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September 2022

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Abstract

This report describes our efforts to develop a partial electrochemical oxidation process to produce formaldehyde selectively from methanol. The effort examined numerous potential anode materials in pursuit of 70% Faradaic efficiency for conversion of methanol to formaldehyde. Among the various electrode materials tested herein both Pt and PtRu were identified as the most promising catalysts in this process as the Faradaic efficiency obtained in these cases are 40% and >70% respectively. Several other 3d transition metals, Pt group metals and their alloys were also studied in which the Faradaic efficiency was obtained within 5-30%. In case of Pt and PtRu bulk metal electrode shows higher selectivity to formaldehyde compared to their nanostructured materials. Based on the literature, nanostructured Pt and PtRu are considered as active catalysts for methanol fuel cells, thus, lower selectivity to formaldehyde with nano Pt and PtRu in our case was attributed to their preferential oxidation of methanol to CO_2. Severe catalyst deactivation was noted when 0.5 (M) sulfuric acid was used as the electrolyte irrespective of catalyst formulation. On the other hand, much higher activity and selectivity for formaldehyde was noted when alkaline electrolyte was employed during oxidation. Considering selective electrochemical oxidation of methanol to formaldehyde is an area which is underexplored as of today, our findings about catalyst formulation and process condition is noteworthy in this direction. Both bulk metal electrodes of Pt and PtRu may be cost prohibitive and thus present challenges to the scale up this technology. Therefore, we recognize that additional efforts are needed to develop catalysts with high activities and Faradaic efficiencies similar to bulk electrodes for the electrooxidation of methanol to formaldehyde.

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1.0 Introduction

Ethylene glycol is a critical precursor to many consumer products (polyester fibers) and plastics (PET). The proposed pathway will enable production of ethylene glycol at a lower cost than the conventional fossil-based process (IHS). The goal of this project was development or discovery of a suitable anode for electrooxidation of methanol to formaldehyde at high Faradaic efficiencies. Success in the objective would provide a clear path to an improved route to ethylene glycol via conversion of CO_2. The proposed process will use electrochemical oxidation of methanol to formaldehyde to thermodynamically drive the electrochemical reduction of CO_2 to CO. Coupling these two electrochemical steps results in a theoretical total cell potential of 0.02 Volts Figure 1. Together, the two half-reactions form an overall process that produces formaldehyde, which is ultimately converted to EG. By coupling the oxidation of methanol to formaldehyde (anode) in an electrochemical reactor, the reduction of CO_2 to CO (cathode) is "paid" for with energy that would otherwise be wasted in the traditional/current thermochemical methanol oxidation process. Further, this process will require no additional reaction steps compared to the conventional process. The feedstock for the process is readily abundant from a wide variety of sources. For example, a typical ethanol plant produces 1.5x108 kg/year of CO_2, which if converted to EG would replace half of a percent of the worldwide EG supply. The technology development required to enable this process is a suitable anode for oxidation of methanol to formaldehyde. While methanol fuel cells have been shown to fully oxidize methanol to carbon dioxide, little work has focused on partial oxidation of methanol. For this process to be commercially viable, the oxidation of methanol must produce formaldehyde selectively.   As a result, the most important metric pertaining to this work is the selectivity for the partial oxidation of methanol to formaldehyde. Given this critical metric, we note that Pt has shown promise for partial methanol oxidation to formaldehyde, with high selectivities depending on both the catalyst structure and other process variables. Therefore, the focus of the LDRD project efforts will be on development of a suitable anode electrocatalyst with high selectivity for methanol oxidation to formaldehyde. Electrocatalytic reduction of CO_2 will use a Ag catalyst due to its high Faradaic efficiency for CO. The chemical conversion of formaldehyde to MEG is known chemistry.
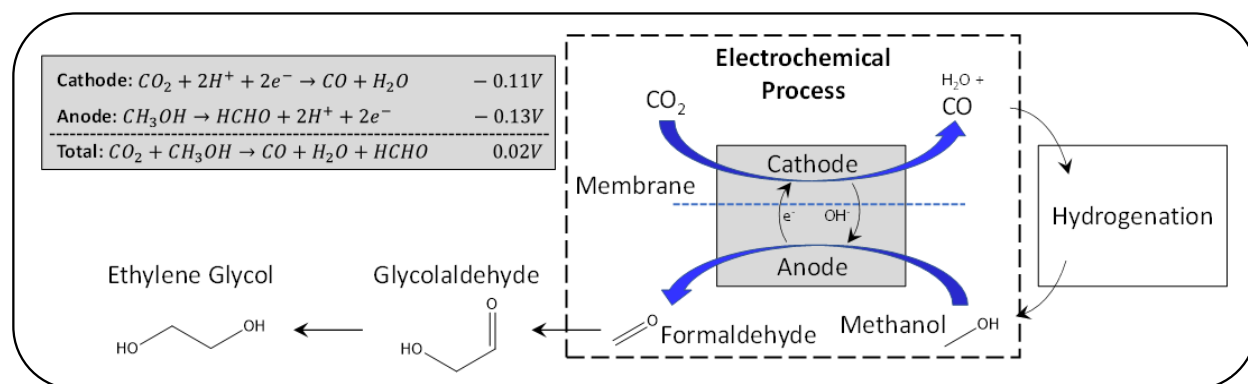

Figure 1. Integrated electrochemical cell matching the reduction of CO_2 to CO and the partial oxidation of methanol to formaldehyde resulting in a total cell voltage of 0.02V

