

Electrochemical Reduction of Carbon Dioxide

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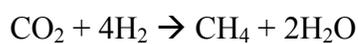
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Introduction

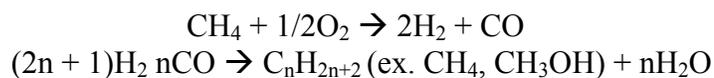
The conversion of carbon dioxide into useable hydrocarbons is a process that has been around since the early 1900s. The Sabatier and the Fischer-Tropsch processes are processes that involve the conversion of hydrogen and carbon oxides into hydrocarbons, but especially into hydrocarbons used for fuels. French chemist Paul Sabatier discovered the Sabatier process and he was awarded the Nobel Prize in 1913. His process involves the conversion of CO₂ and hydrogen gas into methane and water in the presence of a nickel catalyst at high temperatures and high pressures.¹ The process has been considered in the research of alternative fuels.

Sabatier Reaction:



Franz Fischer and Hans Tropsch invented the Fischer-Tropsch process in the 1920s.² The process involves two steps and is also seen as an alternative fuel source. The first step is the partial oxidation of coal or natural gas fuels into hydrogen gas and carbon dioxide. The carbon oxide and hydrogen are then converted into more useful methanol and methane fuels. Although it is still currently being used, the Fischer-Tropsch process was a major factor in the German effort in World War II, because they did not have an abundance of oil, but did have vast amounts of coal to produce synthetic oil.

Fischer-Tropsch Process:



Although both these methods are still being pursued today, the electrochemical reduction of carbon dioxide provides a better result than these historical processes. The electrochemical reduction process involves CO₂ gas and uses H₂ gas or various aqueous electrolytes as the source of the H⁺. It also produces methane or methanol and environmentally friendly water as products, but can also give a variety of other hydrocarbon products and even O₂ gas as a product. Another advantage is better chemical efficiency, the physical yield of product compared to the amount of by-products formed, than the other two processes. Also, depending on the reduction method high

Faradaic efficiency, the energy efficiency with which a species is electrolyzed at a given charge, can be accomplished. High Faradaic efficiencies suggest that the process requires lower energy to complete the reaction making the process more feasible. The consideration that this can be achieved at low temperatures is also a benefit when compared to the Sabatier process which involves both high temperature and pressure.^{3,4,5} The purpose of finding a better method of the reduction of CO₂ to methane and methanol fuels includes the use for *in situ* fuel production for a mission to Mars.⁶ This coupled with the possibility of applications on Earth making the electrochemical reduction of CO₂ promising.

Experimental

The electrochemical reduction of CO₂ was considered at low temperatures^{3,4,5}, high pressures^{7,8}, in a mixed supercritical fluid⁸, with various electrolytes^{3,5}, and on nanotubes and nanoparticles⁹. Faradaic efficiency of various hydrocarbon products and the efficiency of the competing hydrogen formation reaction were found for the different conditions. Various electrodes and reduction potentials were also explored in the electrochemical reduction of carbon dioxide.

Low Temperature. The solubility of CO₂ in methanol is about eight to fifteen times greater at temperatures below 273K than in water so methanol was used as the electrolyte.³ A H-cell with a Cu working electrode, a Pt foil counter electrode and a saturated calomel electrode (SCE) was used for the electrochemical reduction. With a 80 mM benzalkonium chloride solution in methanol as the electrolyte, the cell was cooled to 243K and the system, including CO₂ gas, was electrolyzed at -1.8 to -2.1 V/SCE and voltammograms recorded. The Faradaic efficiency was calculated from the total current or charge passed which was 50 C. The reduction products, were analyzed by gas and liquid chromatography (GC/LC).³

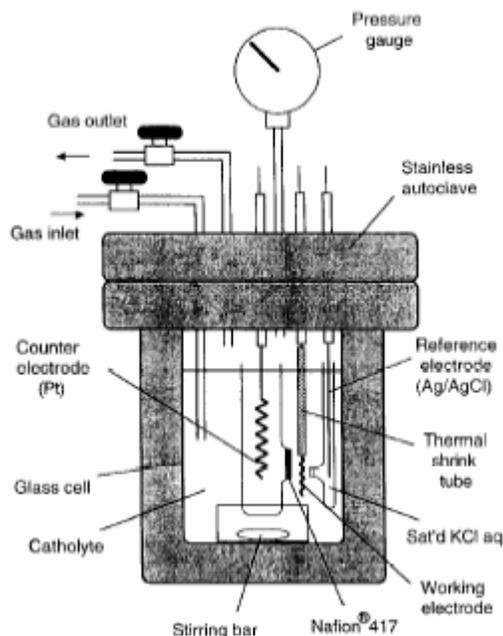
The reduction was again explored using an H-cell and methanol electrolyte.⁵ The electrolyte consisted of 0.8 mol dm⁻³ LiOH/methanol catholyte and 3 mol dm⁻³ KOH/methanol

