

The Electrochemical Reduction of CO₂ into Ethanol Utilizing Novel Doped Cu/SiO₂ Nanoparticles and Electrolytes

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ABSTRACT: With the growing negative anthropogenic impact of the 21st century, it has become imperative to devise alternative means of fuel synthesis. One promising method is the electrochemical reduction of carbon dioxide to ethanol using copper nanoparticles, as it offers a direct conversion of a greenhouse gas to a fossil fuel. However, this process is limited by steep overpotentials, low Faradaic efficiency, and corresponding low selectivity for ethanol. This study aimed to provide a comprehensive overview of factors involved in the reduction reaction. The first phase of this study developed a novel method to produce doped copper nanoparticles, at a size of 2-5 nanometers (based on photon correlation spectroscopy results). The second phase determined that sodium chloride was the most efficient electrolyte at a concentration of 0.4 M. The third phase of this study determined that carbon and lead was the best cathode-anode combination based on consistent high current response at the necessary overpotential of 1 V. The fourth phase of this study utilized Self-Consistent Field calculations, a quantum computational method of approximating the Fermi energy and total energy of a system, to determine the silica supported copper nanoparticle graphene electrode would enable selective reduction to ethanol. This study's novel nanoparticle synthesis methodology is widely applicable to many fields and yields effective particle sizes. This synthesis methodology coupled with analysis of significant factors make the electrochemical reduction of carbon dioxide a more feasible means of fuel synthesis.

KEYWORDS: Electrochemistry; Reduction; Catalyst; Copper; Nanoparticles.

■ Introduction

Mass carbon emissions in the past century have paved the way for the environmental crisis humanity is currently facing. The rate at which carbon is being emitted has been increasing rapidly on an annual basis, resulting in environmental issues such as rising sea levels, increased global temperature fluctuations, air quality degradation, and ocean acidification. The most prominent facilitator of carbon emissions has been the use of fossil fuels as a primary source of energy. According to the Environmental Protection Agency, it accounted for 65% of the total global greenhouse gas emissions in 2014, with the percentage having grown since then.¹ Regarding fuel, the end goal is to decrease the net emissions of carbon generated from fuel consumption. One promising method is to synthesize ethanol, a conventional fuel for motor vehicles, from captured carbon dioxide. As opposed to retrieving fossil fuels from the earth and burning it to expel additional carbon dioxide into the atmosphere, this synthesized fuel would be comprised of carbon dioxide that was previously present in the atmosphere, so when burned, it would emit no additional carbon dioxide (making the fuel inherently carbon neutral). Fortunately, scientists have stumbled across an innovative method of synthesis that may prove applicable. While being a process still in its infancy, this method of fuel synthesis might be the key to an effective production of a carbon neutral fuel. A team of scientists at the Department of Energy's Oak Ridge National Laboratory took "carbon dioxide, a waste product of combustion," and essentially pushed the "combustion reaction backwards with very high selectivity to form a useful fuel."² The process entails a sample of carbon dioxide dissolved in water to be exposed

to a nitrogen-doped copper nanoparticle catalyst with an electrode input of electrons to induce an electrochemical reaction that directly converts the carbon dioxide into ethanol.³ When delving deeper into their methodology, some inconclusive factors appear to foster room for improvement. They explicitly state that the "overpotential (which might be lowered with the proper electrolyte, and by separating the hydrogen production to another catalyst) probably precludes economic viability for this catalyst."³ This begs the question, what optimizes the utilization of copper nanoparticle catalysts in the conversion of carbon dioxide into ethanol through electrochemical reduction on the basis of distinct dopants and electrolytes?

Developments in the electrochemical reduction of carbon dioxide (CO₂) to hydrocarbon products have given rise to its application towards the innovation of modern fuel synthesis, especially for the purpose of environmental conservation. Today's research is quite broad and neglects to tackle various components that could serve pivotal in improving the efficiency of this process. Non-catalytic variables such as the role of doping and the role of differing electrolytes are gaps in research. Investigating the synergistic properties of these variables could bring to light optimizations that have yet to be discovered. This literature review outlines the current state of research in this field and the key aspects that remain the foundation of this investigation.

Ethanol Production from CO₂:

In investigating the procedures for the electrochemical reduction of CO₂ and the potential for ethanol production, it is imperative to study preceding studies and breakdown the various elements that can be applied and tested.

The Department of Physics within the Technical University of Denmark published in *Energy and Environmental Science* the article “How Copper Catalyzes the Electroreduction of Carbon Dioxide into Hydrocarbon Fuels.” Their research focused on the integration of density functional theory calculations to delve into the specifics behind how copper is uniquely able to convert CO₂ into hydrocarbons and the implications of it towards [photo-]electrochemical means of fuel synthesis. Their major gap in research is the high overpotential required for the conversion process that is otherwise efficient in quantity and selectivity through the utilization of copper catalysts. The effectiveness of copper in the reduction of CO₂ using a copper electrode was determined by applying voltage to dissolved CO₂ in water and quantifying the various hydrocarbons products. Their study documented “product distribution and total current produced as a function of applied potential (versus reversible hydrogen electrode, RHE) in the electrochemical reduction of CO₂ at a copper electrode in 0.1 M KHCO₃ (pH 6.8) at 18.5 °C.”⁴ Since copper catalysts commonly have high selectivity for methanol production from a CO₂, CO, and H₂ mixture, the researchers’ discovery that methanol was not the dominant hydrocarbon product demonstrated a discrepancy between conventional electrochemical thought and the implementation of copper catalysts. The significance of a copper catalyst electrode, specifically in the electrochemical reduction of CO₂, is further supported by the Department of Applied Chemistry at Chiba University in their article “Selective Formation of C₂ Compounds from Electrochemical Reduction of CO₂ at a Series of Copper Single Crystal Electrodes.” Their methods described a spherical copper crystal being attached to a copper stick (made from 99.999999% copper) using the Bridgeman method, which employs a graphite crucible after the position of the crystal was deemed sufficient with the use of the X-ray Laue back reflection method.⁵ The results of the study include that the formation rates of the gas products remaining “virtually constant.”⁵ The researchers also state that a higher selectivity in the reduction reaction is desirable for practical applications of the concept such as future reduction into ethanol.

