Electrochemical Reduction of Hexavalent Chromium in Acetonitrile using Glassy Carbon Electrodes

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ELECTROCHEMICAL REDUCTION OF HEXAVALENT CHROMIUM IN ACETONITRILE USING GLASSY CARBON ELECTRODES

A Thesis

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Master of Science in

The Department of Chemistry

by

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B.Tech., Ladoke Akintola University of Technology, 2010
M.Sc., Obafemi Awolowo University, 2016
August 2021
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Abstract

Hexavalent chromium Cr(VI), a form of chromium mainly generated through industrial processes, has attracted great research interests due to its severe toxicity to biological systems. A common way to remove hexavalent chromium from industrial wastes is through reduction to the non-toxic trivalent state. To this end, methods such as chemical reduction, chemical precipitation and coagulation have been used. However, these methods are limited by poor removal efficiency, formation of secondary pollutants (sludge), and are mostly applicable to aqueous solutions. Recently, electrochemical methods have been investigated for reducing hexavalent chromium, but there is a lack of data on the reduction of hexavalent chromium in nonaqueous media. This is a challenge considering the possibility of Cr(VI)-contaminated nonaqueous industrial wastes ending up in water bodies. Therefore, it is crucial to develop methods of treating such wastes before disposal. In this research, an electrochemical method that involves the use of a nonaqueous solvent is presented. Using glassy carbon electrodes and acetonitrile-based electrolyte, a reproducible method of collecting data was established. With the aim of achieving an energy-efficient reduction and making the reduction process electrocatalytic, the effect of Brønsted acids on the reduction process was investigated. In addition, the process of finding suitable electrocatalysts was initiated. Results obtained show reproducible response of glassy carbon electrodes toward hexavalent chromium in acetonitrile and that Cr(VI) reduction proceeds via proton-coupled electron transfer processes.
Chapter 1. Introduction

Pollution of the environment by heavy metals poses a significant threat to life and the environment due to their toxic effects at concentrations above permissible levels. Industrial processes have been identified as the major sources of heavy metals, where heavy metals from improperly handled waste find their way to ground water systems, resulting in the contamination of drinking water. Among these heavy metal contaminants is chromium. Although chromium exists in many oxidation states, the environmentally and commercially relevant states are the 0, +3 and +6 oxidation states. The toxicity of chromium depends on its oxidation state; Cr(0) and Cr(III) at moderate concentrations are not considered threats to life or the environment. Hexavalent chromium, on the other hand, is highly toxic and can have carcinogenic effects on biological systems. Cr(VI) is generated mainly through anthropogenic processes and is used in applications such as: electroplating, leather tanning, wood preservation, pigment production, and metal finishing. Cr(VI) is highly soluble in water and can seep into ground water systems from industrial effluents. Cr(VI) is severely toxic in biological systems due to its participation in intracellular processes that alter enzyme activities, cause DNA damage and cell death. Once in the body, Cr(VI) is readily absorbed by different tissues due to the structural similarity of the chromate anion (CrO$_4^{2-}$) to the sulfate (SO$_4^{2-}$) anion and is mistakenly transported across the cellular membrane via the sulphate uptake pathway. Cr(VI), upon entering the cell, is reduced by cell reductants such as glutathione (GSH), ascorbate and NADPH, resulting in the formation of reduced chromium species (Figure 1.1). Cr(V) and Cr(IV) are short-lived species which can damage DNA via oxidation. Non-oxidative DNA damage can also occur, mostly through the formation of
Cr-DNA adducts. DNA oxidation leads to chromosomal damage and genotoxic mutation (Figure 1.1). Cr(VI) is toxic, even at low concentrations, while Cr(III) is an essential trace nutrient which is required for normal metabolism of fat, protein and carbohydrates in humans. Cr(III) aids in the conversion of glucose into energy and promotes healthy blood glucose and blood pressure levels.

![Figure 1.1. Absorption, metabolism, and effects of Cr(VI) on DNA. Adapted from reference with permission from the American Chemical Society.](image)

The main source of Cr(VI) exposure for humans is through contaminated water. Since Cr(VI)-contaminated non-aqueous industrial wastes can end up in water bodies, it is important to develop methods to remove hexavalent chromium from such wastes before they are disposed.

