations below. Staring with sequential substitutional chlorination of urea:

$$H_2NCONH_2 + Cl_2 \rightarrow H_2NCONHCl + Cl^- \quad (2.17)$$

$$H_2NCONHCl + HOCl \rightarrow CO(NHCl)_2 + H_2O \quad (2.18)$$

$$CO(NHCl)_2 + HOCl \rightarrow Cl_2NCONHCl + H_2O \quad (2.19)$$

$$Cl_2NCONHCl + HOCl \rightarrow CO(NCl_2)_2 + H_2O \quad (2.20)$$

$$CO(NCl_2)_2 + HOCl \rightarrow HCl + CO_2 + NCl_3 + NCl \quad (2.21)$$

$$NCl + OH^- \rightarrow NOH + Cl^- \quad (2.22)$$

$$2\,NOH \rightarrow H_2N_2O_2 \quad (2.23)$$

$$H_2N_2O_2 \rightarrow N_2O + H_2O \quad (2.24)$$

$$NCl_3 + HOCl + 2\,H_2O \rightarrow NO_3^- + 4\,Cl^- + 5\,H^+ \quad (2.25)$$

Chlorine is a stronger electrophilic element than hydrogen. It is considered that chlorination of amines is the common first step in similar reactions. Hydrolysis in equation (2.21) releases amine group in the presence of more OCl^-. In Blatchley's research, it was observed that NCl_3 concentration increases in the beginning and then decreases after a peak. It was assumed that residual free chlorine will continue oxidizing NCl_3. In this regard, NCl_3 is considered as one of the intermediates during reaction. The overall reaction with only final products can be express as:

$$CO(NH_2)_2 + 8\,HOCl \rightarrow CO_2 + H_2O + HNO_3 + 8\,HCl \quad (2.26)$$

$$CO(NH_2)_2 + 3\,HOCl \rightarrow CO_2 + 2\,H_2O + N_2 + 3\,HCl \quad (2.27)$$

In general, low pH, high temperature, high free chlorine and chloride concentrations would give rise to high NCl_3 production. Having an excess of free chlorine can be more effective in chlorinating urea. Most of the carbon is converted into CO_2 (77%) and CO [24]. One should note that this reaction scheme does not include other intermediates and byproducts that can form such as chloroform, nitrogen gas, chlorate and chloroacetonitrile.

Trichloramine

Trichloramine is unstable and very volatile near neutral pH conditions. Ammonia, other chloramines, free chlorine and a low pH environment can make it more stable. Activated carbon adsorption, dechlorination, sunlight, and good ventilation are common removal approach [2]. In addition to chloramines, chloroform ($CHCl_3$) is one of the most abundant DBP that is not detected by DPD combined chlorine test. Related chemistry is supposed to take $CHCl_3$ into account, but little research has been focus on it.

2.4 Oxidation Mechanism

There are a few methods to oxide organic compounds. The method by UV light generated hydroxyl radicals has become a popular topic of water treatment. Fabian et al. has investigated degradation of chloramines by direct photolysis reaction [4]. The UV irradiation leads to cleavage of N-Cl bonding and generate •Cl radical. Trichloramine is especially sensitive to UV light compared to mono- and dichloramine.

However, there are a few significant disadvantages of using UV lights. For one, the existence of free chlorine would rapidly react with both degraded-trichloramine and hydroxyl radical. NCl_3 is largely regenerated and the photolysis efficiency is consequently lower. The regeneration of NCl_3 is especially serious in a big pool with slow water flow. For another, UV light was also found to degrade free chlorine considerably, whose concentration drop as water pass the UV reactor [4]. The chain reactions of UV on HOCl were proposed as follows:

$$\mathrm{HOCl} \xrightarrow{hv} \cdot\mathrm{OH} + \cdot\mathrm{Cl} \tag{2.28}$$

$$\cdot\mathrm{OH} + \mathrm{HOCl} \rightarrow \mathrm{H_2O} + \cdot\mathrm{OCl} \tag{2.29}$$

$$\cdot\mathrm{Cl} + \mathrm{HOCl} \rightarrow \mathrm{HCl} + \cdot\mathrm{OCl} \tag{2.30}$$

$$2\cdot\mathrm{OCl} + \mathrm{H_2O} \rightarrow \mathrm{HCl} + \mathrm{HClO_3} \tag{2.31}$$

The highest absorbance is at 254 nm for HOCl and 292 nm for OCl^-. Similarly, excess sunlight can raise the free chlorine demand in outdoor swimming pools. Yet another is the frequent cleaning of UV lamps to enhance the irradiation. Therefore, oxidation by UV light is considered less favorable.

An alternative method for oxidizing organic compounds is through anodic, electrochemical oxidation. Anodic oxidation has been proved effective in oxidizing, phenol, benzoic acid, aniline, nitrobenzene, and so on [25]. This method does not require the use of toxic chemicals while turning pollutants into less harmful products. The electrochemical oxidation can be either direct or indirect. Direct oxidation involves direct transfer of electrons from target molecule to electrode; indirect oxidation involves transfer of electrons from intermediate species which then oxidize the target molecule.

There are two approaches to reduce chlorination byproducts through electrochemical oxidation. One is getting rid of the source, which is mainly urea. The other is removing the DBPs, which are mainly chloramines. Directly oxidizing source (urea) was considered first. Ideally the complete oxidation of urea produces carbon dioxide, nitrogen and hydrogen, which are all non-toxic. Incomplete oxidation would generate ammonia (NH_4^+) and nitrate (NO_3^-). Boggs et al. have investigated the mechanism for direct oxidation of urea [26].

$$\mathrm{CO(NH_2)_2} + 6\,\mathrm{OH^-} \rightarrow \mathrm{N_2} + 5\mathrm{H_2O} + \mathrm{CO_2} + 6\,\mathrm{e^-} \tag{2.32}$$

$$6\,\mathrm{H_2O} + 6\,\mathrm{e^-} \rightarrow 3\,\mathrm{H_2} + 6\,\mathrm{OH^-} \tag{2.33}$$

$$CO(NH_2)_2 + H_2O \rightarrow N_2 + 3\ H_2 + CO_2 \tag{2.34}$$

Nonetheless, Boggs also pointed out that to efficiently and directly oxidize urea, alkaline conditions and a suitable nickel or nickel (II) hydroxide catalyst are normally required. In neutral solution, nickel is unstable, easily oxidized into Ni^{2+}, and has poor catalyzing capability. It is applicable for generation of hydrogen for fuel cells but not for water treatment purposes. A few other metals have also been tested for direct oxidation but ineffective, including platinum (Pt), iridium (Ir) and ruthenium (Rh). K. Cho and Hoffmann have also tested with bismuth doped titanium oxide to do direct electrolysis of urea at 3 V NHE in Na_2HPO_4 buffered solution, but they could not observe any decrease in urea concentration by direct electron transfer [24, 27].

The indirect oxidation approach have been more prospective. Electrochemically generated free chlorine (Cl_2 and OCl^-) has successfully reduced the amount of urea in controlled experiment containing chloride and urea. Cutting down the concentration of nitrogen source can be more efficient in reducing trichloramine since its formation is rather fast and dynamic. Besides, chloride is naturally abundant in human excreta and waste water, so direct electrolysis of waste water of urine is expected to have a similar effect of reducing urea. For some swimming pools, additional chloride ions, usually in the form of sodium chloride, are added into water to reach a higher salt concentration.

The oxidation process first involves oxidation of chloride into chlorine atom (Cl•) and dichlorine radical anion (Cl_2^-•), which then quickly form free chlorine due to the short life time of radicals [24]. Urea is then oxidized via a similar approach proposed by Blatchley [15] into nitrogen, nitrate, carbon dioxide, and carbon monoxide. It was also found that under higher voltage, higher pH and lower chlorine to urea molar ratio, more nitrogen was produced than nitrate due to competing reaction between chloride and nitrate [28]. Formation of nitrate potentially consumes more electricity than nitrogen, and likely comes from further oxidation of dichloramine.

Electrochemical decomposing urea with anodes made up of mixed metal oxides (MMO) has also demonstrated the ability to produce chlorine for oxidation reaction. These anodes typically contain RuO_2, IrO_2, PtO_2, and other noble metals [29, 30]. Their reaction mechanism mainly involves oxidation of chloride in to chlorine, followed by replacement reaction with water [24, 31]. Then the fresh free chlorine continues to react with urea to produce N_2, CO_2, CO, Cl^-, ClO_3^- and chloramines, etc. A simple mechanism is

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \tag{2.35}$$

$$Cl_2 + H_2O \rightarrow HOCl + HCl \tag{2.36}$$

In this research, both direct and indirect electrochemical oxidation were examined.

3

Methods and Experimental Setup

3.1 Cell Setup

In this research, three-electrode configuration was adopted for all the electrochemical experiments. The three electrodes are working, counter, and reference electrodes. The actual setup and sketch are shown in Figure 3.1 to Figure 3.3. Working electrode is the electrode of interest, and where the desired reaction happens. Counter electrode is an auxiliary electrode, usually platinum or graphite, and its voltage is automatically adjusted by potentiostat to balance voltage on the working electrode. Reference electrode provides a reference for accurate determination of the actual potential that is applied on the working electrode. The reference electrode used in this work was mercury/mercury sulfate, Hg/Hg_2SO_4, since we are using potassium sulfate as electrolyte. It has a stable redox potential at any pH, about 0.64 V against NHE. Cyclic voltammetry and pulse electrolysis are the two major electrochemical techniques used in this work, as discussed in Chapter 2.

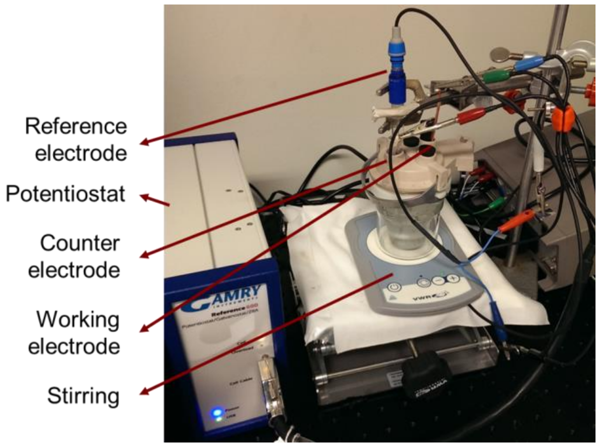

Figure 3.1: The electrochemical setup for three electrode system.

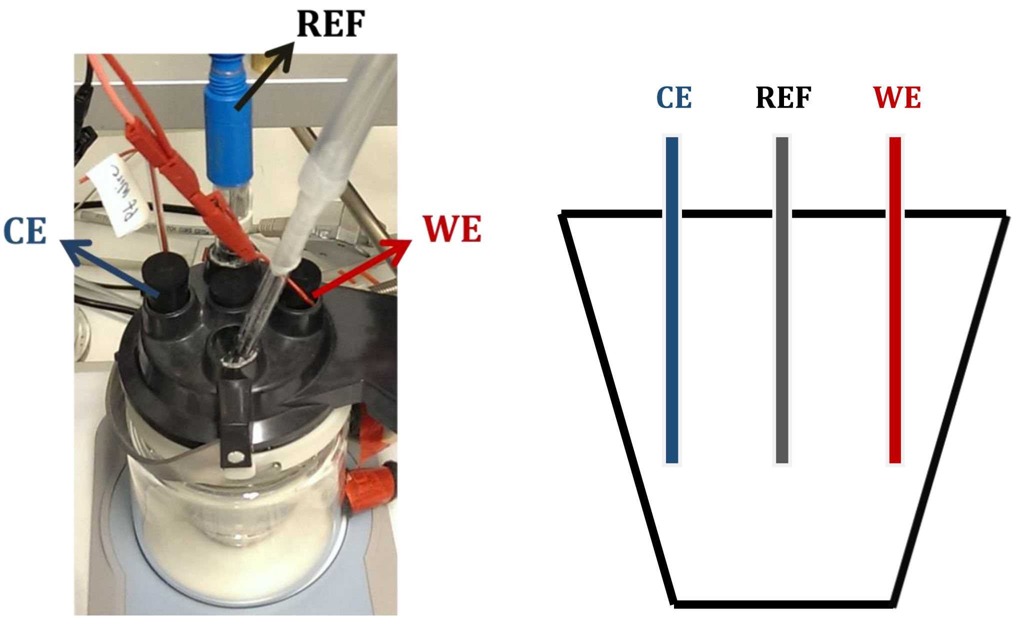

Figure 3.2: Normal electrochemical cell with working electrode (WE), counter electrode (CE), and reference electrode (REF).