Copper Silicon Dioxide Nanoparticles:

The catalyst utilized in the electrochemical reduction of CO₂ into ethanol provides the novelty of such a unique fuel synthesis. Based on research conducted by the Oak Ridge National Laboratory, experimentation of metal-based catalyst in the context of electrochemical reduction has indicated copper as the most electrochemically promising catalyst, having been able to generate over 30 different hydrocarbons.³ Copper has a unique set of characteristics that allows it to serve as an effective catalyst: abundance, conductivity, and corrosion resistance. However, the limitation of copper nanoparticles as a catalyst is that they produce an overwhelming range of resultant hydrocarbons when ethanol alone is the desired product. According to the *Journal of the American Chemical Society*, the moderate binding energy of copper and carbon monoxide, a “major intermediate during the [reduction] reaction,” prevents both high selectivity and faradaic efficiency for desired resultant products.⁶ Corresponding high overpotentials and low selectivity restrict wide application of this reduction

resultant products.⁶ Corresponding high overpotentials and low selectivity restrict wide application of this reduction reaction into fuel conversion. There are developments in the works that seek to limit these obstacles of overpotential while also attempting to increase the selectivity of C₂ and C₃ compounds. The Key Laboratory for Green Chemical Technology of the Ministry of Education in China sought to solve these issues by supporting the copper nanoparticles with silica. Their findings indicated that silica support did achieve the “coexistence of CuO and Cu⁺” and generated such catalytic activity to favor ethanol as the output.⁷ Though in its stages of infancy, the correlation between a greater selectivity for ethanol and silica supported copper nanoparticles provide insight into lowering overpotential and increasing selectivity. Furthermore, an article in *Physical Chemistry Chemical Physics* titled “Electrochemical CO₂ Reduction on Cu₂O-Derived Copper Nanoparticles: Controlling the Catalytic Selectivity of Hydrocarbons” sought to achieve higher levels of selectivity for ethanol. The researchers noted that a stable and robust cathode material that could selectively convert CO₂ and H₂O to useful products at low overpotentials does not yet exist (current methods of electrochemical reduction have high overpotentials and involve rapid degradation of the catalytic activity). The researchers sought to quantify the performance of “electrochemically produced Cu₂O coated copper substrates towards CO₂ reduction” in terms of “selectivity, activity, and long-term stability.”⁸ Thermally produced thick oxide films were reported to decrease the overpotential of reduction without losing activity after an extended period of electrolysis.⁸

Sol-Gel Synthesis Procedures:

Synthesis procedures for copper nanoparticles vary based on chemical needs, but one procedure stands out due to its efficiency and cost-effectiveness: the sol-gel synthesis method. A study published in the *International Journal of Research in Engineering and Innovation* mixed glacial acetic acid with hydrated copper chloride, and then added highly concentrated sodium hydroxide to form a precipitate. The study noted that they were able to produce copper oxide nanoparticles at 16 nm, with reaction time and the concentration of the base playing a major role in the size of the nanoparticles.⁹ While this method does in fact generate fine nanoparticles that are easily applicable to the electrochemical reduction of carbon dioxide, this method lacks the critical silica support necessary for high selectivity for ethanol. A study published in *Chem. Mater.* chose to mix sodium hydroxide (4 mol/L) with copper nitrate (0.5 mol/L) and then add aqueous silica solution to the precipitate to produce a gel. The gel was then aged, filtered, and washed to isolate the catalyst. The addition of silica gel was to provide critical stability for the microparticles.¹⁰ A study published in *Pharmaceuticals* similarly documented the benefits of the sol-gel technique. The study noted that the sol-gel technique ensured “rigorous control of the nanoparticle size,” while optimizing the dimensions of the resultant nanoparticles.¹¹ Altogether, the sol-gel synthesis procedure is both cost-effective and efficient in that it produces uniform nanoparticles with consistent morphology.

Role of Doping in Catalyst Production:

The process of doping entails applying various atoms that function as impurities into the composition of a catalyst substance. Doping a substance can have varying effects, but predominantly results in the formation of a lattice shape structure of a substance used in a reaction. This can cause the substance to become significantly more conductive, where even some doped catalysts have the potential to increase conductivity by a factor of 10^6 .¹² With the foundation of nitrogen-doping (n-doping), new molecules within the catalyst will possess 5 outer elections. Its applicability is apparent in the fact that extra electrons remain unbound by the crystalline structure of the catalyst, transferring freely over the conduction band of the molecule, reducing the band gap that is required to overcome. Though this characteristic implies efficiencies in the electrochemical reduction process, researchers from the University of Qingdao have noted molecules that “occupy at the edge or defect sites” of n-doped catalyst as having reduced the electro-catalytic effect at the center of the reaction.¹³ There is much potential in doping the catalyst to increase efficiency and productivity in the electrochemical reduction of CO₂ into ethanol, meriting alternative dopants to be further investigated.