Conventional methods such as chemical precipitation, coagulation, ion exchange, reverse osmosis and adsorption have been used for the removal of hexavalent chromium. However, these methods are limited by high costs, poor removal efficiencies, and formation of secondary pollutants.
Owing to their sensitivity, cost-efficiency, ease of operation, and scalability, electrochemical techniques have been widely applied for the treatment of many environmental pollutants.\textsuperscript{12–16} Compared to the conventional methods, electrochemical techniques are faster and more environmentally benign as contaminants can be detected or reduced within a short period of time with minimal generation of secondary waste.\textsuperscript{17,18} Consequently, the removal of hexavalent chromium in aqueous media via electrochemical reduction using different electrodes have been reported in literature.\textsuperscript{8,20,21} However, there is a lack of information on the electrochemical reduction of Cr(VI) in non-aqueous media. This is a challenge as Cr(VI)-contaminated nonaqueous industrial wastes can end up in water bodies. This can be avoided by treating such wastes at the source at which they are generated, allowing for the reclamation and reuse of chromium instead of its release to the environment.

Non-aqueous electrochemistry can be effective for the removal of hexavalent chromium in nonaqueous waste for many reasons. First, compared to water, polar aprotic solvents, such as dimethylformamide and acetonitrile, used as solvents in non-aqueous electrochemistry offer solubility and miscibility to a wide range of organic compounds and salts. Also, non-aqueous solvents have wider potential window which allows for electrochemical investigations beyond the potential window of water. Moreover, the reduction of hexavalent chromium in water is complicated by its speciation in water. A diagram showing the speciation of hexavalent chromium in water is presented in Figure 1.\textsuperscript{6} Depending on pH, temperature and total chromium concentration, hexavalent chromium exists in different forms in water.\textsuperscript{6} \(\text{Cr}_2\text{O}_7^{2-}\) is the predominant form at high total
chromium concentrations and acidic to neutral pH, while at low concentration and neutral to basic pH, the predominant form is CrO$_4^{2-}$. At more acidic pH, CrO$_4^{2-}$ is protonated to form HCrO$_4^-$ and H$_2$CrO$_4$. The chromate-dichromate equilibrium is presented as: $2\text{CrO}_4^{2-} + 2H^+ \rightleftharpoons \text{Cr}_2\text{O}_7^{2-} + H_2O$ (Equation 1.1). Polar aprotic non-aqueous solvents, unlike water, do not supply H$^+$ required to keep chromate and dichromate species in equilibrium, hence chromate-dichromate equilibrium is not expected to be a problem. Therefore, non-aqueous electrochemistry could allow the fundamental study of the electrochemical reduction of hexavalent chromium without interference from H$^+$ or H$_3$O$^+$ equivalents. To reduce hexavalent chromium in non-aqueous media, a suitable procedure must be developed, the mechanism of the reduction process must be understood and ways to make the reduction more efficient must be explored. The focus of this research is to develop an energy-efficient method to facilitate the transfer of protons and electrons that will aid in the reduction of hexavalent chromium to benign trivalent chromium in non-aqueous media. To have a fundamental understanding of the electrochemical processes
involved in the reduction of Cr(VI) in nonaqueous media, cyclic voltammetry experiments are carried out using glassy carbon as working electrode.

To compare and understand the chemistry involved in the reduction of hexavalent chromium in non-aqueous media and water using glassy carbon electrodes, we considered literature reports on the reduction of hexavalent chromium in water using glassy carbon electrodes. For example, Welch et al.,\textsuperscript{6} in 2005, reported that the electrochemical reduction of hexavalent chromium in water at glassy carbon electrodes yielded irreproducible results and that expensive noble metal electrodes are required for Cr(VI) reduction. However, in a recent study, Stern et al.\textsuperscript{22} reported a method for obtaining reproducible Cr(VI) detection/reduction in water at glassy carbon electrodes. Stern et al.\textsuperscript{22} also reported that the reduction of hexavalent chromium at glassy carbon electrodes was dependent on pH. No electrochemical response was obtained for the addition of chromate to water in the presence of KCl electrolyte within the potential window studied. However, a reduction peak was observed on the addition of acid, and the peak potential shifted to more positive values as more acid was added, indicating an acid dependent rate limiting chemical step. Moreover, during the titration of chromate into a 0.1 M citric acid buffer at pH 4.75, Stern et al. reported a loss of linearity in current response at high chromate concentrations, and a sharp shift in peak potential to less negative values at about 3 mM chromate concentration (Figure 1.3). These changes in peak currents and peak potentials were attributed to the equilibrium between chromate and dichromate (Equation 1.1).