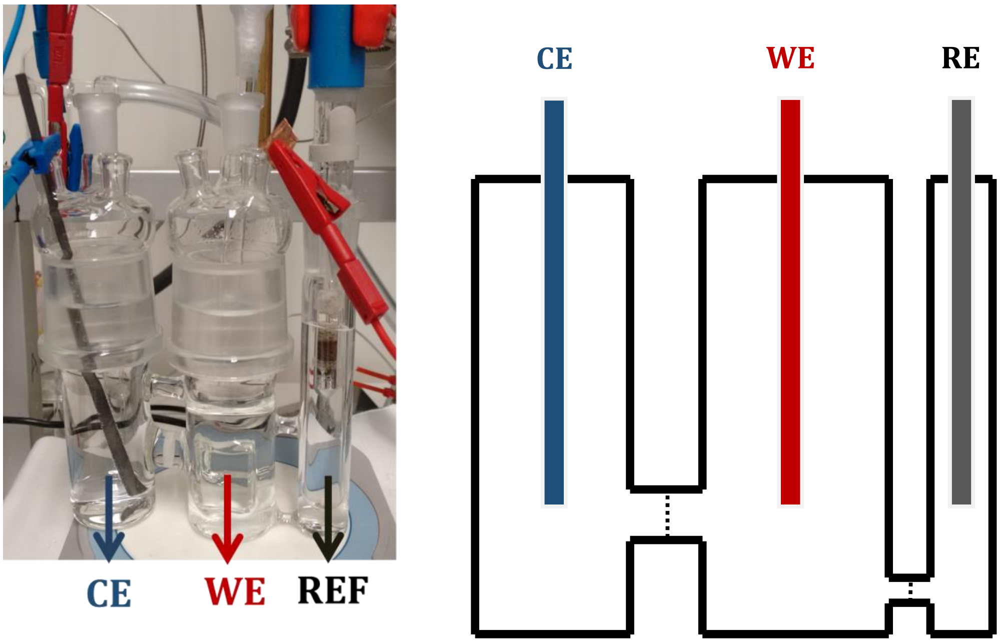

Figure 3.3: Electrochemical cell with membrane-separated compartments, called H cell.

3.2 Samples, Materials and Chemicals

3.2.1 List of Chemicals and Tools

a. Electrochemical cell: titration vessel with thermostat jacket from Metrohm (model 6.1418.220 and 6.1418.250) and corresponding vessel lid with 5 openings.
b. H-cell: Three compartment cell separated with porous fritted glass disk
c. Potentiostat: BioLogic SP-300 and Gamry Reference 600. Both of them provide stable voltage and current. The former allows changing experimental conditions after starting the experiment. The latter is occasionally used for electrolysis.
d. UV-vis spectrophotometer: Cary 5000 UV-Vis-NIR from Agilent Technologies
e. Analytical balance: LA 214i from VWR, precision 0.0001 g
f. Water: Milli-Q® Ultrapure Water
g. Chemicals:
    a) Potassium sulfate: 99% powder from Alfa Aesar, CAS number 7778-80-5
    b) Urea: ≥99.5%, pellets from Sigma Aldrich, CAS number 57-13-6
    c) Sodium hypochlorite: 14% Cl2 in aqueous solution from VWR, CAS number 7681-52-9
    d) Thiosemicarbazide (Hydrazinecarbothioamide): ≥98% from Acros Organics, CAS number 79-19-6
    e) Diacetyl monoxime (2,3-butanedione monoxime): ≥98% from Alfa Aesar, CAS number 57-71-6
    f) Iron(III) chloride hexahydrate: 99% from Sigma Aldrich, CAS number 10025-77-1
    g) DPD free/total chlorine reagent: VWR powder pack reagents with absorption at 510 nm
h. Electrodes: platinum wire* (diameter 0.5 mm), graphite rod (length 150 mm, diameter 3 mm, 99.995%, from Sigma Aldrich), metallic thin film (50-200 nm) deposition on glass substrate (15*15 mm^2) by Lesker evaporator PVD 225 attached to a metal wire with copper tape and hot glue
i. Reference electrode: mercury/mercury sulfate electrode model B3610+ from SI Analytics

*The adhesion between platinum film and hot glue (ethylene-vinyl acetate and petroleum resin) in chlorinated water is poor, so platinum wire was used to avoid any undesirable reactions on the glue.

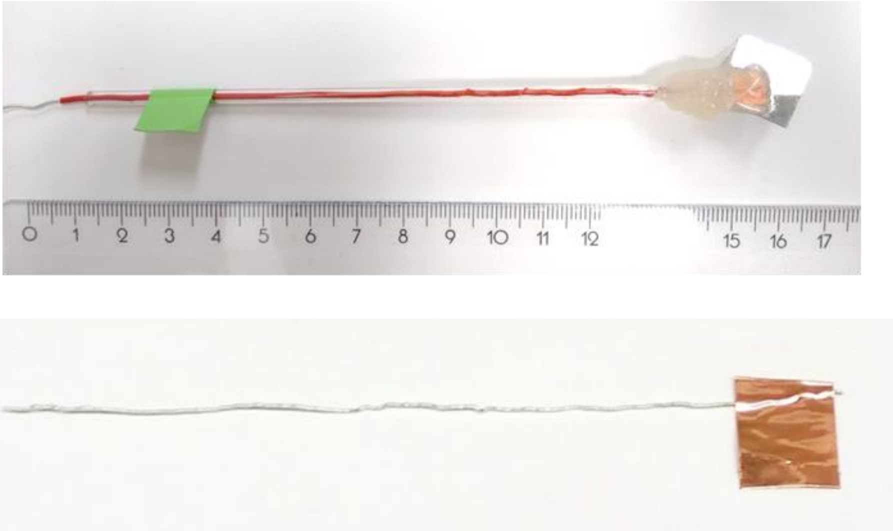

Figure 3.4: Pictures of electrodes of metallic thin films (top), and platinum wire with copper tape as contact pad (bottom).

3.2.2 Sample Preparation

Standard solutions of chlorine and urea were prepared with volumetric flasks and weighted gravimetrically to fourth decimal precision.

The immersion depth of Pt wire had been controlled to about 4 cm, which give a surface area of 0.63 cm^2. After each time of electrolysis, the platinum wire was cleaned in propane flame several times to get rid of all possible contamination from urea and chlorination by-products. The platinum wire was confirmed clean and ready-to-use by checking characteristic CV curves in 0.5M H_2SO_4 solution and by comparing the curves with fresh platinum wire in 0.1M K_2SO_4 solution.

The electrochemical experiments are carried out at room temperature about 21 ℃, which was controlled by the air condition and was supposedly stable any time the year. No external thermal bath was applied.

3.3 Colorimetric Measurements

The concentrations measurement was done by colorimetric method with Cary spectrometer and WinUV system. The wavelength window used was 400-800 nm.

3.3.1 Urea Concentration

The approach for urea concentration is a modification of Cozzi's recipe [14]. First part, step (a) to (e), is the preparation of batch solutions. Second part, step (f) to (o) is the mixing of chemicals and reaction.

a. Diacetyl monoxime 0.7 g/250 mL
b. Thiosemicarbazide 0.5 g/100 mL
c. $FeCl_3 \cdot 6H_2O$ 10 g/100 mL
d. Urea 0.6 g/1000 mL. (10 mM, 1 μL contains 0.6 μg of urea)
e. Keep (a) and (b) in a refrigerator for use afterwards. The other two in a cabinet.
f. Pre-heat the oven to 95°C
g. Take 5 mL of diacetyl monoxime solution (a) in a small glass vial with lid. (Target concentration is 1.4 g/L)
h. Add 2.25 mL H_2SO_4 98%
i. Add 0.7 mL H_3PO_4 85%
j. Add 0.8 mL thiosemicarbazide solution (b). (Target concentration is 0.4 g/L)
k. Add urea solution (d). Add water to reach 100 μL every sample.
l. Add water to 10 mL (about 1 mL extra water)
m. Heat the prepared samples in the oven. Count down 45 min after it reaches 90°C.
n. Take out the samples and let them cool in the fume hood for 10 minutes. Add $FeCl_3$ solution.
o. Measure the absorption with UV-vis spectrometer.

Notice that the color reagents, diacetyl monoxime and thiosemicarbazide, are not stable for long period of time, so it is recommended to replace the solution every day.

The color formation is also affected by chlorine, causing turbidity. It is corrected by shifting the entire sample spectrum by the mean absorption of three standard curves at 800 nm, as demonstrated in Figure 3.7.

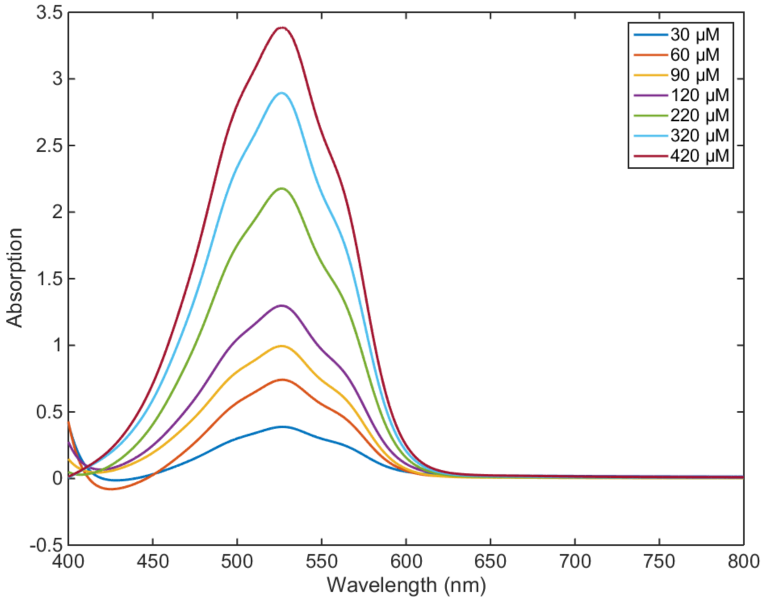

Figure 3.5: Urea concentration is calibrated by area integration of absorption spectrum over 430 to 630 nm.

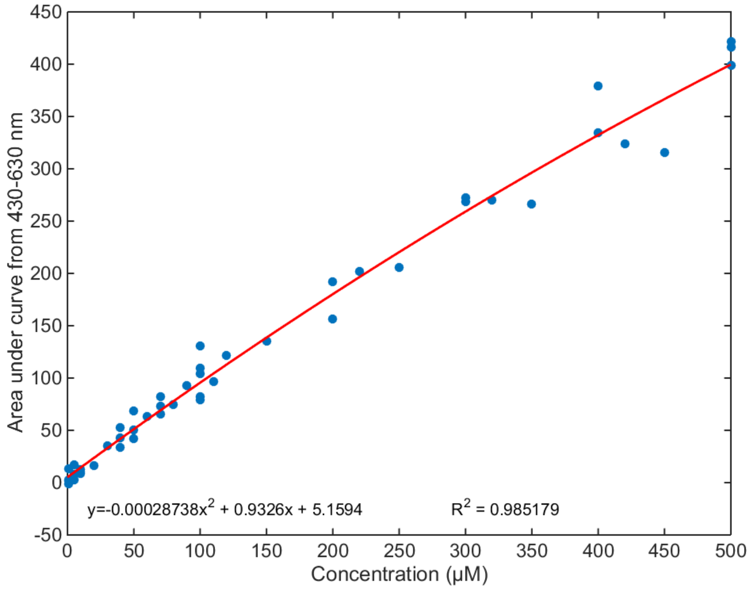

Figure 3.6: Urea concentration calibration curve.