1.1　State of the Art in MEG Production

Currently, nearly all industrial MEG is produced starting from petro-derived ethylene via epoxidation to ethylene oxide as shown in Figure 2. Improvements such as Shell's OMEGA process have maximized the efficiency of this pathway close to 99% but still result in significant carbon emissions and a reliance on petroleum fuels. The recent development of the Eastman/Davey process as the most economical route to ethylene glycol has established a new route to ethylene glycol from CO and syngas-based sources. However, with coal as the primary syngas source, the carbon intensity of production remains just as high as the ethylene pathway. True decarbonization cannot be achieved through the current state of the art processes without leveraging new feedstock sources. Other processes have been industrially explored such as the direct combination of carbon monoxide and hydrogen to MEG. This process pioneered by Union Carbide required pressures as high as 1000-3000 bar using catalysts based on Ruthenium or Rhodium. The selectivity in these reactions were as high as 65% to MEG with methanol being the major side product. Another example is the hydrogenolysis of oxalate esters. This process, developed by Union Carbide and Ube Industries involved synthesis of dibutyl oxalate from n-butanol, carbon monoxide, and oxygen followed by hydrogenolysis of the resulting oxalate ester to yield MEG and n-Butanol. (Witcoff, et al. 174-177). It should be noted that, a now expired patent exists which proposes the electrochemical oxidation of methanol vapor to formaldehyde and methylal with methyl small quantities of methyl formate (Fedkiw, 1993). The general concept of the invention being a continuous electrochemical process in which methanol is oxidized on an anode consisting of a hydrated sulfonated fluorocarbon membrane resin impregnated with a cationic platinum source. The cathode may be either directly contacted to the membrane or separate in the cathode compartment. One key conceptual difference from our work is that the cathode reaction in said invention is the oxygen reducing reaction. The total cell voltage being between 0.6-1.2 V
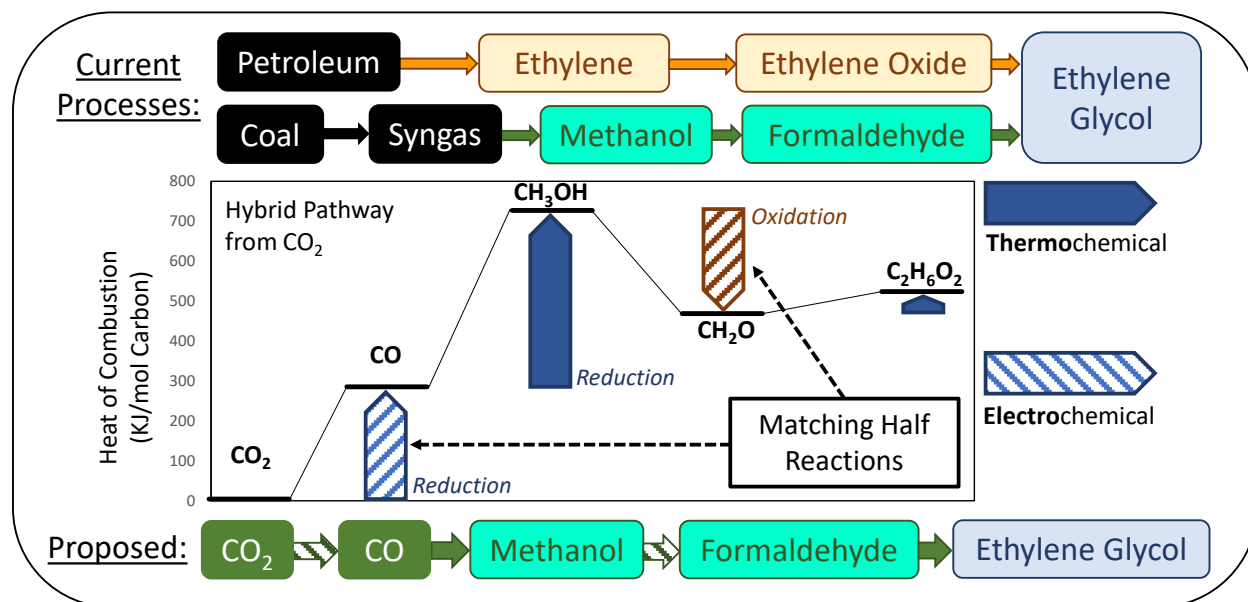

Figure 2. Comparison of current production routes to ethylene glycol with the proposed hybrid thermo/electrochemical route from CO_2

Formaldehyde Production is dominated by two routes: dehydrogenation/oxidation and pure oxidation of methanol. Other pathways have been developed. The dehydrogenation/oxidation route is a silver catalyzed process while the oxidation route is catalyzed by a ferric oxide molybdenum catalyst. While the pure oxidation route results in better yields of formaldehyde, the waste gases are reportedly difficult to manage and, therefore, the silver catalyzed route is prefferd (as of 2013). (Witcoff, et al. 438-439). Other approaches have been developed and patented including the hydrogenation of formic acid to formaldehyde (Masel, 2013)

1.2   Impacts

Our proposed process allows for significant decarbonization of ethylene glycol production by using CO_2 as a feedstock. Though other competitors have also recently begun developing electrochemical pathways from CO_2, their direct approaches also produce a range of C_4 compounds in addition to ethylene glycol (lack of selectivity). Our hybrid process selectively produces ethylene glycol, which is a valuable product with an existing market. In addition, the electrochemical reduction of CO_2 to CO is often coupled with a matching oxygen evolution reaction (OER), which is typically supplied by the inefficient generation of O_2, thus making the CO_2 reduction step extremely energy intensive. Our process uniquely eliminates this major barrier by leveraging the partial oxidation of methanol to formaldehyde as the matching half reaction to bring the total cell voltage to near zero.

While the 6-electron electrooxidation of methanol to CO_2 has been well explored for fuel cell applications ($CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$), the partial electrooxidation of methanol is an underdeveloped pathway which presents a technological gap that we attempted to address in this LDRD project. Success in our proposed approach is the most likely path to rapid industrial implementation, as it is developed around the same chemical reaction steps and unit operations of the existing Eastman/Davey process and can be incorporated into existing facilities without needing additional reactors. Such implementation would leverage the facilities and scale advantages of existing plants without the extremely high risks and costs associated with the development of an entire stand-alone plant based on a new technology.