analyte. The Cu and Pt foil were again used, but with Ag/AgCl, sat. KCl as a reference. The solution was purged with CO₂ and the saturated solution was reduced from -2.0 to -5.0 V/(Ag/AgCl, sat KCl). Voltammetry was applied and Faradaic efficiency calculated at 50 C charge passed. Products were analyzed using GC and HPLC.⁵

Again an H-cell with Cu and Pt foil was used and Ag/AgCl, sat KCl was used as a reference. The electrolyte solution consisted of 0.65 mol dm⁻³ NaHCO₃ and 1.1 mol dm⁻³ KHCO₃.⁴ CO₂ gas was bubbled into the catholyte, NaHCO₃, for 1 hour at 30 cm³ min⁻¹, and the CO₂ saturated solution was reduced at a cathodic potential of -1.6 to -2.0 V/(Ag/AgCl, sat. KCl). Voltammetry was employed to measure the reduction at different temperatures decreasing to 271K. The Faradaic efficiency was calculated assuming 50 C charge passed. Analysis was done by GC and HPLC.⁴

High-Pressure. The high pressure electrolysis was carried out in a glass cell in a stainless steel autoclave as the high pressure cell (Fig. 1).⁷ An aqueous electrolyte was used in the 0.1 mol dm⁻³ KHCO₃ with an Ag/AgCl, sat. KCl reference electrode. The counter electrode was a platinum

Fig. 1. Electrolysis cell and stainless steel autoclave for the electrochemical reduction of CO₂ at high pressures.⁷

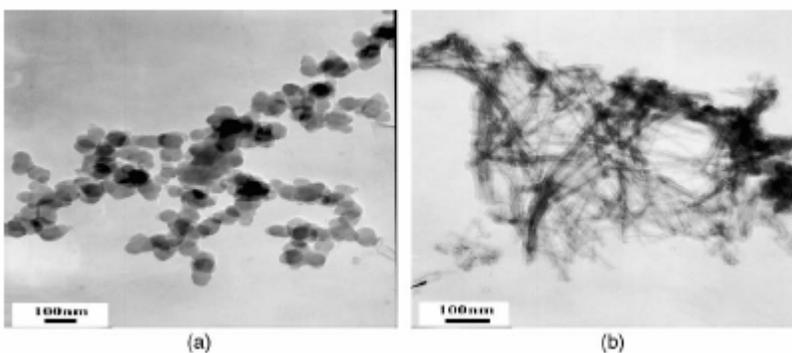


electrode. The reduction was completed for various working electrodes with equal surface areas of 0.16 cm^2 : Ti, Zr, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, Zn, Al, In, C, n-Si, Sn, Pb, and Bi (group 4-15 elements). The electrolyte was deaerated by bubbling with CO_2 and a known pressure of 30 atm CO_2 was entered into the cell at 298K and the charge passed through the cell was 300 C as the electrolysis was carried out galvanostatically. Voltammetric measurements were recorded as potential was corrected. The products were analyzed using GC with a flame ionization detector and by HPLC with a UV detector.⁷

The electrochemical reduction of CO_2 was done in a mixed supercritical fluid of 1,1,1,2-tetrafluoroethane (HFC 134a) and carbon dioxide. The high-pressure system consisting of two electrodes, Pt on Pb and a Ag/Ag^+ pseudoreference electrode, was purged with the 30.6 mol % HFC 134a/ CO_2 mix with a tetrabutylammonium tetrafluoroborate electrolyte.⁸ Voltammetric determinations of the electrolysis were recorded. The bulk electrolysis products were analyzed using GC, HPLC and by UV absorbance at 210 nm.⁸

Modified NT/NP Electrodes. The nanotubes and nanoparticles (NT/NP) were synthesized in ethanol from $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and TiO_2 . The RuO_2 was loaded on to the TiO_2 and the $\text{RuO}_2/\text{TiO}_2$ composite examined by TEM (Fig. 2).⁹ The NTs and NPs were pretreated to form a composite

Fig. 2. TEM images of
(a) $\text{RuO}_2/\text{TiO}_2$ NPs composite
(b) $\text{RuO}_2/\text{TiO}_2$ NTs composite