Role of Electrolytes in Electrochemical Reduction:

Electrolytes are key components to the process of electrochemical reactions. The article “Electrolyte Effects on the Electrochemical Reduction of CO₂” reviewed the influence of electrolytes on the electrochemical reduction of CO₂ and sought to uncover insights on ways to lower overpotential and boost selectivity. Accordingly, the researchers of the study mention that the “addition of salts to form the aqueous electrolyte can induce a salting out effect, further lowering CO₂ solubility in the Electrolyte,” which induces mass transfer limitations in instances of an operation at higher current densities.¹⁴ In cases where gas is diffused in the set-up, a faster diffusion of CO₂ is achieved in the presence of electrolytes near areas of an electrocatalyst surface, sustaining higher current densities. Additionally, they discuss that pH dictated by electrolytes is a critical parameter in controlling the electrocatalytic selectivity due to the formation of OH. It was noted that “local” pH also plays an important role in the electrochemical reduction of CO₂ to hydrocarbons on copper electrodes. While the formation of methane was found to be pH sensitive, the formation of ethylene was found to be pH insensitive, suggesting separate pathways for the production of these hydrocarbons.”¹⁴ This provides information on how selectivity can be achieved through the differentiation of pH based on electrolytes. Furthermore, in “High-Selectivity Electrochemical Conversion of CO₂ to Ethanol using a Copper Nanoparticle/N-Doped Graphene Electrode” from the journal Chemistry Select, the electrochemical scientists comment on electrolytes within their experimentation on CO₂ reduction and ethanol production through the use of copper nanoparticles and a nitrogen-doped graphene electrode. They reflect on their findings and state overpotential “might be lowered with the proper electrolyte, and by separating the hydrogen production to another catalyst.”³ This provides an inherent gap in research that can be

pivotal in generating a feasible and effective means of ethanol production from the reduction of CO₂.

Software Analysis of the Electrochemical Reduction of CO₂:

For analysis into thermodynamic qualities and ground states of electrochemical systems, there exists two forms of software-based research: density functional theory (DFT) and the chemical process simulators. DFT offers a set of functionals that utilize quantum computing to generate approximations of many-body systems. Singh *et al.*, researchers at the National Laboratory in Berkley, produced a DFT model to answer several key questions for the electrochemical reduction of carbon dioxide using silver particles. The researchers modeled their system by constructing a 3 x 3 x 4 atom cell which represented their electrode surface. Singh *et al.* performed first free energy calculations with 72 explicit water molecules and then replaced 36 of them with an implicit electrolyte. The researchers “treated [the solvent] as a continuum dielectric” and analyzed it with a “linearized Poisson-Boltzmann model.” They finally calculated the electrode potential with the resultant Fermi energy. The analysis of the free energy profiles of the CO₂RR (CO₂ Reduction Reaction) and HER (Hydrogen Evolution Reaction) noted that the first electrons transferred to H₂O split the molecule into H and OH. The second electron acted similarly but joined the two H atoms to produce H₂. The reaction mechanisms indicated that CO₂ is reduced to COOH which is then reduced to CO using H and H₂O.¹⁵ In Huang J. *et al.*, researchers at the Laboratory of Nanochemistry for Energy in Switzerland, utilized Quantum Espresso (QE) and Environ (a module extending the functionalities of QE) to study the degradation of the copper nanoparticles under operation conditions.¹⁶ Huang J. *et al.* first modeled their base nanoparticle and then modified certain parameters to determine variances in the potentials provided.¹⁶ The researchers utilized this methodology to analyze the overpotentials and formation energies of the reduction reaction. The researchers continued their quantum calculations by determining interface energies through first developing copper supercells. They then tested interface energies over a range of potential differences. Their results indicated that the adsorption of either H atoms or CO molecules on the crystal surface would degrade them at a sufficiently negative potential. Their study further showed the smaller nanoparticles indicated a higher selectivity in the CO₂RR.¹⁶ In Kirk *et al.*, researchers at Stanford University, conducted a similar investigation into the electrochemical reduction of carbon monoxide for single metal atoms embedded in graphene.¹⁷ Their modeling consisted of the development of a supercell with a 4 x 4 lateral size. The unit cell was first allowed to relax to decrease the force acting on each individual atom. The researchers further noted the irregularities of the graphene nanostructures at various levels of nitrogen doping; these irregularities were ignored to generate simplified models.¹⁷

■ Results and Discussion

Copper Nanoparticle Synthesis:

The primary goal was to determine the most effective means of obtaining nanoparticle catalysts (smallest aggregates of catalyst). Table 1 provides the results of the nanoparticle synthesis

method seen in the study conducted by Gong *et al.* proving to be ineffectual.⁷ The addition of silica into the catalyst solution suggested initially unexpected results. Photon correlation spectroscopy indicated that the particle sizes of the catalyst were entirely outside of the nanoscale, generating particles in micrometers. Regardless of silica concentration or copper nitrate and sodium hydroxide ratios, the results for the most part were lackluster, leaving clumpy catalysts that would leave suspension overtime. The addition of nitric acid and sulfuric acid produced a significant change in the particles themselves, while boric acid offered little improvement. The particles synthesized without these acids were clearly visible and would not remain in suspension due to their size (Table 1). The copper particles synthesized with dopants were not visible and did remain in suspension, indicating a much smaller size (Table 1). Unexpectedly, photon correlation spectroscopy indicated no difference in doped samples containing silica and doped samples without silica. The high polydispersity index resulting from these subsets of samples indicates nanoparticle aggregation is likely occurring, producing particles in the microscale (Table 1). This supports the idea that silica support alone does not lower the interfacial tension of the particles to a high enough degree. Based on the high polydispersity index, nanoparticles were most likely initially produced, in the range of 2-5 nanometers, but aggregated after being produced. Given that the size of the silica nanoparticles is about 40 nm, this method of synthesis yields copper supported silica nanoparticles rather than silica supported copper nanoparticles, as originally intended. The copper nanoparticles initially being so much smaller than the silica nanoparticles may play a role in silica's inability to properly promote the stability of the copper particles. Research was halted prior to attempting a means of stabilization of the nanoparticles; however, a novel approach to not only catalyze nanoparticle synthesis, but nanoparticle synthesis in general was formed within this phase of experimentation.