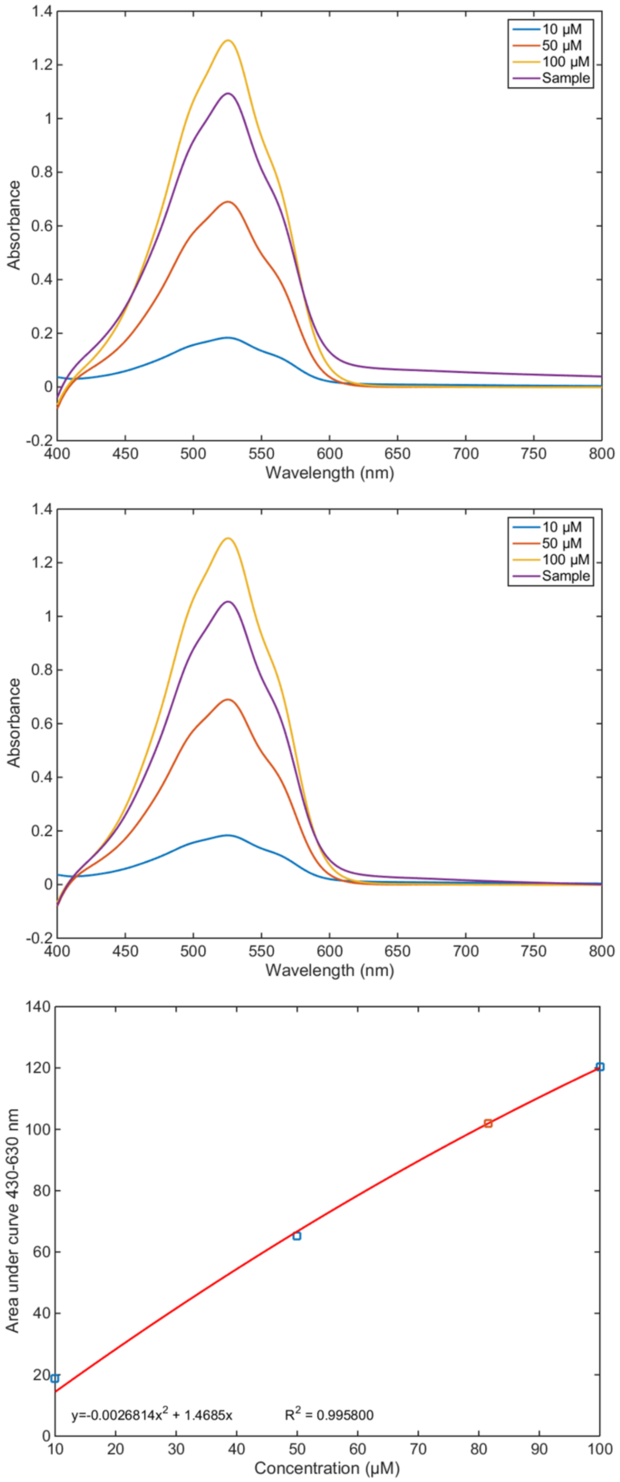

Figure 3.7: Urea concentration measurement by interpolating of three standard concentrations. Original spectra (top), shifted spectra (middle) and concentrations (bottom).

3.3.2 Chlorine Concentration

DPD free/total chlorine reagent powder pillows from Hach were used to determine the chlorine concentrations. The pillow reagents normally contain TBE buffer to keep pH around 6.2-6.8 for better consistency. The concentration measurement needs to be calibrated for readout from absorption spectra to concentration value. The steps are:

a. Prepare 10 mM standard solution by having 0.422 ml hypochlorite stock solution (2.37 M) in some water and then fill it with more water to 100 ml with volumetric flask.
b. The standard solution is then stirred for around one hour.
c. Make various concentrations of diluted hypochlorite solutions from the 10 mM standard by preparing several vials with 10 ml mili-Q water.
d. Take out equivalent volume of water from the vial before adding 10 mM solution. For example, for 100 μM solution, take out 100 μl of water and then add 100 μl of 10 ml NaOCl solution.
e. Add free/total DPD chlorine reagents into the vial right before UV-vis spectrometric measurement.
f. Calibrate the absorption baseline with milli-Q water.
g. Measurement the absorption of the samples.
h. Make the calibration curve of signal against concentration.

After the calibration, we can measure chlorine concentration conveniently. Similarly, we prepare samples vials with 10 ml water and then take out 50 μl target solution with a pipette. Then we do the spectrometric analysis and read out the concentration from the calibration curve.

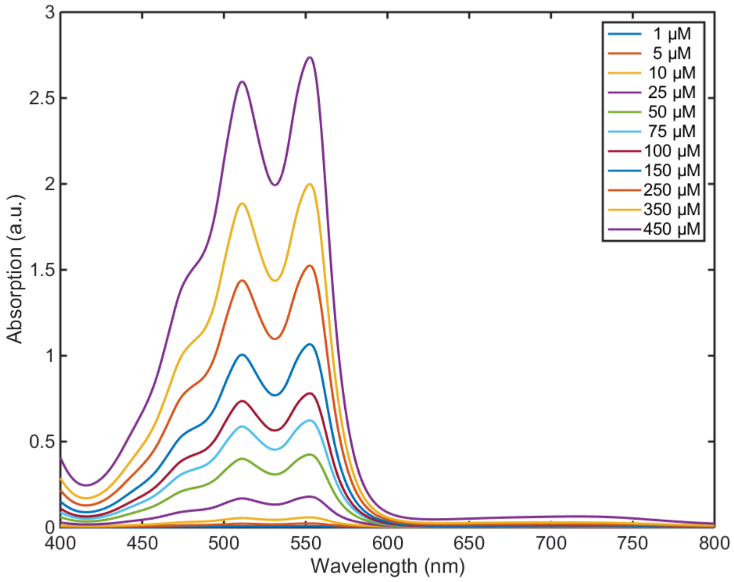

Figure 3.8: Total chlorine concentration is calibrated by area integration of absorption spectrum over 450 to 600 nm.

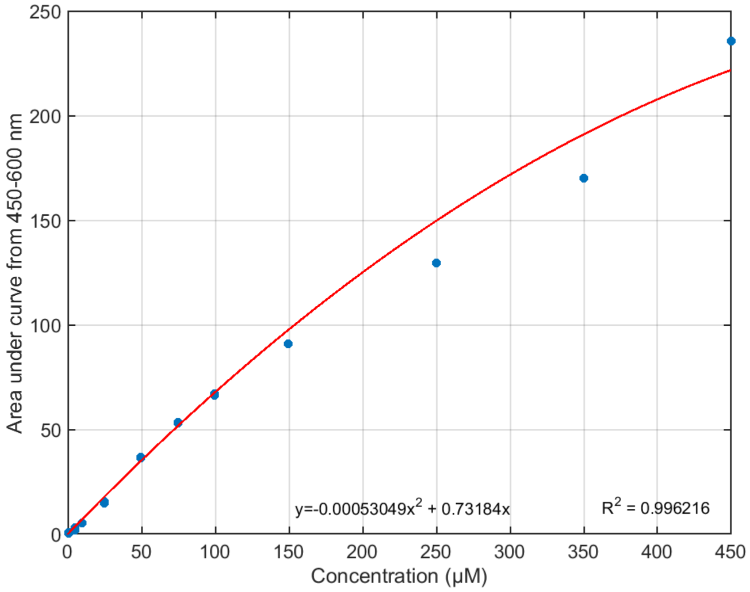

Figure 3.9: Free chlorine calibration curve.

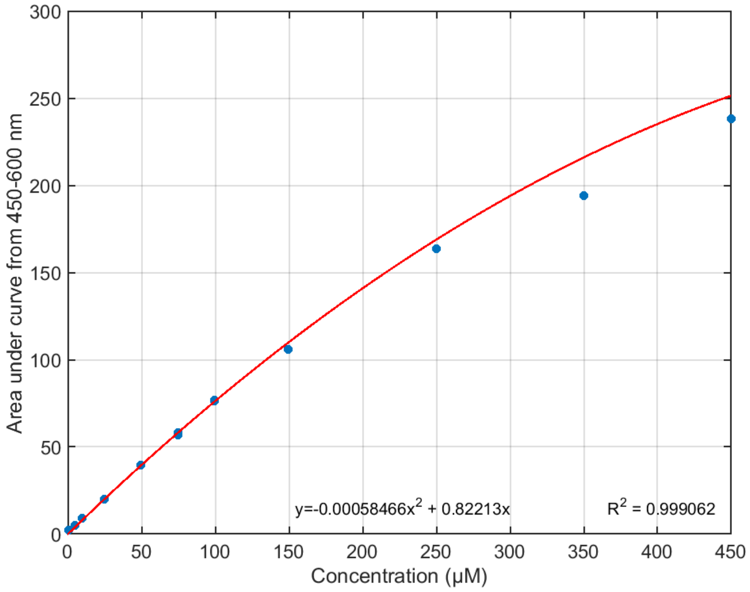

Figure 3.10: Total chlorine calibration curve.

3.3.3 Percent Active Chlorine

In chemistry and science, chemical concentration is usually expressed by molar or mole per liter. In water treatment practice, non-chemists prefer expressing as milligram per liter or ppm. Concentrations of different chlorine species in mg/L cannot be added up directly because they have different molecular weights. For example, 1 mg/L of Cl_2 and 2 mg/L of HOCl does not equal 3 mg/L of all chlorine species. As a result, percent active is created as a convention for comparing oxidizing power of different chlorine solutions. The convention also makes it easier to determine the amount of solution needed and the effectiveness of any chlorine solution.

Percent active chlorine is defined by the oxidizing power of chlorite-based chemicals compared to that of pure chlorine (Cl_2) in weight percentage [2]. In scientific terms, it is determined by the number of moles of iodine (I_2) released from oxidizing iodide (I^-) by one mole of chlorine oxidant. Each mole of hypochlorous acid, sodium hypochlorite, or monochloramine can release one mole of iodine. Calcium hypochlorite and dichloramine can release two moles or iodine by every mole of them.

$$\mathrm{NaOCl} + 2\,\mathrm{I}^- + \mathrm{H_2O} \rightarrow \mathrm{I_2} + \mathrm{Cl}^- + \mathrm{Na}^+ + \mathrm{OH}^- \tag{3.1}$$

$$\mathrm{Cl_2} + 2\,\mathrm{I}^- \rightarrow \mathrm{I_2} + 2\,\mathrm{Cl}^- \tag{3.2}$$

$$\mathrm{Ca(OCl)_2} + 4\,\mathrm{I}^- + 2\,\mathrm{H_2O} \rightarrow 2\,\mathrm{I_2} + 2\,\mathrm{Cl}^- + \mathrm{Ca}^{2+} + 4\,\mathrm{OH}^- \tag{3.3}$$

By this convention, the concentrations of all the relevant chlorine species (NaOCl, HOCl, Cl_2, etc.) can all be expressed by mg/L as Cl_2. These species are considered chemically equivalent.

To convert from mg/L back to molar, different molecular weights have to be considered. Take sodium hypochlorite solution with 14% active chlorine (14% as Cl_2) as an example. The density of this NaOCl solution is about 1.2 g/cm^3. NaOCl can release the same moles of iodine as Cl_2, i.e. equivalent to 1 mole of Cl_2 per mole of NaOCl. So 14% times molecular weight of NaOCl (74.44 g/mol) divided by molecular weight of Cl_2 (70.9 g/mol) results in 14.7 w/w% of NaOCl, or 2.37 M. In brief, 1% active chlorine is about 0.141 M of NaOCl solution.

4

Results and Discussion

4.1 Cyclic Voltammetry Results

4.1.1 Platinum wire in H_2SO_4

Cyclic voltammetry (CV) in 0.5 M H_2SO_4 has been well studied. When going from 0.4 V where no reaction happens toward oxidation potential above 0.6 V, platinum surface first experience surface oxidation and then water oxidation. The surface oxidize is reduced in the backward scan from high to low potential. At even lower potential, hydrogen start to adsorb, which is then oxidized and desorb again in forward scan. The region of no reaction is called double layer region, where no charge transfer reaction takes place on the electrode. The complete picture is presented in Figure 4.1. This curve has been used to check the condition of platinum wire after cleaning.

4.1.2 Platinum wire in chlorinated solutions

In this work, CV is conducted in the order of three situations, (1) K_2SO_4, (2) K_2SO_4 and NaOCl, (3) K_2SO_4, NaOCl and urea. This order is used to minimize poisoning effects. Poisoning is the adsorption of unwanted chemicals on the active sites of catalysts and prevents the adsorption of other reactants. For instance, amines groups (including urea), sulfides and thiols are known to poison platinum [32]. CO and CO_2, which are the major products from urea chlorination, as discussed in Chapter 2, also have poisoning effects [33]. Therefore, desorption of CO or CO_2 is hypothesized as the rate-determining step for electrochemical oxidation of urea. The poisoning result can be seen from CV of platinum in Figure 4.2, where urea is added without NaOCl.