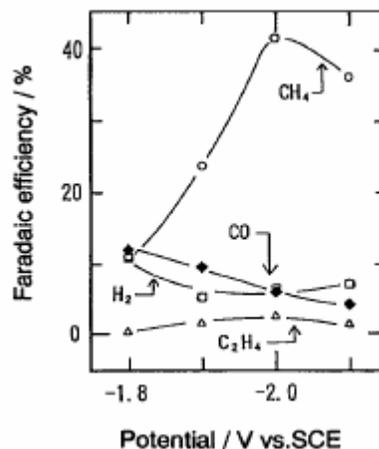


Pt electrode modified with $\text{RuO}_2/\text{TiO}_2$. The reduction of CO_2 at this electrode was explored in 0.5 M NaHCO_3 in an H-cell. Involved was also a Pt counter and SCE reference electrode. The experiment was done at room temperature and cyclic voltammograms, steady state polarization, and current-time curves were all measured for the system. The products in the gas phase were not analyzed; however liquid phase products were explored using GC and mass spectroscopy.

Results

Low Temperature. The first electrochemical reduction of carbon dioxide, in methanol at 243K resulted in a maximum formation of methane at -2.0 V with a Faradaic efficiency of 42.5% (Fig. 3.).³ At -2.0 V, the competing H_2 formation was found to be depressed to less than 8%

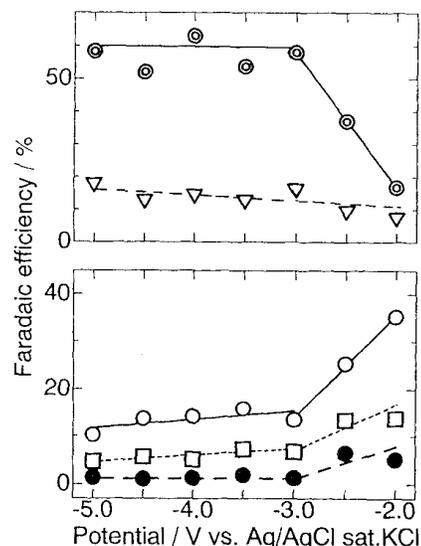
Fig. 3. Faradaic efficiencies for the products of electrochemical reduction of CO_2 in methanol at 243K: \circ CH_4 ; \blacklozenge CO ; Δ C_2H_4 ; \square H_2 .³



efficiency. At ambient temperatures, the methane production was less than 6%. Other products were formed, CO and ethylene. Ethylene did not show significant formation by CO_2 reduction at low temperatures with efficiency of 2.1% as seen in Figure 3. Carbon monoxide was also formed, however, CO production was found to be greater at ambient temperature rather than 243K.

In the $\text{LiOH}/\text{Methanol}$, the hydrocarbon formation also had good Faradaic efficiency.⁵ Methanol and ethylene were produced at 78% at -4.0 V (methane ~63% and ethylene ~15%), as shown in the plot of efficiency vs. potential in Fig. 4. This is much better than the efficiency

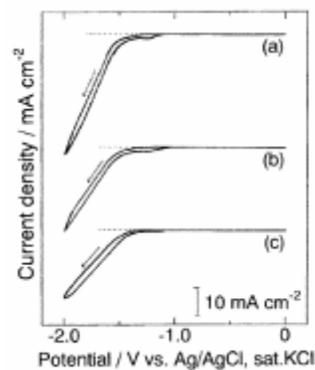
Fig. 4. Effect of potential on the Faradaic efficiencies for the products by electrochemical reduction of CO_2 at Cu electrode in methanol at 243 K: \odot CH_4 ; ∇ C_2H_4 ; \circ CO ; \square HCOOH ; \bullet H_2 .⁵



found when the electrochemical reduction occurs in water, an average efficiency of 27.3%. The competing hydrogen reaction was found to be depressed in LiOH/Methanol vs. in water with efficiencies less than 2% for polarizations less than -3.0 V. Also, partial current densities were found to be greater for potentials less than -3.0 V.⁵

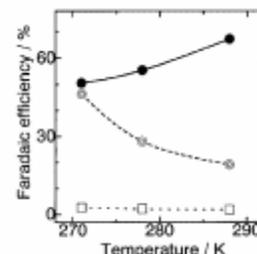
For the procedure in which temperatures were reduced to 271K, the effect of higher than ambient temperatures on the reduction of CO_2 was seen in extreme H_2 efficiencies.⁴ Figure 5 shows how the decrease in temperature affected the voltammograms of the electrolysis and Figure 6 shows the change in the efficiency vs. temperature. The formic acid production has little to no