The second major impact will be the decarbonization of a significant portion of the petroleum chemical market. Ethylene oxide-based production for ethylene glycol is currently ranked in the top 10 most GHG emission intensive chemical industries (2.6% global share). This problem will only become greater as demand for PET and polyester products derived from MEG increases, with estimated MEG market growth at 4% CAGR. The growing use of coal as a feedstock on the horizon will increase carbon emissions even further compared to the standard process. Successful implementation of this technology using renewable electricity would help eliminate 0.512 tons CO_2/tons MEG, the current emission rate for ethylene glycol production using the ethylene oxide process. Furthermore, effective development of this anode technology will provide an energy efficient and economically viable half reaction to drive the carbon capture of CO_2 to produce syngas. The production of syngas and syngas-derived methanol represents an even greater source of carbon emissions (9.2% global share GHG), that may be reduced using this technology.

The most significant impact will be the economic benefit to existing MEG manufacturers. By leveraging low-cost CO_2 feedstocks, feedstock costs can be reduced by 27% relative to the conventional route to produce EG today, from $26.2/kg-mol EG to $19.2/kg-mole EG (average 2009-2018 USGC price basis and including a 0.5V overpotential). The existing market is highly competitive and dependent on competitively priced ethylene and coal resources; using CO_2 as a feedstock would help decouple ethylene glycol production from the volatility of the petroleum market.

Alternatively, one could consider the impact to the formaldehyde market and producers. The formaldehyde market is expected to surpass a valuation of USD 6,160 million by 2027 (Global Market Insights Inc.). As of 2020 the market size for formaldehyde exceeded 4,350 million $US with projections to expand with a CAGR of 5% from 2021 to 2027. Formaldehyde can be used to directly and indirectly produce several chemicals and products including urea formaldehyde resin, ethylene glycol, melamine resin, phenol formaldehyde resin, polyoxymethylene plastics, 1,4-butanediol, and methylene diphenyl diisocyanate. Formaldehyde is also a precursor to polyfunctional alcohols such as pentaerythritol, which is used to make paints and explosives. Other formaldehyde derivatives include methylene diphenyl diisocyanate, an important component in polyurethane paints and foams, and hexamine, which is used in phenol-formaldehyde resins as well as explosives.

2.0   Materials and Methods

The potentiostat used to carry out this work was an Ametek Versastat 4. Electrooxidation of methanol was conducted either in an H-Cell with a total volume of 50 mL in each compartment using a 3-electrode configuration or using an H-cell with a working compartment with a volume of 25 mL separated from the smaller auxillary compartment of 10 mL (Basic electrochemical H-cell setup, REDOXME). Except where otherwise indicated, Pt wire was used as the counter electrode to perform the experiments demonstrated herein

In the case of experiments with acid electrolyte, solutions of methanol (approximately 10 wt%) and sulfuric acid (0.5 M) in water solutions were placed in the anode compartment while Sulfuric acid (0.5 M) in water solutions were placed in the cathode compartment.   The reference electrode was an aqueous Ag/AgCl wire in a glass compartment with a vycor plug. In the case of experiments with alkaline electrolyte, solutions of methanol (approximately 10 wt%) and NaOH (0.5 M) in water solutions were placed in the anode compartment while NaOH (0.5 M) in water solutions were placed in the cathode compartment.   The reference electrode was an aqueous Ag/AgCl wire in a glass compartment with a vycor plug. After evaluating cyclic voltammograms, chronoamperometry experiments were carried out at various potentials and time periods.

Initial catalyst development/discovery efforts involved supporting metal on carbon type catalysts or metals on carbon felts or carbon paper by a catalyst ink method. Other electrodes were prepared by electrodeposition on carbon paper or carbon felt. A small number of experiments attempted to use metal precursors deposited on graphite as anodes.

Solution phase products were characterized by HPLC. The HPLC system includes a high performance liquid chromatography (HPLC) equipped with a Waters 2414 refractive index detector and a Bio-Rad Aminex HPX-87H ion exclusion column (300 mm × 7.8 mm) was used for analyte separation. Sulfuric acid (0.005 M) was used as eluent at a flow rate of 0.55 mL/min. Formate, formaldehyde, and methyl formate calibrations were run prior to the start of anode catalyst development and calibrations were checked later in the year to ensure stability.

Gases were sampled from the H-cell using a gas tight syringe connected to a PTFE tube at the cathode outlet. Gases were analyzed on a 4-module INFICON gc system.

3.0   Results and Discussion

Electrochemical methanol oxidation is a well-studied reaction thanks to strong interest in its application in methanol fuel cells (in which methanol is completely oxidized to CO_2). Accordingly, most methanol fuel cells use noble group metals (alone or in combination with other metals) as the anode and operate at potentials sufficient to drive the reaction to complete oxidation of methanol to CO_2. However, it is well known that there are numerous products which may result from the incomplete electrooxidation of methanol including formaldehyde, formate/formic acid, and carbon monoxide (figure 1).

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$CH_3OH + H_2O \rightarrow HCOOH + 4H^+ + 4e^-$$

$$CH_3OH + H_2O \rightarrow CO + 4H^+ + 4e^-$$
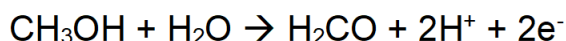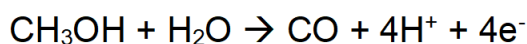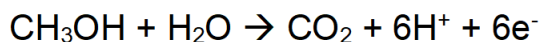$$CH_3OH + H_2O \rightarrow H_2CO + 2H^+ + 2e^-$$

Figure 3. Potential products resulting from electrochemical oxidation of methanol.

Due to the interest in methanol fuel cells, the associated literature has focused on improving the catalysts, ion exchange membranes, electrolytes, and reaction conditions to drive the reaction to complete oxidation of methanol. Perhaps unsurprisingly, there are few examples of published literature focusing on the partial oxidation of methanol to formaldehyde. That said, there have been a handful of notable studies which are focused on partial oxidation of methanol, in some cases, with promising results. For example, using noble metal catalysts and acid electrolytes, Korzeniewski et al achieved a formaldehyde yield of ~30% in a methanol oxidation experiments (Korzeniewski et al. 1998).