Platinum is a good catalyst for water oxidation and reduction. Once its surface is poisoned, it partially loses its catalytic activity for water splitting, resulting in a smaller current. This effect was also noticed by Bunce during electrochemical oxidation of ammonia, possibly from adsorbed atomic nitrogen [34]. Similar effects were also observed on other materials like titanium, iridium and palladium where current got smaller and features got flatten out. Gold and nickel do not exhibit decrease of current by urea [26].

Apart from the poisoning problem, the absence of free chlorine is not common for a normal swimming pool. Also, oxidation of urea by direct electron transfer is slower than by free chlorine reaction as will be discussed in section 4.4. So in the CV work, hypochlorite was always put in before urea. This addition order is also similar to the situation in swimming pools where free chlorine is always present.

Addition method was adopted in CV in various solutions as following steps. First, 0.1 M potassium sulfate solution in the electrochemical cell was prepared. Then, the cell was purged with nitrogen gas for c.a. 15 minutes before tests. After purging, the wires from potentiostat were connected to the electrodes in the cell as in the experimental setup. Then a wide potential window (-0.8 to 2.6 V RHE) was selected for easier observing the evolution of the peaks. When potassium sulfate test had been finished, everything was kept intact except that 2.86 ml hypochlorite (64.4 mM) was added into the cell and stirred for about 30 minutes. Finally, the last step was the addition of 10 mM urea into the solution and waiting for one hour for chlorine to react.

It is clear in Figure 4.3 that the oxidation current for mixture of urea in NaOCl-insufficient situation is more pronounce than that of NaOCl alone. Insufficient free chlorine would keep the reaction in earlier step. From the reaction mechanism by Blatchley et al. [15], the first step, chlorination of urea, is the rate-determining step. Production of final products (chloramines) would be slow if there is no enough free chlorine to further react with chlorourea. In other word, chlorourea or monochloramine can be abundant in the solution and they are easier to oxidize compared to nitrate, chloride or trichloramine. Consequently, the oxidation current is higher. The concentration measurement before start of electrolysis in Figure 4.15 also shows the existence of combined chlorine compared to the case starting with excess chlorine in Figure 4.13. It is also worth noting that the initial mixture curve was measured about 15 minutes after addition of NaOCl. The time was too short to allow chlorine reaction with urea to produce chlorourea and chloramines. Urea possibly blocks the active site in the beginning, so the current appears smaller. Nevertheless, because of the relatively high concentration of chemicals used, observable amount of bubbles could be seen during reaction. There could be very likely a lot of nitrogen and carbon dioxide lost in the air. The gaseous components were not examined in this research.

In the case of excess chlorine, 4.06 ml of NaOCl (90.4 mM) was added. The CV curve after mixing urea looks very different from chlorine-insufficient situation. The oxidizing current is not higher with the addition of urea. The discrepancy between two figures comes from the fact that excess free chlorine can push the reaction toward final products. In other words, mostly NO_3^-, N_2, CO, CO_2, NCl_3 are produced from complete oxidation of urea in the presence of free chlorine. Thus, there exist less chlorinated species which are easier to oxidize as in the chlorine insufficient situation. The concentration measurement in Figure 4.13 also reveals that very little combined chlorine was present in the solution before electrolysis.

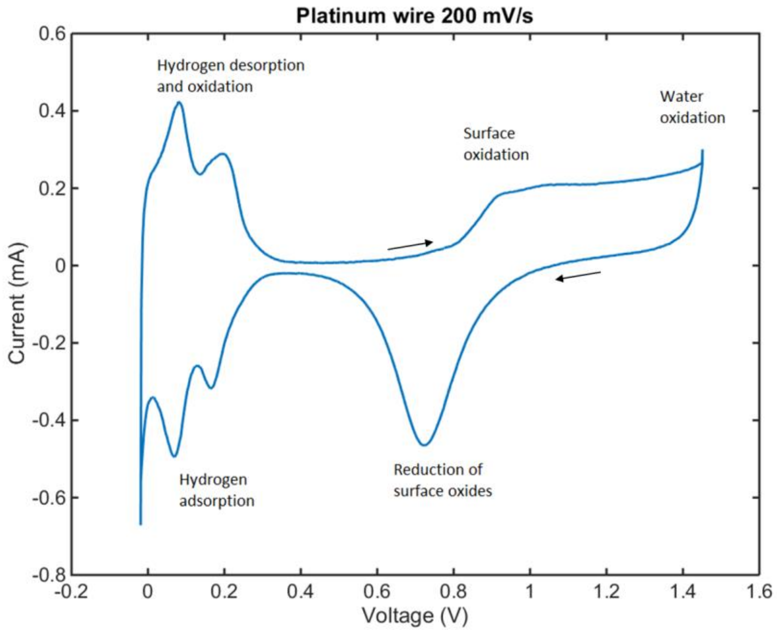

Figure 4.1: Cyclic voltammogram of platinum in 0.5 M sulfuric acid.

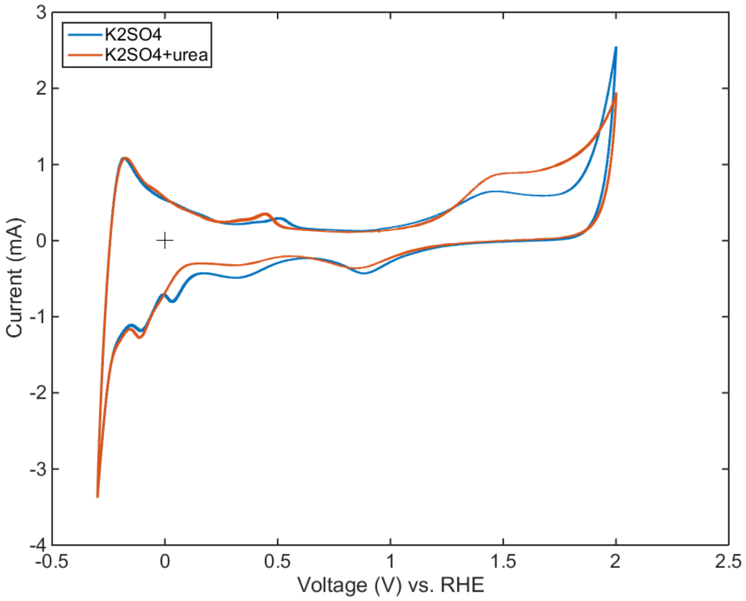

Figure 4.2: CV curve of platinum in 0.1 M K_2SO_4 without urea (blue) and with urea (red) scanning at 100 mV/s.

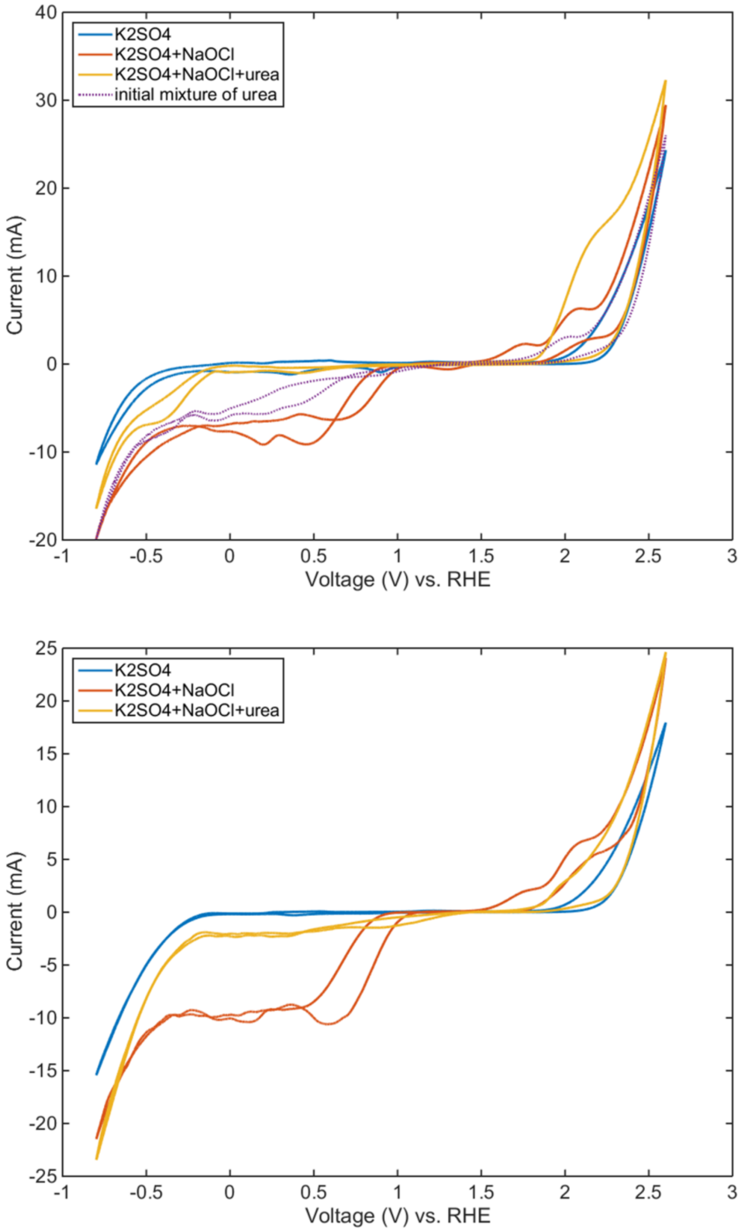

Figure 4.3: Platinum wire CV in K_2SO_4 (blue), addition of NaOCl (red), initial mixture of urea (purple dash) and after an hour (yellow), scanning at 100 mV/s. NaOCl is insufficient in the top figure and excess in the bottom figure.

4.2 Materials Comparison in CV

A variety of metallic materials, gold, nickel, titanium, iridium and palladium, were prepared by evaporation on glass substrate. All the solutions were prepared via a similar method described previously, including 0.1 M K_2SO_4, 64.4 mM NaOCl and 10 mM urea.

4.2.1 Graphite

The diameter of graphite rod was 3 mm, and the immersion depth was about 2 cm. This gave approximately 1.8 cm^2 of surface area, roughly 3 times the surface area of the platinum wire. Graphite electrode looks promising as the current in Figure 4.4 is higher with the presence of urea in NaOCl. This result is similar to the current on platinum electrode.

However, the instability of graphite at oxidizing potential leads to carbon decomposition into CO_2, HCO_3^-, and CO_3^{2-}. The oxidation can be greatly accelerated in the presence of hypochlorite, producing salt and CO_2 [35].

$$\mathrm{C} + 2\,\mathrm{NaOCl} \rightarrow \mathrm{CO_2} + 2\,\mathrm{NaCl} \tag{4.1}$$

This degradation of graphite electrode and its lifetime has to be taken into consideration before anodic oxidation application in water treatment. Graphite was further tested for electrolysis in section 4.4.

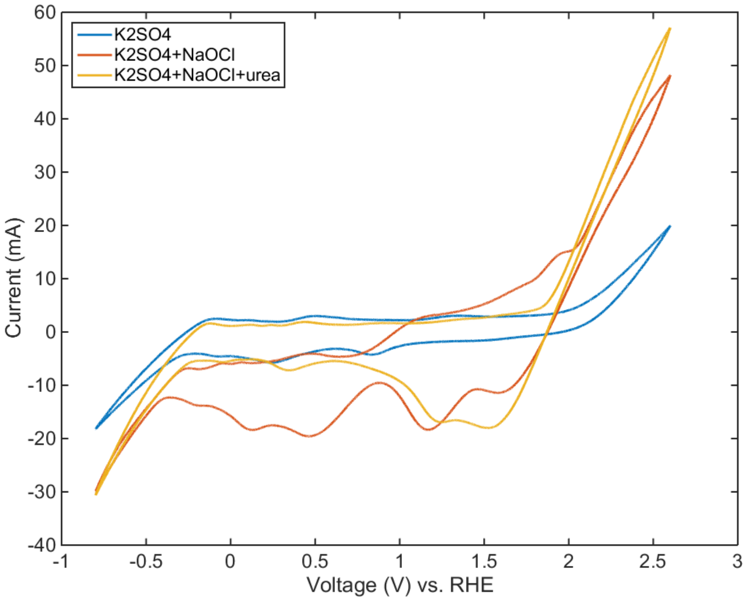

Figure 4.4: Graphite CV in K_2SO_4 (blue), addition of NaOCl (red) and further addition of urea (yellow), scanning at 100 mV/s.