Following up on this previous work, herein is described a method for obtaining reproducible cyclic voltammetric data for Cr(VI) detection/reduction in a non-aqueous medium using glassy carbon electrodes, allowing for a better understanding of the
reduction process. The effect of Brønsted acids on the behavior of Cr(VI) and electrocatalysis using small molecular catalysts are also evaluated. This research is important for the development of a cheap, energy efficient and environmentally benign method for removing Cr(VI) from non-aqueous sources.

Figure 1.3. Evolution of cathodic peak potential with chromate concentration in 0.1 M citric acid buffer at pH 4.75. Figure from reference²² with permission from the copyright holder.
Chapter 2. Experimental

2.1. Analytical Techniques

To have a fundamental understanding of the electrochemical processes involved in the reduction of Cr(VI) in nonaqueous media, cyclic voltammetry experiments are carried out using glassy carbon as working electrode.

Cyclic voltammetry is an electroanalytical technique used for the study of electroactive species. Cyclic voltammetry is usually the first technique in the electrochemical study of a compound, electrode surface, or a biological material since it is a useful technique for obtaining quick information about the thermodynamics of redox processes and electron transfer kinetics.\textsuperscript{23}

Cyclic voltammetric experiments are carried out using a vessel known as an electrochemical cell (shown in Figure 2.1). The electrochemical cell consists of a working electrode where the redox reaction of interest occurs, a reference electrode, which has a

![Figure 2.1. A schematic describing a typical electrochemical cell for cyclic voltammetry experiments. Figure from reference\textsuperscript{24} with permission from the American Chemical Society.](image-url)
well-defined and stable equilibrium potential, to which the potential of the working electrode is referenced, and a counter electrode to complete the electrical circuit.24

In cyclic voltammetry experiment, a potential is applied to the working electrode using a potentiostat, and this potential is varied with time. The current passing through the working electrode is then measured as a function of the applied potential and a plot of current versus applied potential is generated. This plot is known as a voltammogram.23,24

Ultraviolet and visible (UV-vis) spectroscopy involves the measurement of light absorption by a sample and is a useful tool to differentiate components of a sample based on their absorption bands as different molecules absorb radiation at different wavelengths. In UV-Vis experiments, a plot of absorbance against wavelength is generated. This plot is known as a UV-vis spectrum.25

2.2. Analytes and Reagents

Acetonitrile (Millipore Sigma, 99.8%) was degassed with three freeze-pump-thaw cycles and dried over activated molecular sieves. Bis (tetrabutylammonium) dichromate (Sigma-Aldrich, 99%) and phenol (TCI Chemicals, 99.5%) were dried at room temperature under vacuum for 8 hours. Dichloromethane (BDH Chemicals, 99.5%), N,N-Dimethylformamide (Acros,99.8%), Tetrahydrofuran (Millipore Sigma, 99.5%), Pyridinium dichromate (Sigma-Aldrich, 98%), Ammonium chromate (Alfa Aesar, 98%), Ammonium dichromate (Alfa Aesar, 99.9%), Ferrocene (Alfa Aesar, 99%), benzoic acid (Acros, 99.6%), and salicylic acid (TCI Chemicals, 99.5%) were used as received. Tetrabutylammonium hexafluorophosphate [NBu4][PF6] (TCI Chemicals, 98%) was
recrystallized from hot ethanol, filtered, washed with cold ethanol, and dried at room temperature under vacuum for 24 hours.