Other relevant findings include published studies documenting the selective electrooxidation of alcohols to aldehydes. For example, Wang, et al. demonstrated selective partial oxidation of benzyl alcohol to the corresponding aldehyde using carbon anodes in a 99% yield using a continuous-flow reactor (Wang et al, 2019). Further, Suga et al studied carbon-fiber threads supporting Au nanoparticles for catalytic electrooxidation of alcohols in a flow cell with Faradaic efficiencies (F.E.'s) >90%for oxidation of select primary alcohols to corresponding aldehydes and carboxylic acids with oxidation of secondary alcohols, resulting in the formation of the corresponding ketones in approximately 50% F.E. (Suga et al 2021).

Our initial experimental approach to electrocatalyst development/discovery and screening involved deposition of carbon supported metal catalysts on carbon felts ($6.25cm^2$) by typical catalyst ink methods. These initial experiments were conducted in a 3-electrode configuration in an H-Cell with a volume of 50 mL in both the anode and cathode compartments. The electrolyte for this series of experiments was 0.5 M sulfuric acid with methanol at approximately 10 weight percent in water. Under these conditions, we found that the methanol oxidation currents for the resulting anodes produced in this manner were far too low to be practical. It was, therefore unsurprising that no products could be characterized in anode solutions by HPLC. Some of the catalysts evaluated by this method are listed in table 1.

In related studies, metal precursors were deposited on carbon felt via ink methods. Even in this case, oxidative currents were either typically too low to be practical and in many cases, the metals were observed separating from the felt and settling in the anode compartment and the oxidation currents gradually fell to near 0 mA. In another unsuccessful approach, we attempted some experiments in which metal precursors were deposited on graphite which resulted in low currents.

Following these challenges, we decided to pursue metal deposition on carbon felts as potential anode materials. Our evaluation included single metals and combinations of metals. However, using this approach, regardless of metals supported (Pd, Pt, Ni, Cu and combinations thereof), no formaldehyde (nor formic acid/formate) product was observed by HPLC analysis of the anode compartment solutions. This was true even in cases of several Coulombs of charge being passed.

Table 1. Compositional Data for representative M on Carbon catalysts

Example Catalyst	Pt	Ni	Re	Fe	Ir	CeO$_2$	Rh	Co	Pd
	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%	Wt%
1		4	4						
2	0.02	5							
3	1			5					
4					3	3			
5							5		
6				0.72				2.5	0.45
7			4.8					5	0.9
8	1			5					

Following the attempts to support metal on carbon catalysts on carbon cloth, it was clear that higher metal loadings would be required to yield practical currents. Accordingly, we then pursued anodes based on single metal and mixed metal combinations supported on carbon paper. In terms of currents produced, we observed significantly improved results. Some of the representative metals included Pd, Pt, Ni, Cu, Co and bimetallic combinations thereof. However, rather than a full presentation of all experimental results, it is far simpler to summarize that under both alkaline and acidic conditions, in the vast majority of cases, very little formaldehyde was produced. In the case of acidic electrolytes, under chronoamperometry, the currents rapidly tapered to nanoamps range. In the case of alkaline electrolytes, we did observe improved and more steady currents under chronoamperometric conditions, however, in most cases, the main product observed in the anode solution was formate.

To some degree, the results appear to be in agreement with what the literature suggests for partial electrooxidation of methanol – smaller particle sizes tend to result in more complete oxidation of methanol to carbon dioxide. Although we cannot rule out the possibility of future success using this approach, literature precedent and our own results indicate that electrodeposited and nanoscale electrocatalysts may remain a challenging area of research with respect to methanol to formaldehyde electrooxidation without additional research and resources. It is known from previous studies reported in the literature that specific facets exposed in case of bulk metal is

different than its nano congeners. While bulk metal exhibited more planar sites, corners and edge sites are predominant in case of nanoparticles.(Le Valant, et al, 2016)(Van Hardeveld and Hartog, 1969) We speculate that higher selectivity to formaldehyde observed with bulk metal electrode could also be attributed to facet dependent activity. However, further research will be needed to better understand the fundamentals of catalyst composition in conjunction with catalyst size/structure as applied to electrooxidation of methanol to formaldehyde.