4.2.2 Stainless Steel

A corrosion-resistant stainless steel was chosen for CV testing. From Pourbaix diagram, iron at oxidizing potential near neutral pH forms $Fe_2O_3(s)$ or FeO_4^{2-}. This iron oxidation current is greatly enhanced with addition of NaOCl.

In Figure 4.5, two additional peaks also show up in CV at 1.4 and 1.9 V. The reason could be the increased oxidation of steel by hypochlorite:

$$3\ \mathrm{NaOCl} + \mathrm{Fe} \rightarrow \mathrm{FeCl_3} + \mathrm{NaOH} \rightarrow 2\ \mathrm{Fe(OH)_3} + 3\ \mathrm{NaCl} \tag{4.2}$$

At the anode, hydroxyl group (OH^-) is consumed by oxygen production and $FeCl_3$ is continuously produced. Hence, a yellow stream of $FeCl_3$ was seen generating from anode.

From the same CV curve, it can be observed that current gets much smaller after addition of urea into the solution with NaOCl. This drop in current is partially due to urea poisoning and largely due to the decrease of NaOCl concentration after addition of urea. It is also because chlorourea and chloramines are not effectively oxidized by stainless steel at anode.

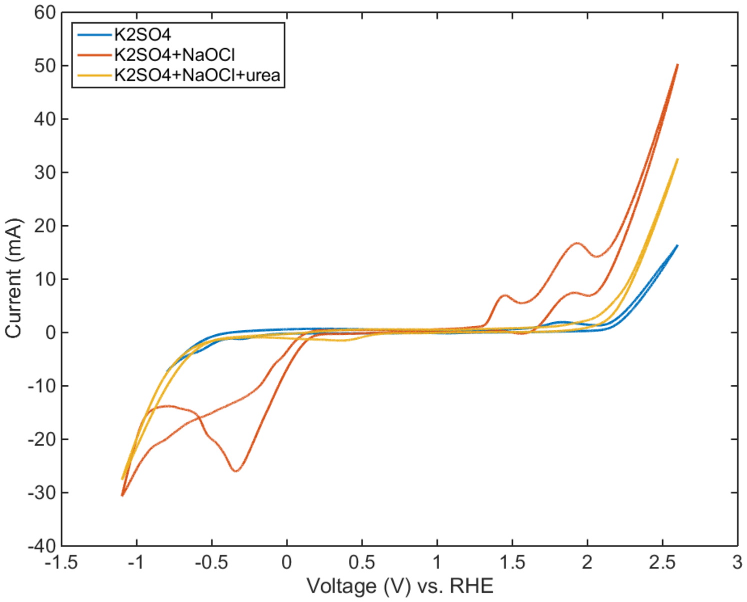

Figure 4.5: Stainless steel CV in K_2SO_4 (blue), addition of NaOCl (red) and further addition of urea (yellow).

4.2.3 FTO

Fluorine-doped tin oxide (FTO) was considered as good candidate for anodic materials since it was just a thin layer of conductive oxide on top of glass. Further anodic oxidation on oxides was supposedly minimized. The stability of FTO can be proved by CV measurement in Figure 4.6, where pure K_2SO_4 solution yields very low current before water splitting. Addition of NaOCl is mainly redox reactions of NaOCl itself. Further addition of urea in chlorine-containing solution decreases the overall current, suggesting that FTO is not a good candidate material.

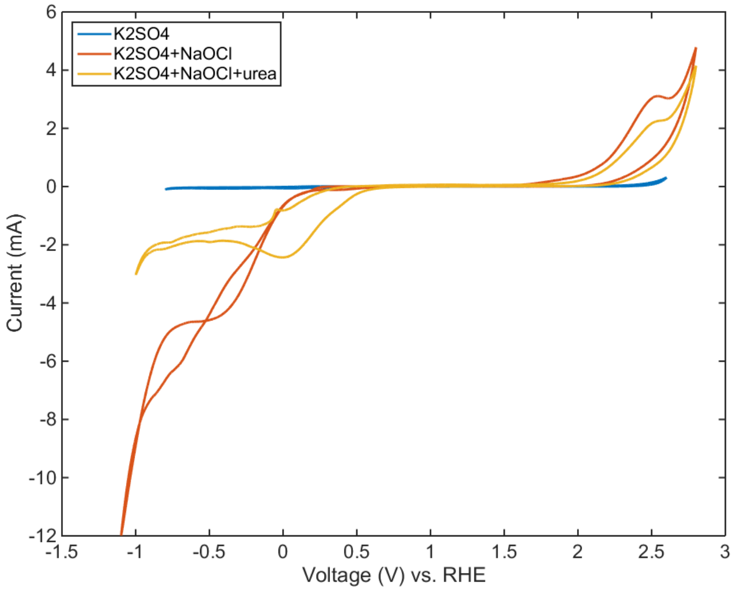

Figure 4.6: FTO CV in K_2SO_4 (blue), addition of NaOCl (red) and further addition of urea (yellow).

4.2.4 Gold

The gold wire had a diameter of 0.5 mm and an immersion depth of about 3 cm. Cyclic voltammogram in Figure 4.7 of gold shows very interesting characteristics for the case of urea and NaOCl. The abrupt oxidation peak appears around 1.9 V, which is not observed in other materials. The current does not sustain if potential if fixed at 1.9 V. To investigate this phenomenon a bit more, similar CV condition was conducted by fixing higher potential at 2.3 V (vs. RHE) but varying the lower potential from -0.6 to 0.7 V. The result indicates that only when potential is cycled below 0.9V can this clear oxidation peak appear. The reason is not understood yet.

Chlorine can react with gold forming $AuCl_3$ or $AuCl_4^-$, both of which are highly soluble in water. It was a popular method to extract gold from ore before the invention of cyanide (CN^-) method. The reaction is simply expressed as [36]:

$$2\,\mathrm{Au} + 3\,\mathrm{Cl_2} \rightarrow 2\,\mathrm{AuCl_{3(aq)}} \xrightarrow{\mathrm{Cl^-}} \mathrm{AuCl^-_{4(aq)}} \tag{4.3}$$

$$2\,\mathrm{Au} + 6\,\mathrm{H^+} + 3\,\mathrm{ClO^-} + 5\,\mathrm{Cl^-} \rightarrow 2\,\mathrm{AuCl^-_{4(aq)}} + 3\,\mathrm{H_2O} \tag{4.4}$$

The locally acidic environment near anode from oxygen production can enhance the rate of formation for gold chloride. The presence of additional chloride from urea and chlorine reaction can intensify the dissolution of gold by developing tetrachloroaurate. However, this chlorine reaction on gold is passivated by gold oxide at higher potential, so the current drops, as the discussion by Michael in the past [37]. The phenomena in Figure 4.8 is probably because when cycling back to lower potential (<1.0 V) the surface oxide is reduced and gold is ready to be oxidized again.

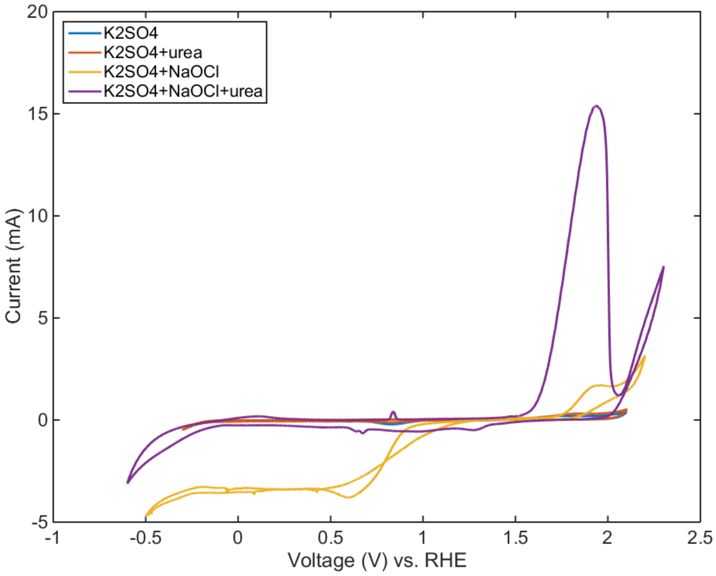

Figure 4.7: Cyclic voltammogram of gold wire in solutions of K_2SO_4 (blue) and addition of urea (red), addition of NaOCl (yellow) and addition of both urea and NaOCl (purple) scanning at 100 mV/s.

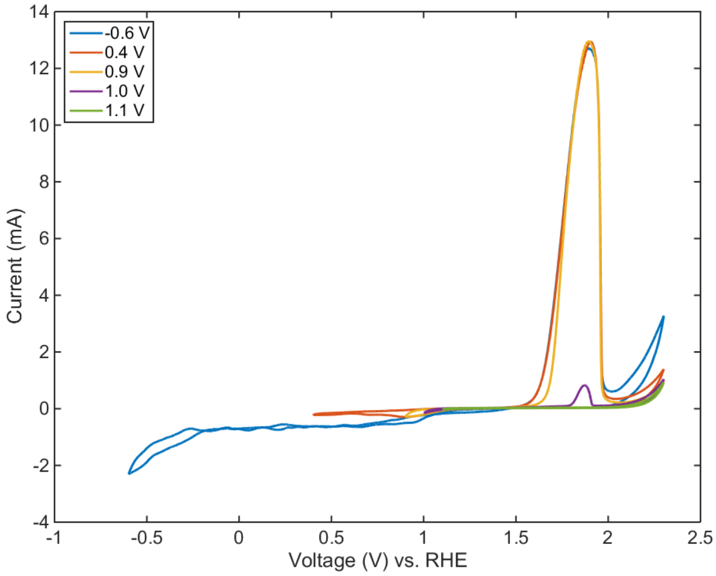

Figure 4.8: Cyclic voltammogram of gold wire in K_2SO_4, urea and NaOCl cycled to various lower potentials, -0.6 V (blue), 0.4 V (red), 0.9 V (yellow), 1.0 V (purple) and 1.1 V (green). Scanning rate is 100 mV/s.

4.2.5 Titanium

A few metals inclusive of titanium (Ti), palladium (Pd), iridium (Ir), and nickel (Ni) films were tested for CV measurement in 0.5 M K_2SO_4 and 10 mM urea as in Figure 4.9. Titanium oxide forms on the surface of titanium metal at oxidizing environment. The oxide is insulating and passivates the surface, preventing the interior from further oxidation. Consequently, the current is very small on titanium anode.

4.2.6 Palladium

Palladium shows very similar behavior as platinum. In Figure 4.9, palladium also appears to be poisoned by urea as well. By virtue of the similarity to platinum, Pd was not further investigated in this research.

4.2.7 Iridium

Iridium and ruthenium, including their oxides, were reported to be good catalysts for generation of free chlorine through electrolysis of chloride-containing water [38]. However, their metal forms are unstable from Pourbaix diagram, and they quickly buildup oxide/hydroxide layers on top or get corroded in cyclic voltammetry scan. Repetitive cycling between reducing and oxidizing potentials continuously builds up and peels off the oxide on the surface. The 50 nm iridium film actually vanish very quickly in CV experiment. From Juodkazyte's work, iridium has the tendency of building up thick oxide layer by oxidizing at 1.2 V (vs. RHE) or higher [39].

Another problem is still the obvious decline in oxidation current due to possible poisoning. As a result, electrolysis with iridium film was not considered.

$$\mathrm{Ir} + 3\,\mathrm{H_2O} \rightleftharpoons \mathrm{Ir(OH)_3} + 3\,\mathrm{H^+} + 3\,\mathrm{e^-} \tag{4.5}$$

$$\mathrm{Ir} + (\mathrm{n}+2)\mathrm{H_2O} \rightleftharpoons \mathrm{IrO_2}\cdot \mathrm{nH_2O} + 4\,\mathrm{H^+} + 4\,\mathrm{e^-} \tag{4.6}$$

4.2.8 Nickel

Nickel clearly shows catalytic activity for urea. The reason could be the formation of nickel hydroxide during anodic oxidation, and it then serves as a catalyst for conversion of urea into nitrogen and hydrogen as discussed in section 2.4. Boggs have demonstrated treating 0.33 M urea in 5 M KOH and found nickel as the only material exhibiting catalyzing activity for urea by examining cyclic voltammetry properties [26]. PtIr, Pt and Rh do not have similar properties. Instead, the oxidation currents drop for other materials in the same solution.