2.3. Electrochemical Methods

To prevent oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) which are competing reactions, electrochemistry was carried out in a nitrogen-filled glovebox with a Bio-Logic SAS potentiostat using a three-electrode cell system. The cell was composed of a disposable 20 mL borosilicate glass scintillation vial with a Teflon cap bearing openings for the three electrodes and openings for degassing or reagent addition. The three-electrode system contained a glassy carbon working electrode (3 mm diameter, CH Instruments), a platinum counter electrode (3 mm diameter, CH Instruments), and a silver wire pseudo-reference (CH Instruments). The potentiostat was situated outside the glovebox, and the electrode leads were connected through a shielded electrode cable feedthrough. Glassy carbon working electrodes and the platinum counter electrode were polished manually with 0.05 µm alumina powder (CH Instruments)-Milli-Q water slurry for 2 minutes on Microcloth polishing pads, rinsed, and sonicated for 20 seconds in water from the Milli-Q system to remove residual polishing powder followed by drying in a flux of nitrogen gas. The pseudo-reference silver wire electrode was submerged in a glass tube fitted with a porous glass tip containing 0.25 M [NBu4][PF6] in acetonitrile. Each working electrode was pre-treated with several cyclical scans in 0.25 M [NBu4][PF6]/acetonitrile solution. In all the experiments, background voltammograms at the respective scan rate were taken. The solution was stirred between scans. A fresh, pretreated working electrode was used for each scan, and to account for the drift in
potential in non-aqueous solvents, all measured potentials were externally referenced to the ferrocene/ferrocenium couple.

2.4. Optical Methods

UV-vis experiments were carried out using a benchtop Ocean Optics UV-vis spectrometer. The light source is a DH-2000-BAL, a dual light source consisting of Deuterium and Halogen lamps. The light source is coupled to an OCEAN-FX-XRI-ES detector via optic fibers. All experiments were carried out using a 1 cm pathlength Spectrosil® quartz cuvette.
Chapter 3. Results and Discussion

3.1. Choice of Analyte and Solvent

For the determination of suitable solvent and Cr(VI) analyte, solubility experiments (Table 3.1) were carried out to determine the solubility of four Cr(VI) compounds (Bis(tetrabutylammonium) dichromate, pyridinium dichromate, ammonium dichromate, and ammonium chromate) in acetonitrile, dimethylformamide (DMF), dichloromethane, and tetrahydrofuran (THF).

<table>
<thead>
<tr>
<th></th>
<th>CH$_3$CN (5 mL)</th>
<th>DMF (5 mL)</th>
<th>CH$_2$Cl$_2$ (5 mL)</th>
<th>THF (5 mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bis (tetrabutyrammonium) dichromate (25 mg)</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Soluble</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>Pyridinium dichromate (25 mg)</td>
<td>Slightly soluble</td>
<td>Soluble</td>
<td>Sparingly soluble</td>
<td>Slightly soluble</td>
</tr>
<tr>
<td>Ammonium dichromate (25 mg)</td>
<td>Insoluble</td>
<td>Soluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
<tr>
<td>Ammonium chromate (25 mg)</td>
<td>Insoluble</td>
<td>Slightly soluble</td>
<td>Insoluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

As shown in Table 3.1, three out of the four compounds tested were completely soluble in dimethylformamide while only one compound was completely soluble in acetonitrile, tetrahydrofuran, and dichloromethane. Even though dimethylformamide showed the best results, acetonitrile was chosen for this research because of the availability of data on the behavior of acids in acetonitrile on glassy carbon electrodes.\(^\text{26}\) Also, the $pK_a$ values of a large number of Bronsted acids have been reported in the literature.\(^\text{27–29}\) Bis (tetrabutylammonium) dichromate was selected because it is the only compound that dissolved completely in acetonitrile among the compounds tested.
In this document, moving forward, Cr(VI) concentrations given refer to Bis(tetrabutylammonium) dichromate.

3.2. Cyclic Voltammetry at Glassy Carbon Electrodes in Acetonitrile

Due to the advantages of glassy carbon electrodes, such as their relative low cost, wide cathodic potential range, and chemical inertness, the behavior of hexavalent chromium in acetonitrile was evaluated using these electrodes. The voltammetric response of 2 mM tetrabutylammonium dichromate on a glassy carbon working electrode in acetonitrile is shown in Figure 3.1. The voltammogram shows a background trace of

![Figure 3.1](image_url)

Figure 3.1. A cyclic voltammogram showing the response of a glassy carbon electrode to 2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution. Scan rate: 50 mV/s. The electrode (in black) and one reduction peak in the presence of hexavalent chromium (in blue). The Cr(VI) reduction current increases as scan rate increases (Figure 3.2).
Figure 3.2. Voltammograms showing the effect of varying scan rates on the voltammetric response of glassy carbon electrodes to 2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution.