The small particle size hypothesis is exemplified in a comparison of platinum foil and platinum electrodeposited on carbon paper. For example, in our hands, the best results for Platinum foil catalyzed conversion of methanol to formaldehyde realized 40% F.E. while the best results observed for platinum deposited on carbon paper was an 18% F.E. to formaldehyde (figure 4). Relatedly, the phenomenon is observed yet again in the case of PtRu catalysts. In our studies, PtRu foil (90:10) was found to have a much higher F.E. (66%) to formaldehyde compared to PtRu on cloth (<5% F.E.) (figure 5). In both cases, the current per unit mass of the supported nanoparticle cases is significantly higher than the bulk metal or alloys on a mass basis (catalyst area not available for the nanoparticle catalysts).   A reasonable hypothesis for this phenomenon is given by Korzeniewski et al. that more complete methanol oxidation is enabled in nanoscale catalyst due to the increased odds of partial oxidation products encountering active catalyst sites which are dispersed on the electrode surfaces. (Islam et al., 2007), (Childers et al, 1999), (Korzeniewski et al, 1998)
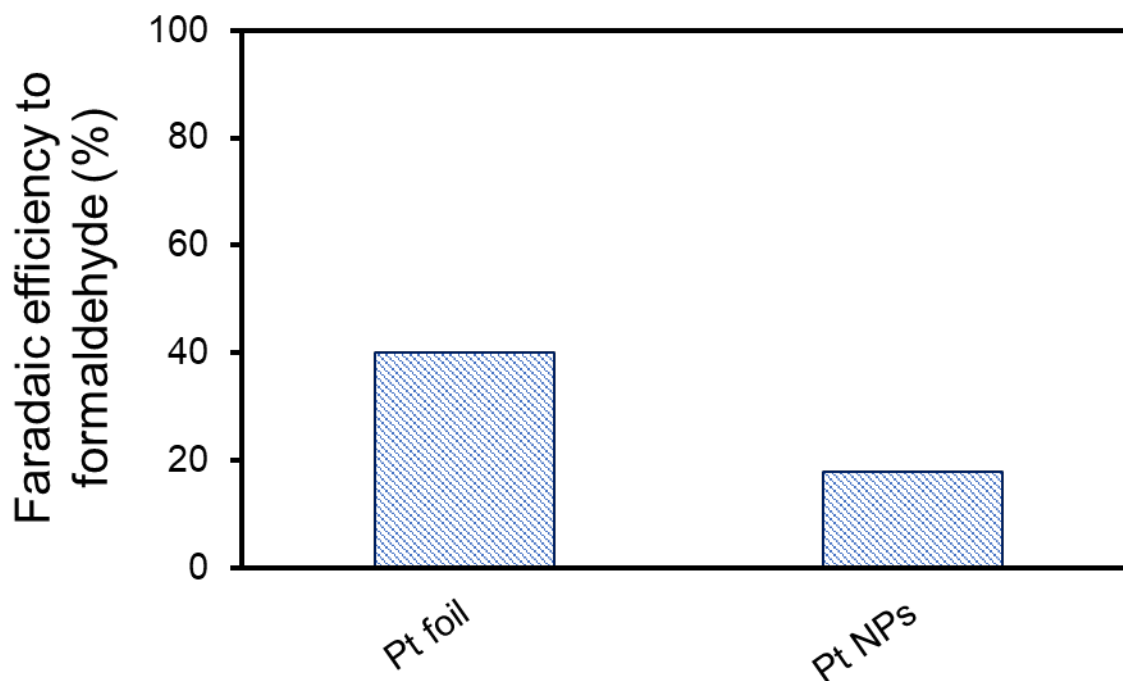

Figure 4. Direct Comparison of bulk Pt foil vs, electrodeposited Pt on carbon paper for MeOH oxidation to Formaldehyde. Experiments carried out at ~0.4 V vs ref in aqueous NaOH electrolyte
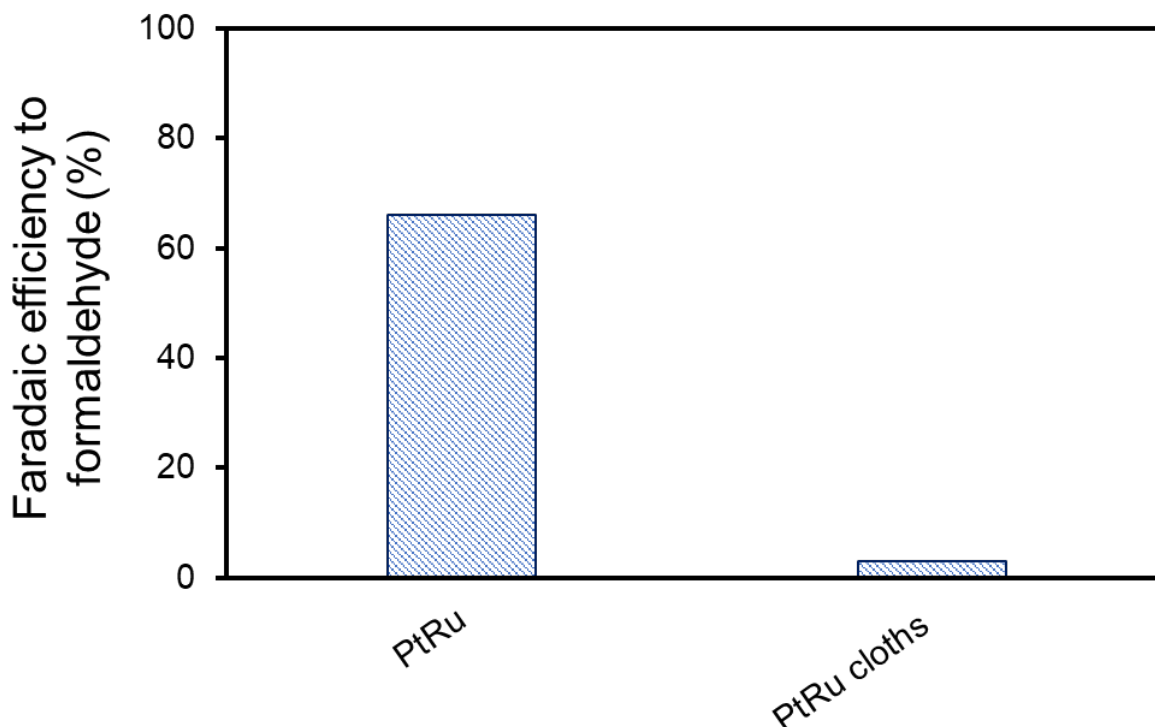
Figure 5. Faradaic Efficiencies of PtRu vs PtRu foil for MeOH oxidation to Formaldehyde. Experiments carried out at ~0.4 V vs ref in aqueous NaOH electrolyte