Electrolyte Conductivity Investigation:

Of the collected voltage outputs from sodium chloride, a concentration of 0.4 M was the most conductive while a concentration of 0.5 M performed the least for this particular electrolyte, producing on average a voltage of 0.84 V and 0.79 V respectively (Table 2). Among the sodium chloride voltage averages for the various concentrations, there was a standard deviation of 0.043. As for the electrolyte potassium bicarbonate, 0.2 M generated the greatest voltage with 0.824 V while 0.4 M generated the least with 0.809 V (see Table 2). There was a standard deviation of 0.010 for the average voltages across the varying concentrations of potassium bicarbonate. Lastly, for calcium chloride, the most conductive concentration was 0.1 M with 0.79 V and the least conductive concentration was 0.5 M with 0.740 V (see Table 2). Calcium chloride's standard deviation regarding its average voltage per concentration was 0.021. Accordingly, sodium chloride was the electrolyte that generated the greatest voltage for the electrolytic cell on average. It was followed by potassium bicarbonate and then calcium chloride that performed the weakest in terms of conductivity. There appears to be no specific trend for the concentration of

electrolyte and generated voltage, and based on the low standard deviations, the differences are not significant; however, there is a clear differentiation among voltage output and the type of electrolyte. Across all three electrolytes, the highest generated voltages occur at different concentrations. Regardless, based up the collected data, the applicable electrolyte can be implemented into an electrochemical reduction process based upon desired conductivity now that voltage outputs have been determined.

Table 1: The size, ability to plate an electrode, suspension, and visibility of copper nanoparticles following varied inductions of silica and doping acids. Unless otherwise specified, the synthesis procedure will use 4 M sodium hydroxide, 0.5 M copper nitrate, and no silica.

Variation of nanoparticle	Results of photon correlation spectroscopy (μm)	Ability to plate an electrode	Suspension in distilled water	Visible particles
Cu particles with 10 mL of silica after precipitation	~ 30	No	No	Yes
Cu particles with 7.5 mL of silica after precipitation	~ 30	No	No	Yes
Cu particles with 5 mL of silica after precipitation	~ 30	No	No	Yes
Cu particles with 2 mL of silica after precipitation	~ 30	No	No	Yes
Cu particles with 1 mL of silica after precipitation	~ 30	No	No	Yes
Cu particles from 0.5 M copper nitrate	> 30	No	No	Yes
Cu particles from 0.3 M $\text{Cu}(\text{NO}_3)_2$	> 30	No	No	Yes
Cu particles from 0.1 M $\text{Cu}(\text{NO}_3)_2$	> 30	No	No	Yes
Cu particles oxidized with 12 M H_2SO_4	NA	Yes	Yes	No
Cu particles oxidized with 12 M HNO_3	NA	Yes	Yes	No
Cu particles oxidized with 6 M HNO_3	~ 25	Yes	Yes	No
Cu particles oxidized with 6 M H_2SO_4	~ 25	Yes	Yes	No
Cu particles oxidized with 0.5 M H_3BO_3	~ 25	NA	Temporary suspension	Yes
Cu particles oxidized with 6 M HNO_3 with 2 mL of silica	~ 25	Yes	Yes	No

Concentration (M)	Avg NaCl (V)	Avg KHCO_3 (V)	Avg CaCl_2 (V)
0.1 M	0.840 V	0.803 V	0.799 V
0.2 M	0.810 V	0.824 V	0.769 V
0.3 M	0.823 V	0.823 V	0.749 V
0.4 M	0.846 V	0.809 V	0.748 V
0.5 M	0.795 V	0.831 V	0.740 V

Table 2: The average electrolytes' (sodium chloride, potassium bicarbonate, and calcium chloride) impact on generated voltage at differing concentrations from 0.1 M - 0.5 M.

		CO Present in the System	CO ₂ Present in the System
Graphene Electrode	Change in Fermi Energy	0.16 eV	-0.28 eV
	Change in Total Energy of the System	-43 Ry	-74 Ry
Graphene Electrode Plated with Copper Nanoparticles	Change in Fermi Energy	0.15 eV	0.19 eV
	Change in Total Energy of the System	-41 Ry	-72 Ry
Graphene Electrode Plated with Silica Supported Copper Nanoparticles	Change in Fermi Energy	0.08 eV	0.18 eV
	Change in Total Energy of the System	-42 Ry	-74 Ry

Cathode-Anode Electrochemical Analysis:

Normal Pulse Voltammetry allows for identification of potentials at Faradaic reactions through application of increasing amplitudes of potential differences in steps or “pulses.” For selective reduction to ethanol, the ideal cathode anode combination would exhibit the highest Faradaic response at -1 V, the overpotential of the reduction to ethanol. The carbon-aluminum and carbon-lead combinations (see Figures 1 and 4 respectively) were the only two that exhibited the ideal sigmoid shapes around -1 V. The carbon and lead combination visibly displayed the greatest consistency with a current increase of 2000 μ A, while carbon and aluminum displayed the second greatest consistency with a current increase of 22000 μ A. The carbon and iron (Figure 2) combination’s sigmoid shape was not present for the first trial, preventing accurate analysis. The potentials corresponding to the spikes in its data were -1.9 V and -2.7 V, far removed from -1 V. The potentials corresponding to the trials for carbon and zinc (See Figure 3) were even more sporadic. Carbon and iron had a current increase of 30500 μ A, and carbon and zinc had a current increase of 6100 μ A. Differential Pulse Voltammetry allows for the identification of potential differences of faradaic current activity. The average potential difference for the carbon and aluminum, carbon and iron, carbon and zinc spikes (see Figures 5, 6, and 7 respectively) correspond to -1.5 V, -2.4 V, and -0.27 V. Furthermore, the carbon and aluminum and carbon and iron each had one trial omitted due to irregular results, while carbon and zinc had two trials omitted. Carbon and lead (Figure 8), however, had an average potential difference of -1.2 V with three consistent trials, two of which were centered around -1 V. Thus, the data display overwhelming support for a carbon cathode and lead anode combination, due to higher consistency around -1 V. The fluctuations in data across trials for the other combinations may have resulted from minor changes in the orientation of the electrodes; however, the carbon and lead combination did not exhibit these fluctuations. Additional data is necessary to draw a clear conclusion regarding the most efficient combination.

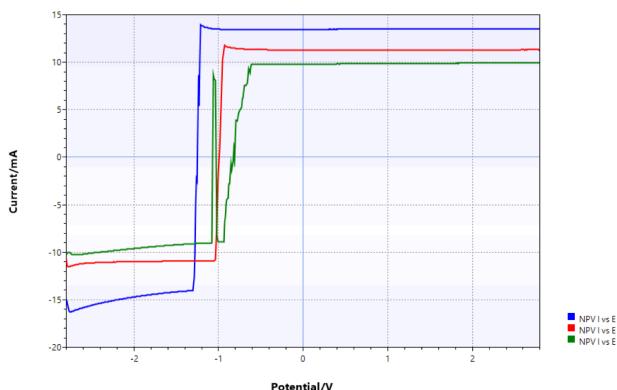


Figure 1: The normal pulse voltammograms for the three separate trials of the carbon and aluminum combination. The blue, red, and green curve correspond to the first, second, and third trial, respectively. The carbon and aluminum combination exhibit faradaic reactions around -1 V.

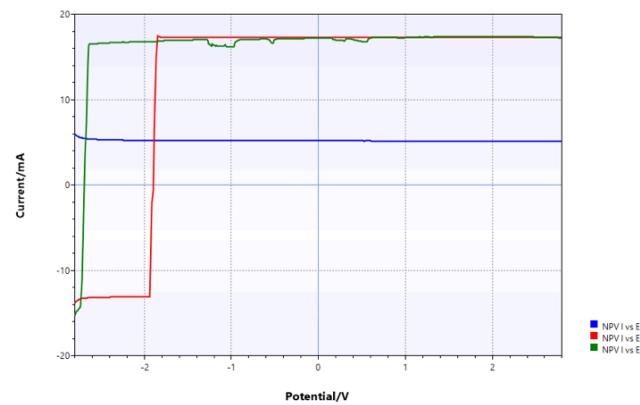


Figure 2: The curves depicting the normal pulse voltammograms for the three separate trials of the carbon and iron combination. The blue, red, and green curves correspond to the first, second, and third trial, respectively. For the blue curve, no significant data was derived due to its irregularity and is not considered in the data analysis. The carbon and iron combination displayed inconsistent faradaic reactions across different potentials.

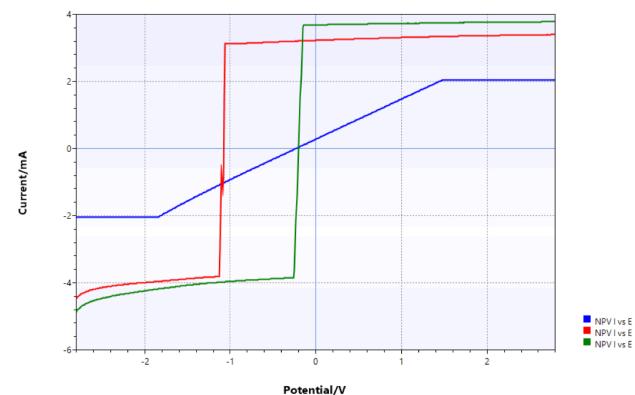


Figure 3: The normal pulse voltammograms for the three separate trials of the carbon and zinc combination. The blue, red, and green curve correspond to the first, second, and third trial, respectively. Carbon and zinc displayed inconsistent faradaic reactions at varying potentials.

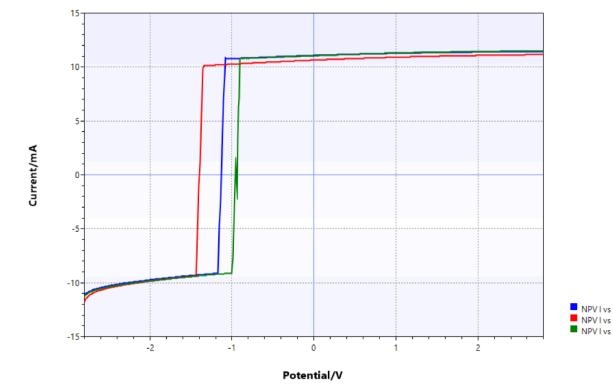


Figure 4: The normal pulse voltammograms for the three separate trials of the carbon and lead combination. The blue, red, and green curve correspond to the first, second, and third trial, respectively. Carbon and lead displayed consistent faradaic reactions around -1 V.