Figure 3.3. Plot of the cathodic peak current versus square root of scan rate. Cr(VI) concentration: 2 mM. Standard deviation error bars are from triplicate analyses.

Concentration on the reduction process was investigated by varying the concentration from 0.2 to 6.6 mM (Figure 3.4). As shown in Figure 3.5, the peak currents showed a linear variation with Cr(VI) concentration with a $R^2$ value of 0.9991, indicating the linear dependence of peak current on Cr(VI) concentration. This suggests that this method
could be efficient for the determination and quantification of Cr(VI) concentration in CH$_3$CN.

Figure 3.4. Voltammograms showing the effect of varying concentration on the voltammetric response of glassy carbon electrodes in 0.25 M [NBu$_4$][PF$_6$]/CH$_3$CN electrolyte solution.

Figure 3.5. Evolution of peak current with increasing concentration of Cr(VI) in 0.25 M [NBu$_4$][PF$_6$]/CH$_3$CN electrolyte solution. Scan rate: 100 mV/s. Standard deviation error bars are from triplicate analyses.
3.3. Chromate-dichromate Equilibrium

The fundamental study of the electroreduction of hexavalent chromium in water is complicated by the equilibrium between chromate and dichromate (shown in Equation 1.1). This equilibrium causes hexavalent chromium to shuttle between the chromate and the dichromate form, depending on concentration and pH. At low concentrations and basic pH, chromate is the predominant species while at high concentrations and acidic pH, dichromate is the predominant species. In aprotic non-aqueous solvents, there are no “H+” or “H_2O^+” equivalents. Hence the chromate-dichromate equilibrium is not expected to be a problem. As shown in Figures 3.4 and 3.5, there is a linear increase in current as the concentration of dichromate increases from 0.2 mM to 6.6 mM. The linearity of the plot suggest that dichromate is the only hexavalent chromium species at the low and high concentrations tested. To confirm this observation, reduction peak potentials from data in Figure 3.4 were plotted against log[Cr(VI)] (Figure 3.6) in a manner like Figure 1.3. The reduction peak potential shifts linearly to more negative values as the concentration of dichromate increases, which further indicates that dichromate is the only species at all concentrations. This is contrary to the loss of linearity observed at high chromate concentration by Stern et al. during the addition of increasing amount of chromate in water. The outcome of this experiment is that it is possible to investigate the reduction of dichromate at both low and high concentrations.
3.4. Acid-mediated Reduction of Cr(VI)

As shown in the dichromate reduction equation:

\[ \text{Cr}_2\text{O}_7^{2-} + 14H^+ + 6e^- \rightarrow 2\text{Cr}^{3+} + 7H_2O, \]

many protons and electrons are required for the reduction of hexavalent chromium. This translates to a large activation barrier, making the direct electrochemical reduction of hexavalent chromium energy demanding. To supply the required protons, three organic Brønsted acids (benzoic acid, phenol, and salicylic acid) were investigated as proton donors. These acids were chosen because their \( pK_a \) values, behavior and potential window in acetonitrile have been reported in the literature. Izutsu reported a \( pK_a \) value of 16.7 for salicylic acid in acetonitrile. The \( pK_a \) of benzoic acid in acetonitrile was reported as 21.5 by Agnes Kutt et al. in 2006, while that of phenol was reported as 29.14 by Agnes Kutt et al. in 2008. The potential range at which these acids get reduced was reported by McCarthy et al. in their study of the
behavior of Brønsted acids in acetonitrile using glassy carbon electrodes. This allows us to choose a suitable potential window for this study. Voltammograms showing the effect of phenol on the reduction of 2 mM Cr(VI) in acetonitrile are shown in Figure 3.7. The reduction peak shifts to less negative potentials as the concentration of phenol increases (Figure 3.7, black arrow). This suggests acid dependent rate determining chemical steps. Similar shifts in potentials to less negative values are observed with increasing concentrations of benzoic acid (abbreviated as BA in Figure 3.8) and salicylic acid (abbreviated as SA in Figure 3.9). As shown in Figure 3.7, the reduction peak current increased with the addition of 50 mM of phenol (Figure 3.7, orange trace) while subsequent additions of phenol (Figure 3.7; yellow, green, and blue trace) yielded no significant change in peak currents. This can be attributed to the change in the rate determining step of the reduction as the number of protons available increases. The large currents observed on the addition of acid can be attributed to new species from the protonation of the dichromate ions.