Pursuing yet another avenue, bulk metal and bulk alloys were evaluated as potential anode materials. In figure 6 and table 7, select results for bulk metal and bulk alloys as anodes are summarized. The results of chronoamperometry experiments (primarily conducted at ~0.4 V vs. Ag/AgCl reference) are compared. The standouts among these results, at least in terms of Faradaic efficiencies to formaldehyde, are PtRu foil and PdNi gauze at 66% and 49% respectively. The results of our evaluation of Pt foil as an anode is within range of other studies at ~39% F.E. for methanol to formaldehyde. In addition to the results discussed herein, we note that other bulk materials were screened as anodes which resulted in solutions of formate and little to no formaldehyde being present or even cases with neither product present at detectable levels.
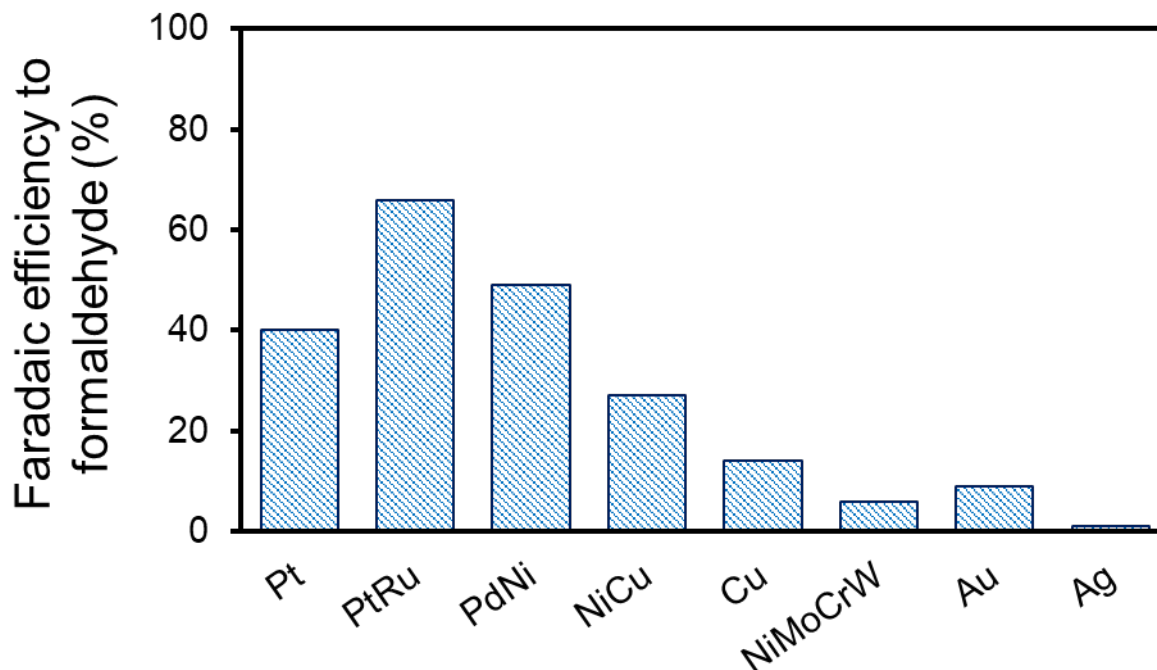
Figure 6. Comparison of bulk metal/bulk alloy electrodes for MeOH oxidation to Formaldehyde. Experiments carried out at ~0.4 V vs ref in aqueous NaOH electrolyte

Table 2. Faradaic Efficiencies of Bulk Metal/ Bulk alloys in MeOH oxidation to Formaldehyde.

| Catalyst	FE	Potential vs. Ref
Pt	40	0.4
PtRu	66	-0.2
PdNi	49	0.4
NiCu	27	0.4
Cu	14	0.35
NiMoCrW	6	0.5
Au	9	0.4
Ag	1	0.35

Our results with respect to PtRu electrodes are somewhat different than those observed by Islam, et al, in which they found that in that, in our course of experimentation, we found that PtRu bulk electrodes (foil) were capable of producing formaldehyde with >65% Faradaic efficiency while in their work, a maximum of 41% FE was recorded.(Islam, 2007) It is important to note the significant differences in our particular conditions, however. For example, the work by Islam was carried out exclusively in a solution of 1.0 M CH_3OH in 0.1 M H_2SO_4 with only short durations of chronoamperometry (180 s). Also important to note, their work was carried out in microliter volumes with the formaldehyde characterized by Hantzch-type derivatization followed by spectrofluorimetric analysis.(Nash, 1953)

Looking to thermochemical catalysis for inspiration, we evaluated bulk materials which are relevant to methanol to formaldehyde partial oxidation. It is established in the literature and industry that silver based catalysts are quite common in thermochemical oxidation of methanol to formaldehyde with yields typically ranging from 82 to 92% and catalyst lifetimes up to 12 months (Millar and Collins, 2017). Knowing this, we evaluated a silver mesh as a potential anode material. Under the conditions studied, there was no formaldehyde observed in the electrooxidation conversion of methanol. Rather, the only solution product characterized in the anode compartment was formate. Assuming purely electrochemical conversion of methanol without complicating chemical side reactions, the F.E. of methanol to formate was ~80%. However, this may not be a safe assumption as discussed below. In any case, we hope to emphasize that catalysts used in thermocatalytic transformations are not necessarily suitable in analogous electrochemical trasnsformations.

Although there are different electrochemical pathways proposed which allow for formation of formate, presented in Figure 4 is a simplified mechanism for electrooxidation to formaldehyde and formate.(Yuda, et. Al, 2022). The steps of this reaction involve adsorption of the methanol to the anode surface followed by oxidation to formaldehyde. The resulting formate could be a result of either electrooxidation or other chemical processes such at a Cannizzaro-like disproportionation to methanol and formate. (Haisch et. al., 2019).