However, for swimming pool application, the pH is kept constant around 7. Nickel is very unstable at neutral solution, and only in alkaline condition can it form $Ni(OH)_2$. So, nickel was also disregarded.

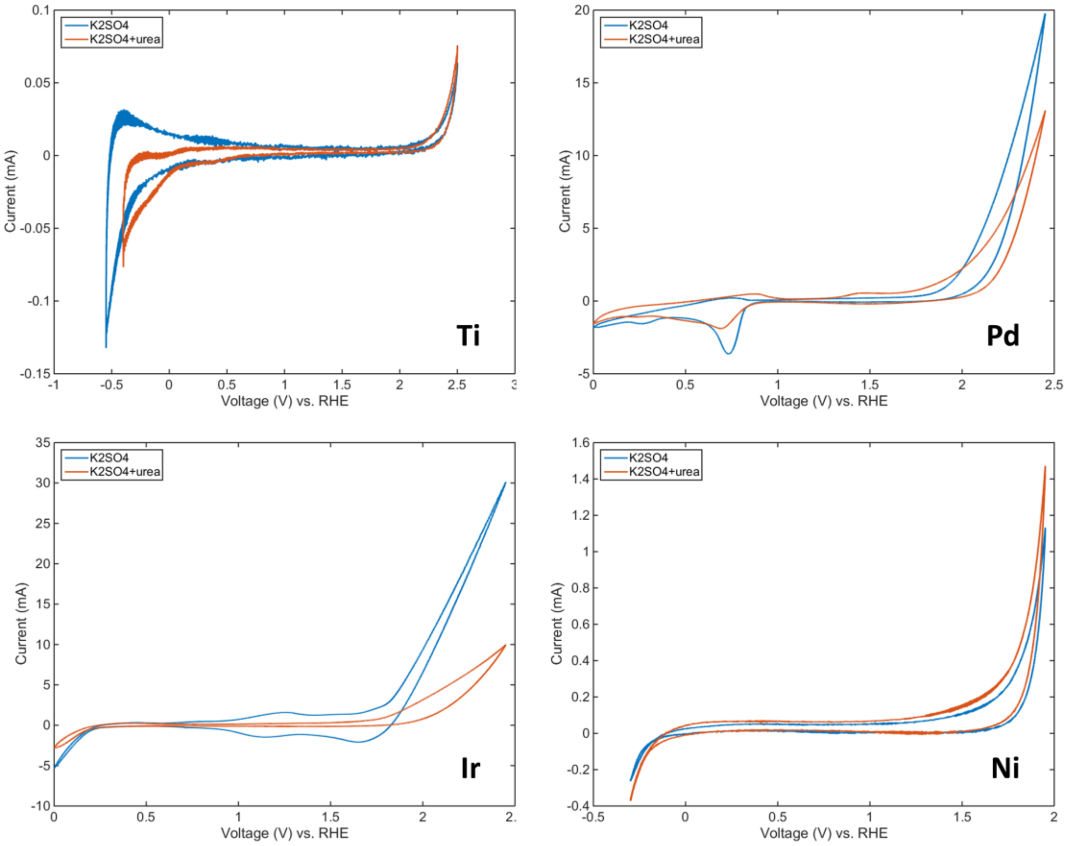

Figure 4.9: Cyclic voltammogram of titanium, palladium, iridium and nickel films in solutions of K_2SO_4 (blue) and addition of urea (red) scanning at 100 mV/s.

4.3 Pulse Voltage Probing

The pulsing principles were sketched in Chapter 2 and Figure 2.4. To determine the voltage for later pulse electrolysis, a test for probing required pulse voltage was done by fixing the higher potential at 2.6 V (vs. RHE) for 30 seconds and varying the lower potential from 2.5 to -0.8 V for 5 seconds. Each cycle had 35 seconds (0.58 minute) and each voltage step was repeated 30 times (1050 sec, 17.5 minutes). Only the first voltage was repeated 40 times.

The higher voltage was chosen based on the cyclic voltammetry results that a minimum of 2.6 was needed to generate enough current. Choosing an even higher potential can increase the rate of electrolysis but also loss more energy to water splitting. The duration time of lower potential was chosen for easier observation of changes and was not optimized for best efficiency in this work. As discussed in the general electrochemistry, constant voltage/current electrolysis leads to buildup of diffusion layer. By having the polarity altered, this diffusion controlled region, also called depletion zone, can be diminished and the current can regenerate again.

The sudden switch of polarity would bring about capacitive discharge in a short time, creating a current spike in the beginning of the switch as in Figure 2.4. The current-time plots have removed these spikes by selecting the current at the end of 30-second oxidation.

Platinum wire was selected for most of the electrolysis experiments due to its excellent stability and ease of cleaning. The probing result with platinum in Figure 4.10 indicates the need to go below 0.2 V to regenerate enough current. Note that the current at 2.5 V is not representative, because the initial current is always high when there is a sudden increase of voltage. The current would slowly decrease and reach a more steady state after two or three hours. What we can see from the figure is that the current is not regenerated and is decreasing.

Same method was also applied on graphite in Figure 4.11, and it exhibited a bit different behavior so that the potential is as low as 0.4 V is enough. Voltage below 0 V (vs. RHE) would evolve a lot of hydrogen product in theory and was consequently avoided.

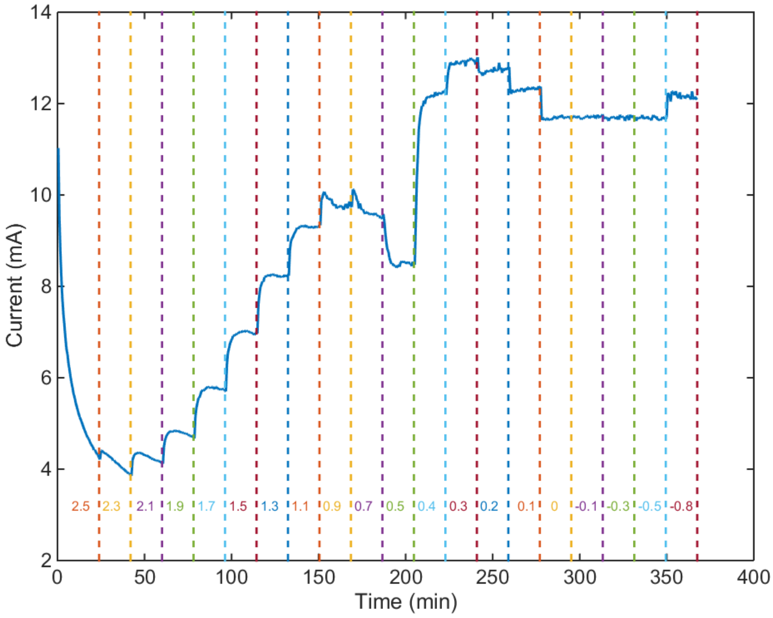

Figure 4.10: Platinum wire pulse voltage probing varying lower potential from 2.5 to -0.8 V (vs. RHE). The numbers between the lines are the lower potential values expressed in volts vs. RHE.

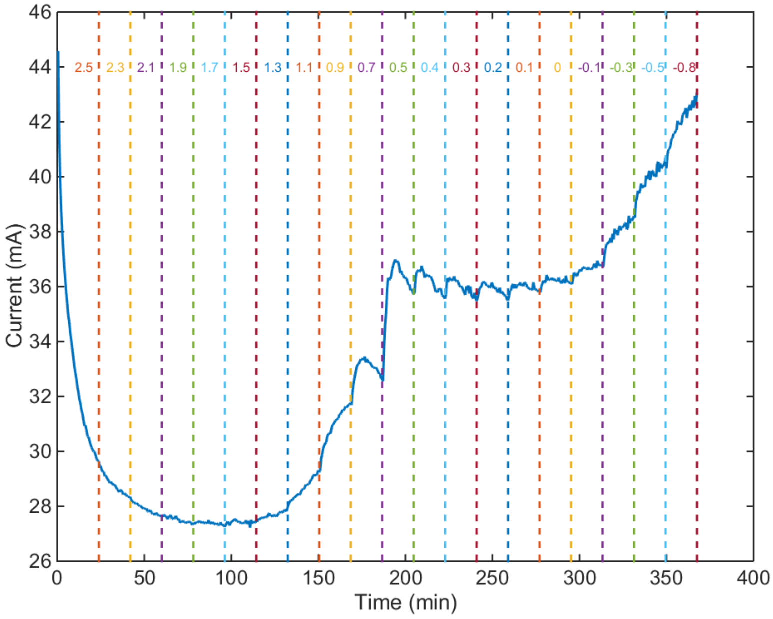

Figure 4.11: Graphite pulse voltage probing varying lower potential from 2.5 to -0.8 V (vs. RHE). The numbers between the lines are the lower potential values expressed in volts vs. RHE.

4.4 Electrolysis Results

For better comparison between different results, the displayed concentrations are either normalized by the concentration at the start of electrolysis (C_S) of the concentration at time zero (C_0). The difference between total chlorine and free chlorine is the combined chlorine, i.e. chloramines (NH_2Cl, $NHCl_2$, NCl_3). All of the electrolyte was 0.1 M K_2SO_4.

4.4.1 Platinum

Platinum was so far the only stable material tested for the specified experimental conditions. The value of uncompensated resistance was about 4 ohms and the open circuit voltage was about 0.4 V. The iR drop during electrolysis was considered negligible and not taken into account. Based on the pulse voltage probing results, a higher potential at 2.6 V for 30 seconds and a lower potential at 0.2 V (vs. RHE) for 2 seconds were chosen. It had been applied for all the electrolysis experiments.

Direct electrolysis of urea

Direct oxidation through electron transfer from urea to Pt electrode was examined in the first place. The electrolysis was carried out under fixed current (100 mA) with platinum, corresponding to a current density of 68 mA/cm^2 and voltage about 3.7 V. Pulse method was not adopted in this experiment. The starting concentration of urea was 10 mM, and 0.1 M K_2SO_4 was added as electrolyte. Nevertheless, the decrease of urea concentration at such high current is still very slow, approximately 5% decrease per hour from Figure 4.12. The current efficiency calculated by reaction (2.32) is less than 10%. This implies the direct oxidation of urea is possible yet inefficient. It is advantageous to have free chlorine in the water to react with urea since the reaction between chlorine and urea is relatively fast compared to direct oxidation of urea.

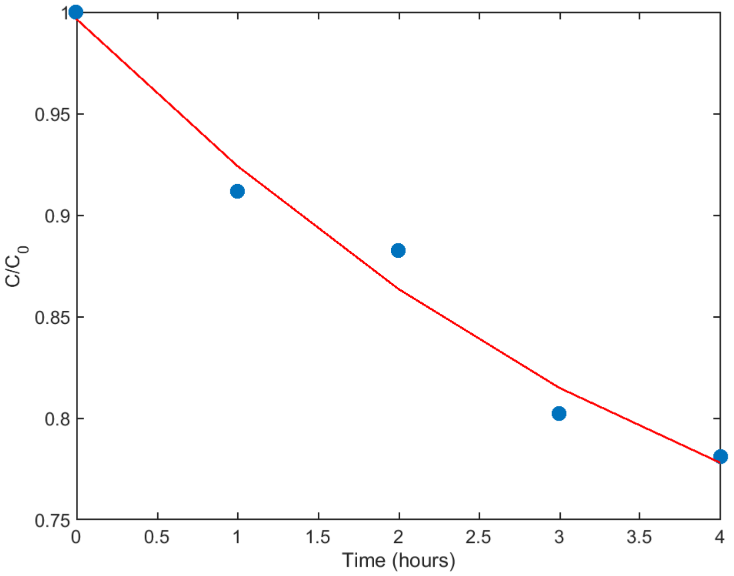

Figure 4.12: Direct urea electrolysis. Concentrations normalized by the initial concentration C_0.

Excess free chlorine condition

Direct oxidation was not efficient, so indirect oxidation was examined. The electrolysis was performed with initial concentrations of 0.1 M K_2SO_4, 10 mM urea and 90.4 mM NaOCl. The timer started right after the addition of 4.06 ml NaOCl into the reaction vessel. The sampling was done by taking 50 μL of the solution from the cell and diluting it to 10 ml in a vial. That was equal to 200X dilution of the original concentrations. The sampling decreased the bulk volume by only 0.05% so that variation in volume neglected. The concentration measurement was accomplished by DPD chlorine method, accompanied with UV-vis spectrometer as described in experimental section. Too low concentration of chlorine makes the measurement difficult and suffers from variations.