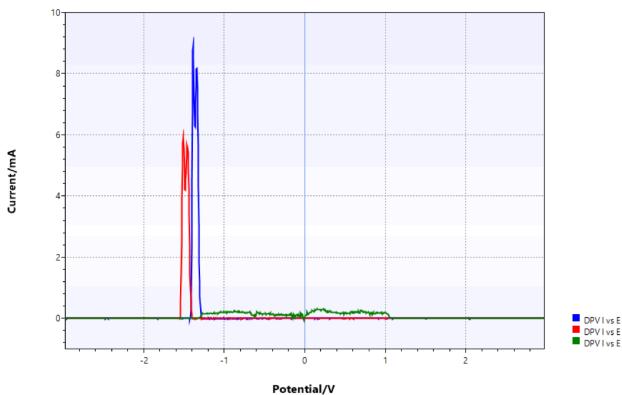


Figure 5: The various differential pulse voltammograms for the carbon and aluminum combination. The blue, red, and green curves correspond to the first, second, and third trial in the data table. The third trial was omitted from the data analysis due to its irregularity. Carbon and aluminum displayed erratic current spikes beyond -1 V.

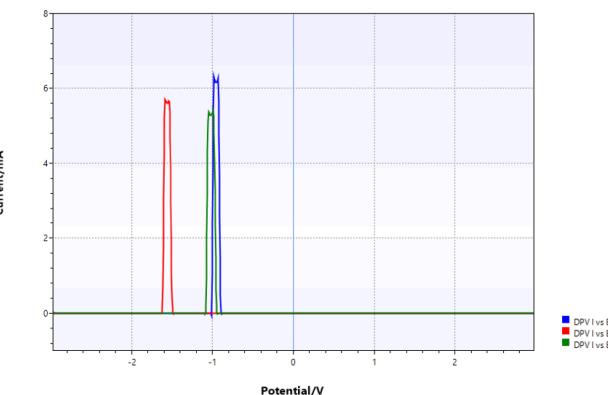


Figure 8: The various differential pulse voltammograms for the carbon and lead combination. The blue, red, and green curves correspond to the first, second, and third trial in the data table. While not the highest, carbon and lead's current response was around -1 V.

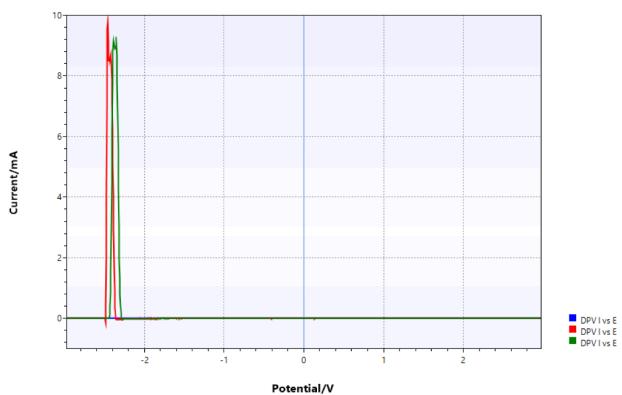


Figure 6: The various differential pulse voltammograms for the carbon and iron combination. The blue, red, and green curves correspond to the first, second, and third trial in the data table. The first trial was omitted from the table as it did not exhibit a significant spike. Carbon and iron displayed current response around -2.4 V.

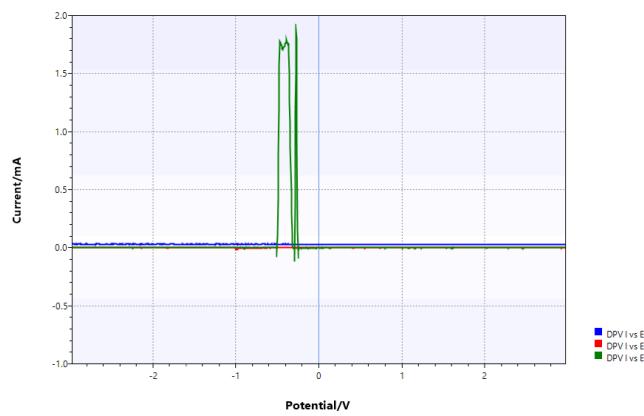


Figure 7: The various differential pulse voltammograms for the carbon and zinc combination. The blue, red, and green curves correspond to the first, second, and third trial in the data table. The first and second trials were omitted from data analysis due to their irregularity. Carbon and zinc displayed minimal current response across three trials.