When considering electrolytes, our early efforts emphasized the use of H_2SO_4 as the electrolyte. However, it is known that performance of platinum containing electrodes typically are improved in alkaline medium relative to acidic environments. This is thought to be due to weak binding of the products on the surface of the catalyst under alkaline conditions relative to in acidic media. Further, in alkaline environments, critical hydroxide ions are readily available in solution and can be absorbed on the anode surface resulting in methanol oxidation taking place at lower potentials. (Yuda et. al., 2022) The balanced reactions for methanol oxidation with alkaline electrolytes is as follows:

1a) $CH_3OH + 6OH- \rightarrow CO_2 + 5H_2O + 6e^-$

1b) $CH_3OH + 8OH- \rightarrow CO_3^{2-} + 5H_2O + 6e^-$
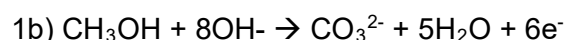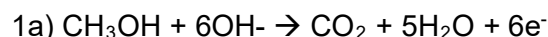
In 1b, the equation considers that under alkaline aqueous conditions, carbonate is likely to form.
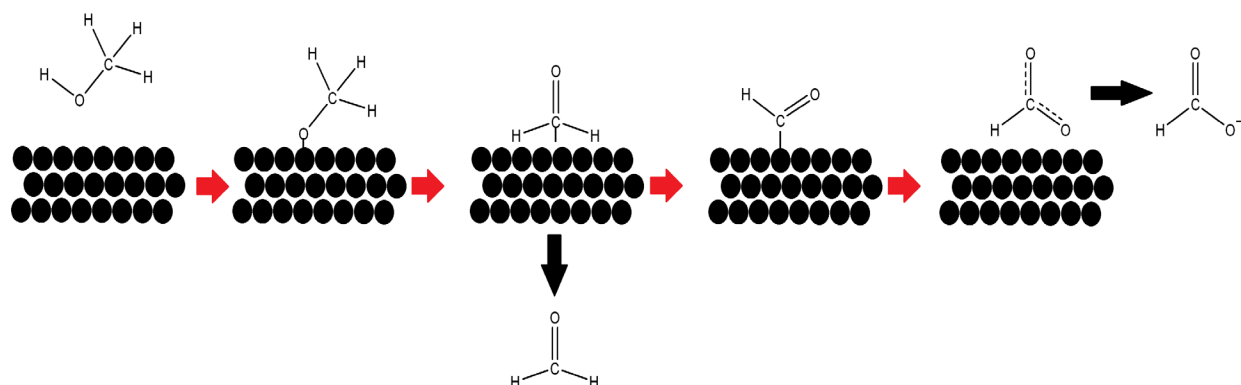

Figure 7. Simplified Mechanism for Electrooxidation of methanol to formaldehyde and formate under alkaline conditions.

In our early proposal, we proposed to evaluate metal oxide materials as potential anodes. One example of this approach is use of a RuO-Mo3 ($Ru_{0.8}Mo_{0.2}O_2$) catalyst deposited on carbon felt (10 mg catalyst on 6.25cm^2 carbon felt). This anode was evaluated in both acidic and alkaline electrolyte. In the alkaline electrolyte case, there was no formaldehyde detected in the anode compartment after chronoamperometry. When using acidic electrolyte (H_2SO_4), formaldehyde was produced with ~20% F.E. along with formate at ~30% F.E. On one hand, it is encouraging that any formaldehyde was detected at all; on the other, these values are quite low overall. Although the particle size of the catalyst is not specifically known, it is likely that the small particle size was a contributor to the low F.E. to formaldehyde.
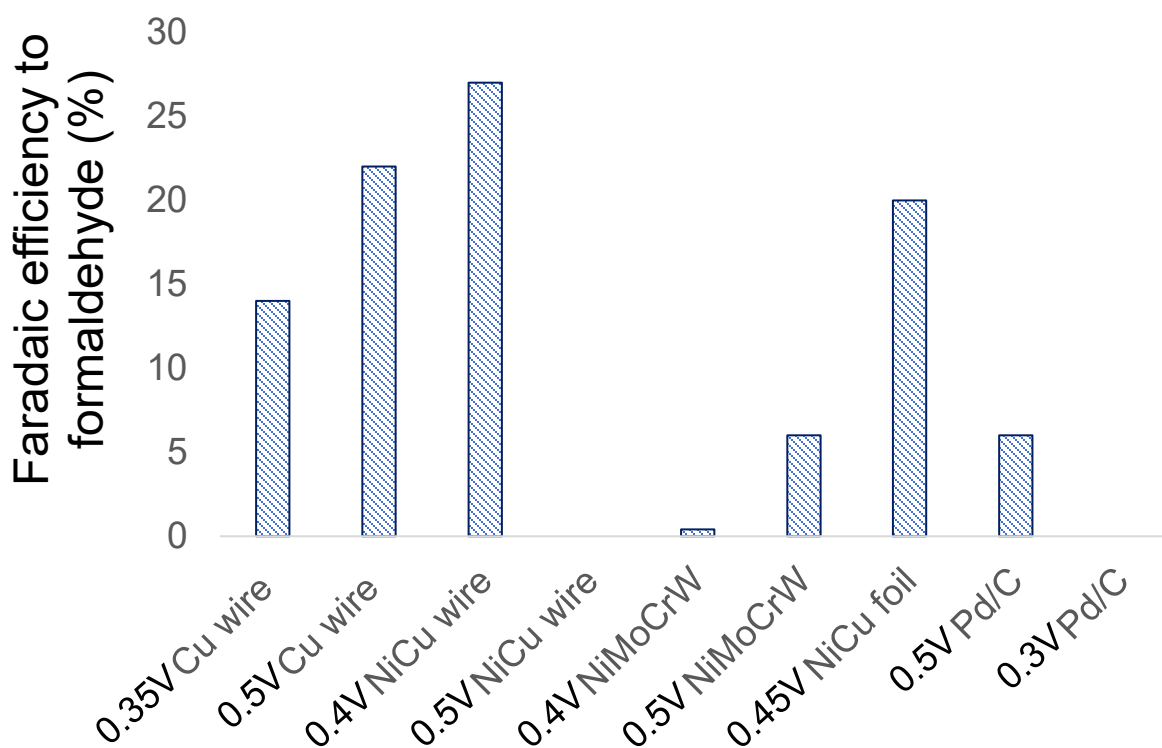

Figure 8. Faradaic Efficiencies of various bulk metal and bulk alloys for MeOH oxidation to Formaldehyde. Experiments carried out at varied potentials vs Ag/AgCl in aqueous NaOH electrolyte

In evaluation of the combined cell, we carried out experiments using a platinum wire as the anode with various cathode materials under alkaline conditions. The cathode compartment was constantly bubbled with CO_2 while the anode was as in previous experiments with ~10 wt% methanol in a 0.5M KOH anolyte. The cathode materials evaluated were NiCu foil (6.25 cm^2), NiCu on carbon paper, and CoCu on carbon paper. It should be noted that the gaseous products observed from the anode compartment were a mixture and not pure CO. The use of NiCu foil resulted in currents far too low to be practical while the experiments involving CoCu on carbon paper and NiCu on carbon paper had F.E.'s ranging from 10-33% for methanol oxidation to formaldehyde.