Figure 3.7. Cyclic voltammograms of 2 mM Cr(VI) with varying concentration of phenol in 0.25 M [NBu₄][PF₆]/CH₃CN solution. Scan rate: 100 mV/s.
Figure 3.8. Cyclic voltammograms of 0.2 mM Cr(VI) with varying concentration of benzoic acid in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution. Scan rate: 100 mV/s.

Figure 3.9. Cyclic voltammograms of 0.2 mM Cr(VI) with varying concentration of salicylic acid in 0.25 M [NBu₄][PF₆]/CH₃CN electrolyte solution. Scan rate: 100 mV/s.

To compare the effect of the acids on Cr(VI) reduction and to correlate acid behavior to their strength, plots of peak potential against log of acid concentration (Figure 3.10) were made and a correlation between potential and acid strength was observed, with salicylic acid and benzoic acid shifting the potentials to more positive values.
3.5. Homogenous Electron Transfer to Cr(VI)

Due to the large number of protons and electrons required for the reduction of Cr(VI), there is an energy barrier that must be surmounted to achieve efficient reduction. While Bronsted acids have been identified as proton donors for Cr(VI) reduction, there is still a need to make the reduction process less energy demanding. A way to combat this is through catalysis using suitable catalysts that can facilitate the transfer of electrons to Cr(VI) ions. In selecting a catalyst for the reduction of hexavalent chromium, small molecules that can be oxidized by Cr(VI) and reduced back are desirable. Ferrocene is an electron donor and is capable of mediating electron transfer by switching between its oxidized state (ferrocenium) and its reduced state (ferrocene). This suggests that ferrocene could act as a catalyst for Cr(VI) reduction. To investigate this hypothesis and get a fundamental understanding of the role and reactions between the various entities...
involved, electron transfer from ferrocene to dichromate ions in acetonitrile was monitored using UV-vis spectroscopy. As shown in Figure 3.11., the dichromate shows an absorption maximum at 377 nm (orange trace), while the absorption maximum of ferrocene can be seen at 440 nm (grey trace). Benzoic acid showed no signal in the wavelength range studied. Also, there was no change in the ferrocene signal on the addition of benzoic acid. Similarly, there was no change in the UV-vis signal of either Cr(VI) or ferrocene when they were added together. This implies the lack of reaction between ferrocene and benzoic acid, or between Cr(VI) and ferrocene. However, the dichromate absorption peak at 377 nm disappears and two new peaks at 365 nm and 450 nm appear on the addition of benzoic acid. These peaks can be attributed to the products of the protonation of the dichromate ions; however, further study is required to determine their speciation. On the addition of ferrocene and benzoic acid to Cr(VI) (Figure 3.11, pink trace), the ferrocene peak at 440 nm, the Cr(VI) peak at 377 nm, and
the peaks at 365 nm and 450 nm are not observed. Instead, two new peaks appear. The first one at 460 nm can be attributed to the reduction of the products formed from the protonation of dichromate ions, while the more prominent peak at 620 nm can be attributed to ferrocenium formed by the oxidation of ferrocene by Cr(VI). These new peaks show that ferrocene can donate the electrons needed to reduce Cr(VI), albeit in the presence of protons, and could act as a small molecule catalyst for the reduction of Cr(VI). Overall, the UV-vis experiments reinforce our observations from electrochemical studies which suggest that the reduction of Cr(VI) proceeds via proton-coupled electron transfer (PCET).