Catalyst Structure and Catalyst-Cathode- CO_2 Interaction

Computational Analysis:

Self-consistent field calculations (SCF) generate approximate Hamiltonians and solve the Schrödinger equation to obtain a more precise set of orbitals. Hamiltonian refers to an operator that contains the sum of all the kinetic and potential energies in an observed system. These calculations continue to run with the new data points until the difference between two calculations is lower than the threshold value established. The Fermi energy refers to energy of the highest occupied state of the system. This means that even if the system were cooled to near absolute zero, the electrons in the system would have a kinetic energy close to the Fermi energy. Existing literature indicates the formation of carbon monoxide is an important intermediate in selective reduction to ethanol; thus, the ideal electrode variant would require minimal energy for the adsorption of carbon monoxide and much more energy for the adsorption of carbon dioxide. The graphene electrode's data provides that lower energy is necessary to be in thermodynamic equilibrium with carbon dioxide, resulting in decreased adsorption of carbon monoxide (Table 3). This indicates the graphene electrode would not enable selective reduction to ethanol. The lower energy required to be in thermodynamic equilibrium with carbon dioxide would likely result in higher adsorption of carbon dioxide than adsorption of carbon monoxide. The graphene electrode plated with copper nanoparticles required 41 Rydbergs for the adsorption of carbon monoxide and 72 Rydbergs for the adsorption of carbon dioxide. The graphene electrode plated with copper and silica nanoparticles required 42 Rydbergs for the adsorption of carbon monoxide and 74 Rydbergs for the adsorption of carbon dioxide. The increase in Fermi energy with carbon monoxide for the electrode with copper and silica nanoparticles was 0.08 eV, while the increase in carbon monoxide for the electrode with copper nanoparticles was 0.15 eV. Thus, despite the electrode with silica and copper nanoparticles requiring minimally more energy for the adsorption of carbon monoxide, the lower increase in Fermi energy suggests an ability to enable selective reduction to hydrocarbons.

Table 3: Values for the change in fermi energy and total energy of the system with the inclusion of carbon dioxide and carbon monoxide in the specified system. The graphene electrode plated with silica supported copper nanoparticles will enable selective reduction to ethanol as it requires lower energy for the adsorption of carbon monoxide.

		Fermi Energy	Total Energy of System	Harris-Foulkes Estimate
Graphene Electrode	No Additional Compounds	5.7375 eV	-1458.61 Ry	-1458.61 Ry
	Carbon Dioxide in System	5.4606 eV	-1532.76 Ry	-1532.76 Ry
	Carbon Monoxide in System	5.9146 ev	-1501.09 Ry	-1501.09 Ry
Graphene Electrode Plated with Copper Nanoparticles	No Additional Compounds	11.6081 eV	-9076.97 Ry	-9076.97 Ry
	Carbon Dioxide in System	11.7937 eV	-9149.22 Ry	-9149.22 Ry
	Carbon Monoxide in System	11.7553 eV	-9117.99 Ry	-9117.99 Ry
Graphene Electrode Plated with Silica Supported Copper Nanoparticles	No Additional Compounds	11.7711 eV	-7142.28 Ry	-7142.28 Ry
	Carbon Dioxide in System	11.9534 eV	-7216.36 Ry	-7216.36 Ry
	Carbon Monoxide in System	11.8538 eV	-7184.60 Ry	-7184.60 Ry

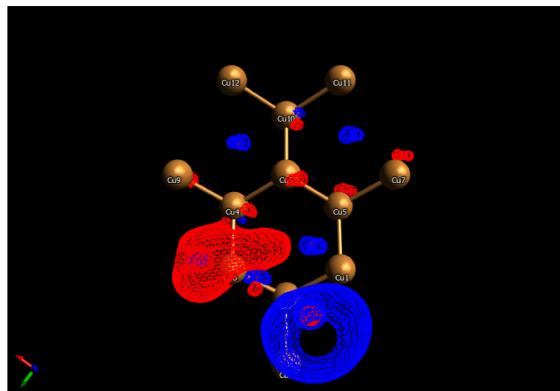


Figure 9: A visualization of the LUMO of copper mimicking the shape of the graphene molecule. In this instance, geometric optimization was implemented to derive a molecular structure with high stability, with the structure's lowest unoccupied orbital depicted above.

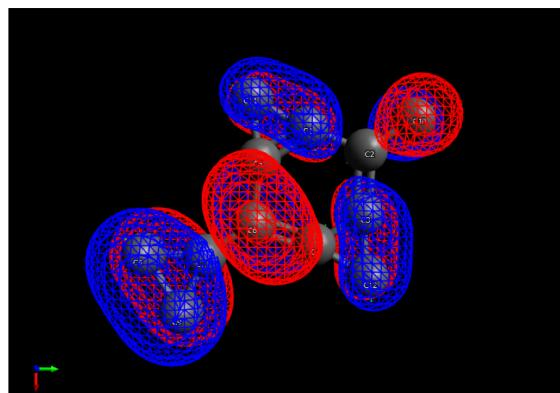


Figure 10: A visualization of the LUMO of the graphene molecule. Geometric optimization was utilized to discover the molecular structure in which energy is the lowest; therefore, yielding the highest stability.

Conclusion

Although the focus of this investigation was solely on concrete electrochemical aspects, the integration and culmination of findings from each phase has significant implications in innovating fuel synthesis for generations to come. The aspects of electrochemical reduction were isolated and tested to determine the optimal variance, and when put together for potential wide scale application, it can become greatly beneficial to remediating human environmental impact. It is known that most of the environmental deterioration of the Earth is caused by human fuel consumption. Mass carbon emissions are polluting the atmosphere and leading to a rise in global temperatures. If the current infrastructure moved away from fossil fuels and towards carbon dioxide reduced ethanol, especially with the implementation of captured carbon dioxide and renewable energy, the net output of carbon dioxide would reduce substantially, and the adverse effects of carbon emissions along with it.