Additional experiments were carried out in aqueous alkaline electrolyte using gold mesh or silver wire as a cathode an PtRu foil or Pt wire. Figure 9 shows the cyclic voltammogram of the PtRu anode in aqueous alkaline electrolyte in orange and the same anode after the addition of methanol (potentials vs. Ag/AgCl reference).
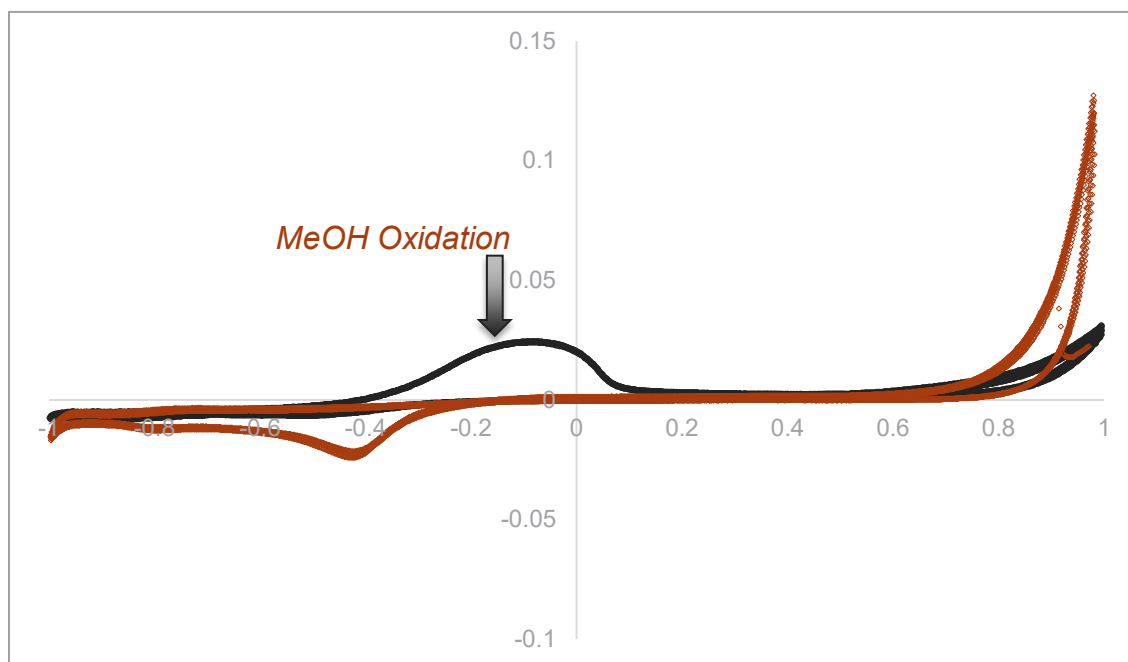

Figure 9. Cyclic voltammograms of and PtRu electrode in 1.0M KOH (orange trace) and PtRu electrode with 10 wt% methanol added (black trace).

The results from the experiment using a gold cathode and PtRu anode resulted in Faradaic Efficiency of >70% for formaldehyde from methanol. Like other similar experiments, the gases collected from the cathode compartment were a mixture of products. It should be noted that the current densities were quite low at ~0.05 mA/cm^2. However, when switching to a fresh anion exchange membrane, current density improved to 0.5 mA/cm^2 with the Faradaic efficiencies toward formaldehyde for the same electrode configuration remaining in in excess of 70%. These results meet the project objective of 70% F.E. using a well-known material and leave us encouraged that further research and development will lead to an improved catalyst with higher F.E. and improved current densities.

4.0   Conclusions

While the project objective of >70% Faradaic Efficiency *with new catalysts* was not achieved, we did find conditions using bulk metal alloy electrodes in which F.E.'s appear to exceed 70% (in a few cases appearing to exceed 80% F.E.). These findings in combination with, albeit limited, literature precedent lead us to believe that the project goal is achievable with additional investment. Our research leads us to the conclusion that any future work should emphasize the integrated cell rather than focusing only on the anode. Further, additional research efforts might be directed toward development of anodes composed of bulk metal alloys and/or nanocatalysts with large facial areas or containing facets similar to bulk electrodes.

Some challenges encountered in this work were related to the difficulty of quantifying formaldehyde in aqueous solutions at low concentrations. While chemical derivatization and analysis by spectrofluorimetric methods would have allowed for improved sensitivity, the time investment required to quantify the presence of such low quantities of formaldehyde would have been of limited return value. Due to these challenges, oxidation experiments conducted by chronoamperometric experiments had to be carried out such that concentrations of formaldehyde were detectable by HPLC without derivatization. By passing these quantities of current through the cell, it is highly likely that significant quantities of any formaldehyde formed were converted to higher oxidation products at the anode. Ideally, characterization of the products would happen with process instrumentation OR with a rapid turnaround time. Future efforts should consider a dedicated process GC and a dedicated or priority use HPLC system.

Although additional catalyst development would benefit a potential process, we generated sufficient data to move forward with IP protection, filing a patent application in FY 2022. Further, our understanding of partial methanol oxidation was significantly improved, and the data generated through this LDRD should provide a pathway for future proposals related to this work. With appropriate project partnering, we believe that this pathway to ethylene glycol can be advanced to TRL's which will attract additional industrial interest and funding.

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