The results of electrolysis are in Figure 4.13 and Figure 4.14. Excess of free chlorine implies most of the nitrogen containing compounds would have been converted to nitrate after 3 hours of reaction. Nitrogen is assumed to be less since high chlorine to urea ratio would promote higher oxidation state. The amount of gaseous products, N_2, NCl_3, and CO_2 was not determined in this study, but a clearly visible amount of bubbles were seen generating in the solution. The other major chemical remained in the solution was the chloride ions, as discussed earlier in the reaction mechanism [2]. As a result, chloride is believed to be the major chemical that is being oxidized during electrolysis. NCl_3 is considered as the major reaction intermediate and byproduct, however it could have escaped a lot as gas. Therefore, the amount of increase is only about 50% in this case. The increase stops when most of the chloride is consumed. Note that there were almost no chloramines (the difference between total and free chlorine) left in the solution from the beginning, meaning that little increase of free chlorine was from chloramine oxidation.

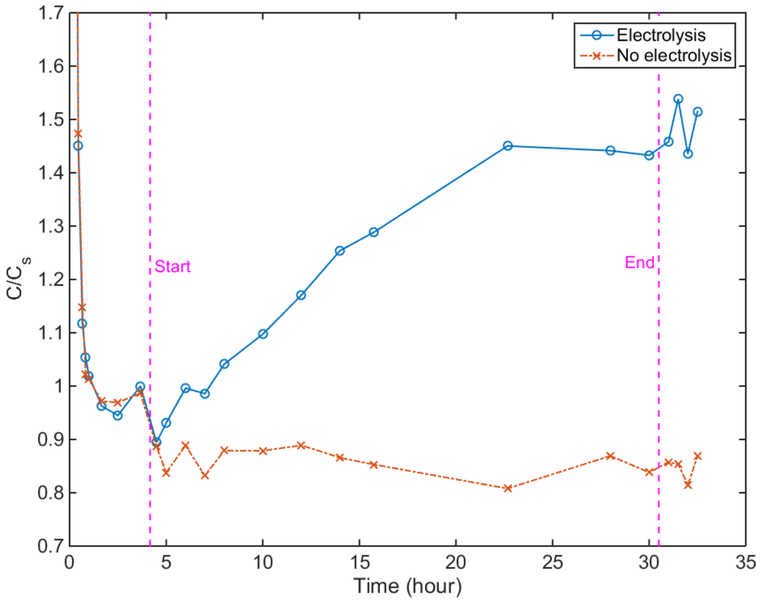

Figure 4.13: Electrolysis with platinum wire as electrode. Free chlorine concentrations with and without electrolysis were measured. Concentrations were normalized by the free chlorine concentration at the start of electrolysis C_S.

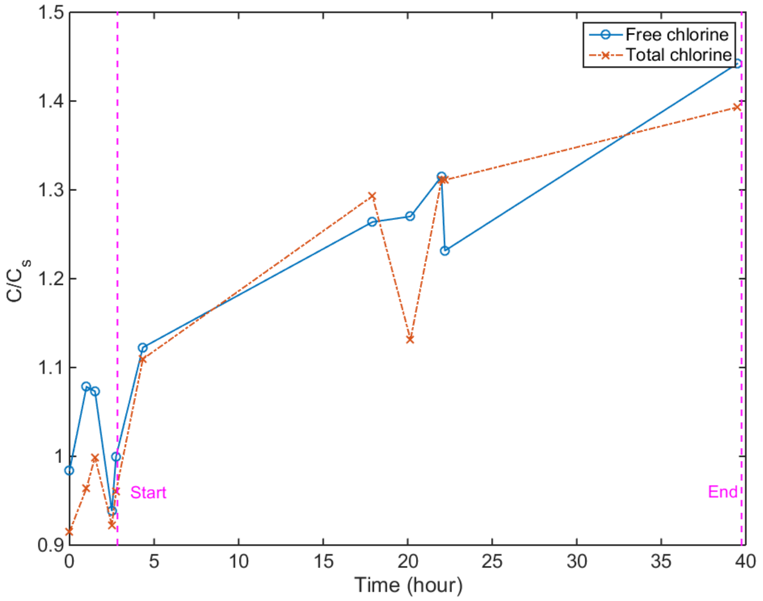

Figure 4.14: Electrolysis with platinum wire as electrode. Free and total chlorine concentrations were measured as a function of time.

Insufficient free chlorine condition

Seeing that excess free chlorine leave very little chloramine for oxidation, the condition with insufficient free chlorine was conducted. If the free chlorine drops to negligible concentration (<100μM) compared to the original concentration of 64.4 mM, it is considered insufficient. The result is exhibited in Figure 4.15.

From the chlorine-urea reaction mechanism in Chapter 2, products from the electrolysis include NH_4^+, NO_3^-, NH_2Cl, $NHCl_2$, NCl_3, n-chlorourea and Cl^-. Chloramines are considered as reaction intermediates during chlorination or speciation from trichloramine and can further undergo disproportionation to N_2 or NO_3^- [15]. It can be proved by the detection of chloramines in the experiments. The presence of chloramines means the incomplete reaction by NaOCl and thus chlorourea can also be present. Therefore the anodic reaction could have oxidized chlorourea and chloramines indirectly via generated free chlorine by equation (2.25). The resulting increase of free concentration is very impressive, more than 200 times higher compared to the concentration at the start of electrolysis.

Excess urea condition

Electrolysis in 10 mM urea, 0.1 M K_2SO_4 and 13 mM NaOCl was also demonstrated in Figure 4.16. There were little chlorourea and chloramines for oxidation. The urea concentration only decreases about 10% after electrolysis for 20 hours. The decrease was mainly from regenerated chlorine. This result further proves that direct oxidation of urea is not a very efficient process.

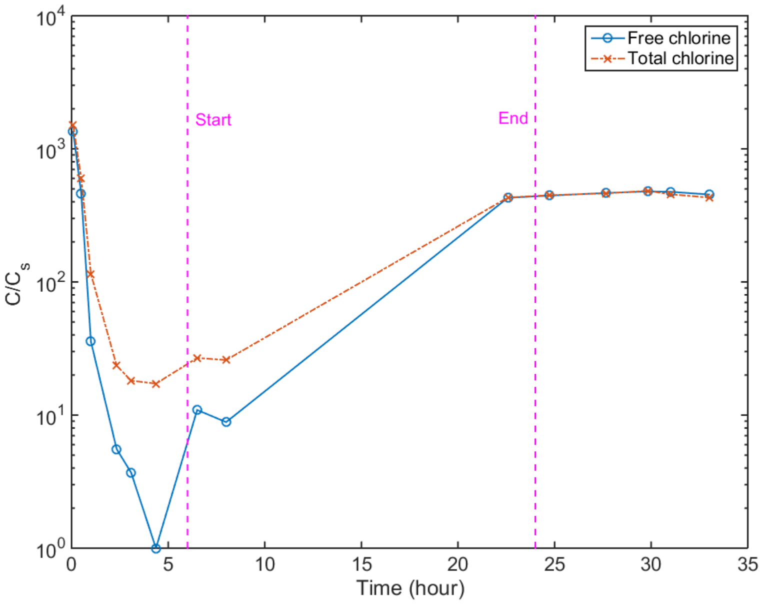

Figure 4.15: Free and total chlorine concentration under insufficient chlorine condition. Free chlorine dropped to a very low value (a few µM) before start of electrolysis; while total chlorine remained at a higher concentration before start.

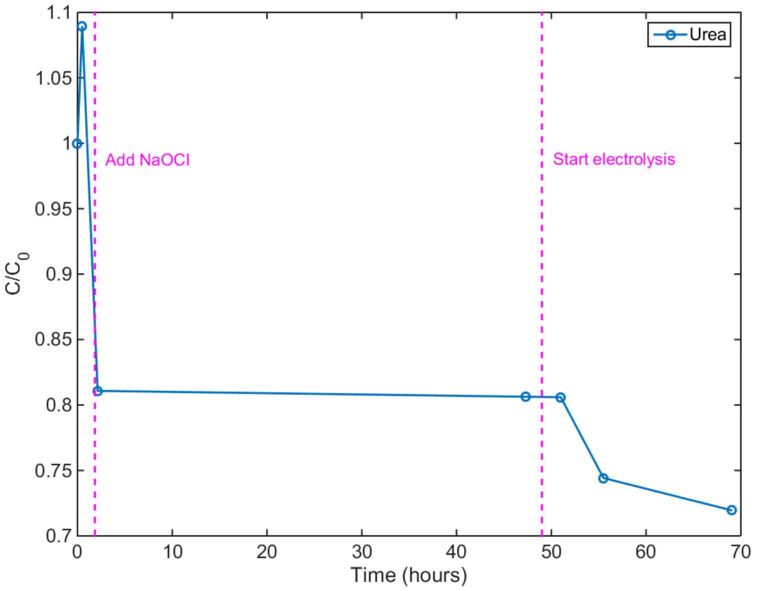

Figure 4.16: Platinum wire electrolysis of excess urea with a little NaOCl. Data normalized by starting concentration at time zero (C_0). The time was recorded by the instant of sampling.

NaOCl Electrolysis

One more thing to check is whether electrolysis with only NaOCl can have similar increase of free concentration. Pulse electrolysis of 90.4 mM NaOCl in 0.1 M K_2SO_4 was also done as a comparison. In Figure 4.17 the decrease of free chlorine concentration during electrolysis can be ascribed to the oxidation reaction of free chlorine (Cl_2 and OCl^-) creating chlorate (ClO^{3-}) [40]. There was no Cl^- left from urea chlorination. Reduction at cathode was believed to be secondary since the potential at counter was not very reductive before 20 hours. After 20 hours the oxidation and reduction processes slowly reached equilibrium on working and counter. ClO^{3-} was the major byproduct of free chlorine oxidation while not detected by our DPD chlorine method.

Pulse Electrolysis in H-Cell

The reaction happening on the working electrode is worth investigating. H-cell configuration allows separation of reaction species from counter electrode compartment. Counter compartment was graphite rod with 45 ml of 0.1 M K_2SO_4. Working compartment was platinum wire with 50 ml of 0.1 M K_2SO_4, 10 mM urea and 90.4 mM NaOCl. Reference compartment was Hg/Hg_2SO_4 reference electrode with 5 ml 0.1 M K_2SO_4.

The result in Figure 4.18 shows that free chlorine regenerated fast in the beginning (50% per hour) but kept decreasing afterward, even after turning off potentiostat. One of the reasons was that chlorourea was prevented from reduction at cathode, so the initial increase of free chlorine was faster than in single-compartment cell. Besides, presumably acidic environment at anode also kept the chlorourea from decomposition.

Nevertheless, free chlorine concentration did not keep on increasing. The reversal was very likely owing to the further oxidation of free chlorine into chlorate, which became non-detectable by DPD chlorine approach. In a single compartment two major equilibria were reached. One was between the reduction of chlorate into hypochlorite at the cathode and oxidation of hypochlorite into chlorate at the anode. The other was between anodic oxidation of chloride and cathodic reduction of hypochlorite [41].

$$\mathrm{ClO^- + 3\,H_2O \rightleftarrows 2\,ClO_3^- + 4\,Cl^- + 6\,H^+ + \tfrac{3}{2}\,O_2 + 6\,e^-} \tag{4.7}$$

$$\mathrm{ClO^- + H_2O + 2\,e^- \rightleftarrows Cl^- + 2\,OH^-} \tag{4.8}$$

$$\mathrm{3\,ClO^- \rightleftharpoons ClO_3^- + 2\,Cl^-} \tag{4.9}$$

In two-compartment H-cell, the above balance was broken. Consequently, the cell ended up with continuous decrease of free chlorine after most of the chloride had been oxidized as free chlorine. This explanation is also validated by the NaOCl electrolysis in the next part. All these reactions were also competing with water splitting, so decrease of hydrogen and oxygen bubbles was expected when most of electron transfers occur for the above equations.

The further decrease of chlorine concentration after stopping electrolysis was because the depletion of chloride shifts the equilibrium and ClO^- decomposed into ClO_3^- and Cl^- by Le

Chatelier's principle. In single cell, there is usually more chloride left from reduction at cathode.