From a purely economic standpoint, the utilization of synthesized ethanol from the reduction of ethanol has significant implications in the future of national expenditures, as well as the energy industry as a whole. The current most abundant source of energy are fossil fuels such as coal, petroleum, and natural gas. These products are becoming increasingly scarce with each coming year. As a result, it is becoming more of a financial burden. Eventually, human consumption of these fossil fuels will inevitably outpace Earth's supply, forcing humans to become entirely fossil fuel independent. Until then, their costs will continue to become a deeper economic pit. One of the greatest benefits is that synthesizing ethanol from carbon dioxide is a renewable process in which the ethanol output will not run out. Furthermore, ethanol is compatible with the vehicle infrastructure of today. As opposed to hydrogen fuel and other biofuels, entirely new engines do not have to be developed for the fuel to be implemented. This means that the hundreds of millions of cars do not need to be modified, saving even more money. Ethanol from carbon dioxide is essentially carbon neutral as well, therefore the costs of environmental remediation that fossil fuels are associated with do not apply here. In looking towards a more economically beneficial fuel alternative, let alone environmentally friendly, ethanol from reduced carbon dioxide is optimal.

Suggestions:

The means of precipitation-gel catalyst synthesis, while cost-effective, does not amount to the mass production of the electrochemical reaction that other methods can. One example that could be further investigated is chemical vapor deposition in which precursor chemical reactions are able to coat substrates with immense precision. Additionally, the implementation of molecular beam epitaxy has the ability to grow catalyst crystals at the atomic level. A last suggestion for the future of this investigation is to delve into utilizing Environ in Quantum Espresso. This would enable linearized Poisson-Boltzmann models with the addition of an electrolyte, taking in an additional factor for computation.

■ Methods

Copper Nanoparticle Synthesis:

Three groups of copper silicon dioxide nanoparticles were synthesized (unaltered, nitrogen-doped, and sulfur-doped). To generate the initial copper silicon dioxide nanoparticles, 2.6 mL of 4 M sodium hydroxide was added to a 50 mL beaker. 10.2 mL of fully saturated copper nitrate was then introduced into the solution where it was placed on a magnetic stirrer. A stirrer was placed in the beaker and the solution was let to stir for 10 minutes, after which 5 mL of colloidal silica was immediately added. This was repeated with 1/3 of the samples being nitrogen-doped by pouring 5 mL of 6 M nitric acid and another 1/3 of the samples being sulfur-doped by pouring 5 mL of 6 M sulfuric acid to the catalyst solutions. Subsequent trials modified the amount of doping acid and the amount of silica. All samples were then placed under photon correlation spectroscopy, a technique that utilizes light diffraction patterns from collisions with nanoparticle samples, to determine the particle sizes of each catalyst.

Electrolyte Conductivity Investigation:

Three electrolytes (sodium chloride, potassium bicarbonate, and calcium chloride) were tested on the basis of conductivity. Beginning at 0.5 M, 300 mL of each electrolyte was poured into a 500 mL beaker. A copper cathode and a zinc anode were inserted, secured by a sheet of parafilm. A voltmeter was then attached accordingly and utilized to measure the voltage output in the initial 5 seconds. The electrolyte solutions were then diluted and tested for potential difference at 0.4 M, 0.3 M, 0.2 M, and 0.1 M. Measurements were recorded over 3 trials per electrolyte per concentration.

Cathode-Anode Electrochemical Analysis:

A single compartment electrochemical cell was created using 2 electrodes and a beaker (capped off with parafilm). The cell was filled with 355 mL of carbonated water to act as carbon dioxide dissolved in water. A carbon electrode was utilized as the constant cathode for the entire experimentation while the anodes tested varied from aluminum, iron, lead, and zinc. To test each anode combination an EmStat3 Potentiostat applied to the cathodic and anodic compartments of the electrochemical cell was then connected to a recording device and PSTrace Software was opened. The techniques conducted were Normal and Differential Pulse Voltammetry with the following specifications: -2.98 V (E begin), 2.98 V (E end), 0.005 V (E step), 0.025 V (E pulse), 0.07 s (t pulse), and 0.025 V/s (scan rate). Measurements for each technique were collected in real time. This process was repeated for 3 trials for each anode variation set up (contents cleaned upon reuse).

Catalyst Structure and Catalyst-Cathode-CO₂

Interaction Computational Analysis:

For the generation of the Quantum Espresso model, a graphene electrode had to be created. In the Burai interface, the graphene electrode was produced by importing the molecule from Materials Project. A supercell was then produced to accurately depict an electrode. The dimensions of 3 x 3 x 2 were used to create the electrode surface. Atoms that made up

the outside of the supercell along with relevant interior atoms were changed to copper to simulate the plating. The top layer of the supercell had no copper atoms as copper nanoparticle plating will not cover the upper portion of the electrode. To generate the variation necessary for carbon monoxide, a carbon atom and an oxygen atom were manually inserted into the supercell. To generate the variation for carbon dioxide, a carbon atom and two oxygen atoms were manually inserted into the supercell. Depending on the interface used, the calculation was completed by setting the Burai mode to SCF and autogenerating the necessary values. The threshold energy necessary for convergence, however, was lowered by an order of magnitude of two in order to be able to achieve convergence in a reasonable amount of time. The calculation was run through command prompt by first pasting the path of the plane-wave self-consistent field executable into the command window. The path of the -input file was then pasted into the command window, surrounded by a less than symbol on the left side and a greater than symbol on the right side. The path of the blank output file was then pasted into the command window to complete the command. Additionally, to perform Orca software specific calculations, Avogadro first needed to be opened. A graphene molecule was created rather than importing from Materials Project. A geometry optimization was conducted to optimize bond angles and the positioning of the atoms. An input file was created through extensions. The auto-generated basis sets (a set of DFT functions) were used, but the type of calculation was changed to geometric optimization rather than single point energy. This process was repeated but rather than producing the shape of a graphene molecule with carbon atoms, the same shape was produced with copper atoms.

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