3.6. Reproducibility Studies

In this study, different factors affecting the collection of reproducible data were discovered. First, the cathodic peak potentials for Cr(VI) in acetonitrile were found to be affected by the presence of trace amount of water. As shown in Figure 3.12, the

![Figure 3.12. Voltammograms obtained for 0.2 mM Cr(VI) in 0.25 M [NBu₄][PF₆]/CH₃CN solution showing peak potentials before and after changing the molecular sieves in the solvent. Scan rate: 100 mV/s.](image-url)
reduction of Cr(VI) occurred at a less negative potentials when a solvent which was suspected to contain trace of water was used. The peak potential shifted to more negative values after replacing the molecular sieves in the solvent, suggesting that water is acting as a proton donor. This could be helpful in making the reduction of hexavalent chromium less energy demanding, however, it is difficult to account for the number of protons supplied by H$_2$O compared to externally added acids, making the mechanism of the reduction process difficult to understand. Therefore, to have a better understanding of the behavior of hexavalent chromium in nonaqueous media and obtain reproducible data, the effect of water must be minimized. This was done by carrying out all experiments in a nitrogen-filled glove box with solvent that had been degassed and dried with activated molecular sieves. Another reproducibility parameter is the residence time of electrodes in solution during experiments. This was discovered during time dependency experiments. As shown in Figure 3.13, results from 15 seconds and 30 seconds residence time were compared and it was found that reproducible data are obtained at 30 seconds residence time.

Figure 3.13. Voltammograms obtained at 15- and 30-seconds electrode residence time for 0.2 mM Cr(VI) in 0.25 M [NBu$_4$][PF$_6$]/CH$_3$CN solution. Scan rate: 100 mV/s.
time. As shown in Figure 3.14, by applying the new method of data collection, data were obtained for the reduction of 0.2 mM Cr(VI) in three consecutive experiments with some degree of reproducibility. Statistical analysis of the peak potentials for the three experiments was carried out and a mean ± standard deviation value of $-1.972 ± 0.005$ V was obtained with a low relative standard deviation value of 0.26%. This study shows that reproducible Cr(VI) data in acetonitrile can be obtained at glassy carbon electrodes.

Figure 3.14. Voltammograms for the reduction of 0.2 mM Cr(VI) in three different experiments. Scan rate: 100 mV/s.
Chapter 4. Conclusions

This work has shown that Cr(VI) in acetonitrile can be reduced at glassy carbon electrodes under certain conditions. The reduction of Cr(VI) at glassy carbon electrodes was found to be irreversible and diffusion controlled. The reduction potential for the electroreduction of Cr(VI) was also found to be energy demanding as indicated by the high potential value. This can be attributed to the kinetic barrier caused by the huge numbers of protons and electrons required for the reduction process. However, this study has shown that this kinetic barrier can be overcome using Bronsted-Lowry acids as proton mediators. Electrochemical and UV-Vis studies suggest that the reduction of Cr(VI) proceeds via a proton-coupled electron transfer process.

Outstanding challenges include understanding the mechanism of the reduction process, nature of the products formed and identifying suitable electrocatalysts that can efficiently mediate the transfer of protons and electrons between Cr(VI) and the electrodes. Finding solutions to these challenges will boost Cr(VI) remediation efforts in non-aqueous sources.
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Appendix C. Reuse Permission Request and Permission for Figure 1.2

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Thu 5/27/2021 12:16 PM
To: Noemie Elgrishi <noemie@lsu.edu>
5/27/2021
Department of Chemistry,
Louisiana State University,
Baton Rouge, Louisiana,
United States.
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Appendix E. Reuse Permission for Figure 1.3

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______________________________
Noémie Elgrishi, PhD
Assistant Professor, Department of Chemistry
Louisiana State University
office: 225-578-6917 | CMB 301A
noemie@lsu.edu

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From: Temitope O Jegede <tjeged1@lsu.edu>
Sent: Thursday, May 27, 2021 12:16
To: Noemie Elgrishi <noemie@lsu.edu>
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Appendix F. Reuse Permission Request for Figure 3.1

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Image Title: Figure 4. Schematic representation of an electrochemical cell for CV experiments.

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Sincerely,
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Appendix G. Reuse Permission for Figure 3.1

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Image Title: Figure 4. Schematic representation of an electrochemical cell for CV experiments.
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Sincerely,
References


Vita

Temitope Oluwaseyi Jegede, born in Ilesa, Nigeria, obtained his bachelor’s degree from Ladoke Akintola University of Technology, Nigeria. He later got a Master of Science degree from Obafemi Awolowo University during which he focused on geochemistry. Having witnessed the devastation of the environment due to poor exploration practices, he developed an interest in environmental remediation and clean energy studies. He joined the Department of Chemistry at Louisiana State University where he investigated the remediation of toxic hexavalent chromium in acetonitrile. He plans to receive his master’s degree in August 2021.