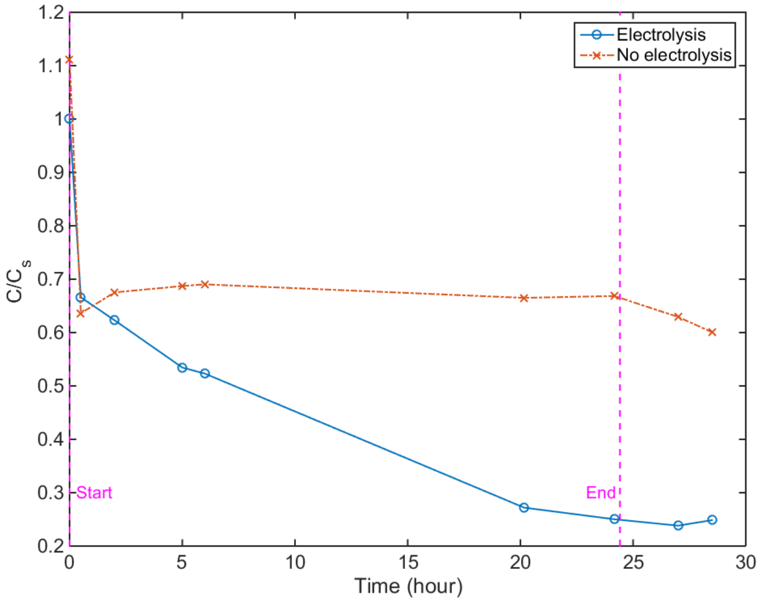

Figure 4.17: Platinum wire electrolysis of NaOCl without urea in a normal cell, measuring free chlorine concentrations with electrolysis (-o-) and without electrolysis (-x-).

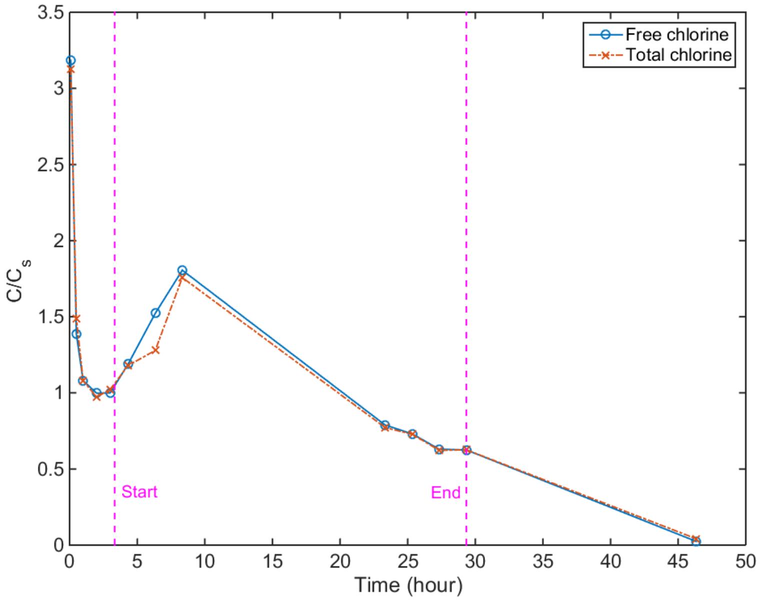

Figure 4.18: Platinum wire electrolysis with urea and excess free chlorine in H-cell, measuring free chlorine (-o-) and total chlorine (-x-).

Counter electrode potential

The potential on the working electrode had been kept at 2.6 V during 30 seconds of oxidation pulse for pulse electrolysis. The potential on counter electrode was also recorded as a function of time during electrolysis in single cell setup to understand the reduction at counter. The results in excess NaOCl with and without urea are shown in Figure 4.19. Curves are plotted by fifth degree polynomial fitting to the raw data.

The result shows that the CE potential could get lower than -0.4 V (vs. RHE), which is lower than the onset potential of hypochlorite reduction from CV in Figure 4.3. Therefore, a lot of NaOCl could have been reduced at cathode and then re-oxidized at anode again. This CE potential results support our previous hypothesis that there are chlorine or DBPs reduced at the cathode.

The CE potential during electrolysis of NaOCl alone did not go very negative in the first 10 hours. Mostly hydrogen evolution was taking place, and the reduction of hypochlorite was minimal. However, this voltage slowly got lower afterward, approaching the case with urea. The increasing amount of chlorate reduction was assumed responsible for the gradual change.

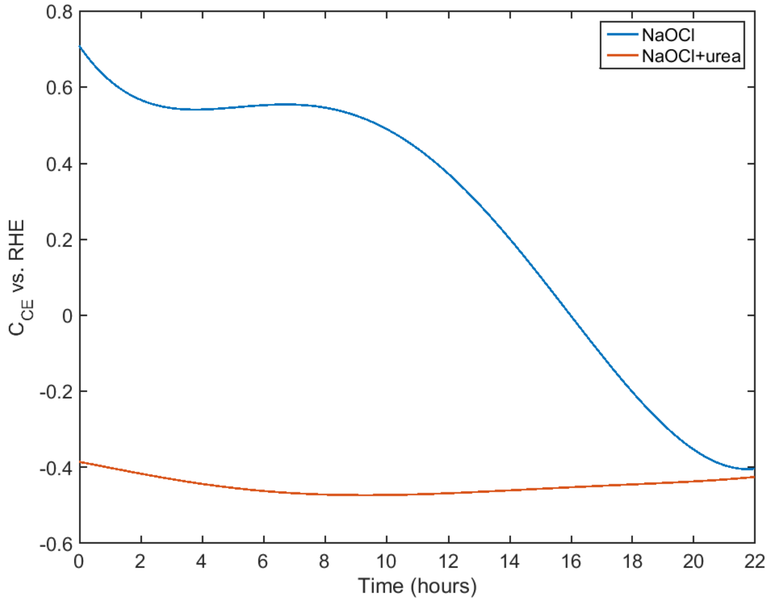

Figure 4.19: Potential on counter electrode during electrolysis in NaOCl alone (blue) and with addition of urea (red).

<u>pH</u>

The pH went from approximately 7.5 to 9 during the electrolysis of urea in excess chlorine due to the competing reaction of hydroxyl group at anode and the hydrogen production on the cathode. See equation (4.10) to (4.14). At this slightly alkaline pH most of the free chlorine will be OCl^- and less Cl_2 and HOCl will be available. The chlorination of urea has thus a slow reaction rate.

Summary of reactions

Based on the above-mentioned analysis and theory of chlorination, the mechanisms of electrochemical oxidation at anode are proposed as follows:

$$2\ Cl^- \rightarrow Cl_2 + 2\ e^- \tag{4.10}$$

$$2\ NH_2Cl + 6\ OH^- \rightarrow Cl_2 + 5\ H_2 + 2\ NO_3^- + 4\ e^- \tag{4.11}$$

$$2\ NHCl_2 + 6\ OH^- \rightarrow 2\ Cl_2 + 4\ H_2 + 2\ NO_3^- + 4\ e^- \tag{4.12}$$

$$2\ NCl_3 + 6\ OH^- \rightarrow 3\ Cl_2 + H_2 + 2\ NO_3^- + 4\ e^- \tag{4.13}$$

$$2\ OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2\ e^- \tag{4.14}$$

Chlorourea would react with hypochlorite, releasing trichloramine, and then further oxidized to form chlorine. Formation of nitrate instead of nitrogen is expected for high Cl to N ratio. Note that the amount of chlorine produced from chloramines depends on concentration, energy barrier and free energy, all of which have not been fully understood.

4.4.2 Graphite

The result of graphite electrolysis in Figure 4.20 says that there are very little chloramines, and, unlike platinum, pulse electrolysis with graphite as working electrode actually leads to decrease of both free and total chlorine concentration.

This can be explained by the increased surface area of carbon that can adsorb chlorine and combined chlorine. It is the basic reason how the activated carbon works. For eliminating chlorine, it is generally known as dechlorination. In the literature, it was shown that activated carbon (C*) can have following reactions with chlorine [42]:

$$C + 2\ Cl_2 + 2\ H_2O \rightarrow 4\ HCl + CO_2 \tag{4.15}$$

Graphite (always with surface hydrogen) has the following reactions.

$$Cl_2 + HC^*C^*H \rightarrow 2\ HCl_{(g)} + C^* = C^* \tag{4.16}$$

$$Cl_2 + C^*H \rightarrow HCl_{(g)} + ClC^* \tag{4.17}$$

For hypochlorite, the reaction is first adsorption and then decomposition [43].

$$C^* + HOCl \rightleftharpoons CHOCl^* \rightarrow CO^* + HCl \tag{4.18}$$

Even worse, combined chlorine reaction rate is much slower than that of free chlorine [2].

$$C_{(s)} + NH_2Cl + H_2O \rightarrow CO_{(s)} + NH_4^+ + Cl^- \tag{4.19}$$

$$CO + 2\ NH_2Cl \rightarrow C_{(s)} + N_2 + 2\ H^+ + 2\ Cl^- + H_2O \tag{4.20}$$

$$C_{(s)} + 2\,NHCl_2 + H_2O \rightarrow CO_{(s)} + N_2 + 4\,HCl \qquad (4.21)$$

After the electrolysis, a yellowish color was also observed in the solution (inset in Figure 4.20). The color is from oxidation activities on the anode that produce graphite oxides and color the solution yellow. The apparent increase in roughness is likely due to chlorine-carbon reaction accompanied by the generation of oxygen bubbles.

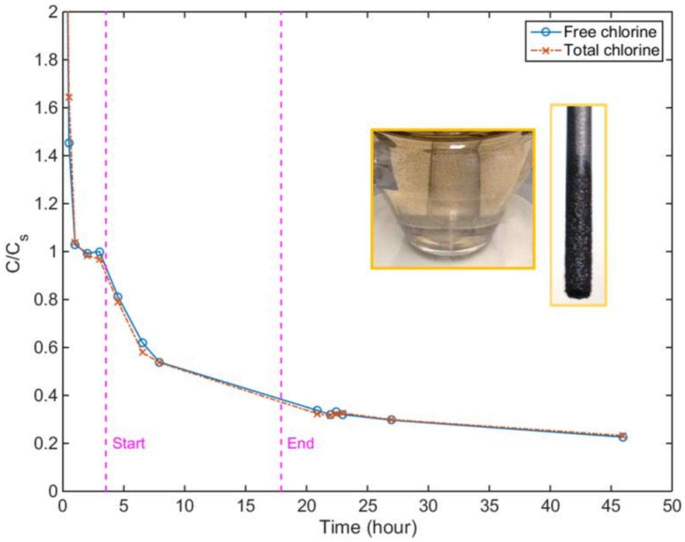

Figure 4.20: Free and total chlorine concentration after electrolysis with graphite rod. The inset photos show the solution (left) and the morphology of graphite rod (right) after electrolysis.

5

Conclusion and Outlook

The mechanism for electrochemical oxidation of DBPs have been studied. A few electrode materials were tested by CV in this work, and platinum wire was chosen for further pulse electrolysis experiments owing to its exceptional stability. Several cases with different initial chlorine concentrations were carried out for pulse electrolysis, including excess free chlorine condition, insufficient free chlorine condition, urea excess condition and urea-free condition. First, the excess free chlorine in the form of Cl_2 would facilitate the degradation of urea. Thus the increase of free chlorine was little. Second, insufficient free chlorine can leave chlorourea and chloramines in the solution and the resulting increase of free chlorine is high. DBPs also decreased during pulse electrolysis process. Third, electrolysis of NaOCl alone did not give rise to an increase. Last but not least, direct anodic oxidation of urea was not very efficient.

The increase of free chlorine is because of oxidation of chloride, which is the major product from reaction between urea and free chlorine. The mechanism of electrochemical oxidation has been proposed.

Nevertheless, this research did not provide straightforward results from trichloramine in water. It is possible to measure trichloramine in water by instrument such as membrane introduction mass spectrometry (MIMS). Direct measurement will provide a stronger evidence for the effect of electrolysis. Measurement of such DBP gaseous components as trichloramine by gas chromatography (GC) or quadrupole mass spectrometer (QMS) during electrolysis is also a topic worth investigating. After that, a more detailed study of electrochemical oxidation mechanism has to be established. In addition to the materials tested in this research, recent research has also focused on the use of mixed metals/metal oxides as anodic electrode. Choosing a suitable catalyst would greatly enhance the efficiency of chlorine conversion and save more energy.

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