Fig. 5. Cyclic voltammograms of Cu electrode in NaHCO_3 aqueous solution: (a) 288 K (b) 278 K (c) 271 K.⁴



change with temperature, but more importantly the methane production is less than half that of the hydrogen produced at 288K, also seen with applied potential. The formation of useable methane was greater at -2.0 V than -1.6 V.⁴

Fig. 6. Effect of temperature on Faradaic efficiencies of the products by electrochemical reduction of CO₂ at Cu electrode in NaHCO₃ aqueous solution at -2.0 V: ◦ CH₄; ● HCOOH; □ H₂.⁴



High-Pressure. As seen in Table I, the various electrodes under high-pressure conditions of 30 atm resulted in a number of various products and efficiencies.⁷ On Ag, Au, Zn, Pb, and In,

Table I.⁷ The Electrochemical Reduction of CO₂ Under 30 atm Pressure

Electrochemical reduction of CO ₂ under a pressure of 30 atm on various electrodes at 163 mA cm ⁻²												
Group	Electrode	<i>E</i> ^a /V	Faradaic efficiency/%								PCD(CO ₂ red.) ^c /mA cm ⁻²	
			CH ₄	C ₂ H ₆	C ₂ H ₄	CO	HCOOH	H ₂	CO ₂ red. ^b	Total		
4	Ti	-1.57	0.18	0.01	0.08	Trace	4.6	80.8	4.9	85.7	8.0	
	Zr	-1.73	0.13	0.01	0.01	32.5	7.6	44.2	40.3	84.5	65.7	
5	Nb	-1.45	0.56	0.05	0.01	n ^d	3.5	81.4	4.1	85.5	6.7	
	Ta	-1.51	0.55	0.05	Trace	Trace	7.0	74.4	8.2	82.6	13.4	
6	Cr	-1.49	0.53	0.05	0.07	11.8	8.2	68.6	20.7	89.3	33.7	
	Mo	-1.34	0.40	0.05	0.03	n	6.5	83.3	7.0	90.3	11.4	
	W	-1.61	0.38	0.04	0.01	Trace	31.9	53.1	32.3	85.4	52.6	
7	Mn	-1.69	0.68	0.10	0.06	2.8	2.8	78.8	6.5	85.3	10.6	
8	Fe	-1.63	2.03	0.40	0.16	4.2	28.6	51.6	35.4	87.0	57.7	
9	Co	-1.54	3.09	0.17	0.38	15.8	21.9	46.9	41.5	88.4	67.6	
	Rh	-1.41	0.26	0.03	0.01	61.0	19.5	13.1	80.8	93.9	131.7	
	Ir	-1.55	0.62	0.05	0.05	17.5	22.3	48.3	40.5	88.8	66.0	
10	Ni	-1.59	0.72	0.08	0.11	33.5	31.3	26.0	65.7	91.7	107.1	
	Pd	-1.56	0.13	0.01	Trace	46.1	35.6	12.8	81.8	94.6	133.3	
	Pd ^e	-1.76	0.21	0.01	0.02	35.2	44.0	13.8	79.4	93.2	397.0	
	Pt	-1.48	0.22	0.02	Trace	6.1	50.4	33.6	56.7	90.3	92.4	
11	Cu	-1.64	9.95	0.06	3.74	20.1	53.7	2.5	87.6	90.1	142.8	
	Ag	-1.48	0.20	0.01	Trace	75.6	16.8	3.9	92.6	96.5	150.9	
	Au	-1.30	0.21	0.02	0.11	64.7	11.8	15.4	76.8	92.2	125.2	
12	Zn	-1.70	0.31	0.03	Trace	48.7	40.5	2.8	89.5	92.3	145.9	
13	Al	-1.97	0.66	0.01	n	n	1.3	86.5	2.0	88.5	3.3	
	In ^f	-	0.28	Trace	0.04	3.8	90.1	5.6	90.5	99.1	147.5	
14	C ^g	-1.68	0.45	0.03	0.04	44.0	30.2	15.6	74.7	90.3	37.4	
	C	-2.14	0.66	0.02	0.05	3.6	6.8	75.5	11.2	86.7	18.3	
	n-Si	-2.04	0.87	0.01	0.02	2.0	46.3	40.6	49.2	89.8	80.2	
	Sn	-1.39	0.06	Trace	Trace	8.0	92.3	1.3	100.4	101.7	163.0	
	Pb	-1.57	0.20	0.01	Trace	Trace	95.5	1.2	95.7	96.9	156.0	
15	Bi ^h	-1.42	0.17	0.01	Trace	3.3	82.7	6.3	86.2	92.5	140.5	

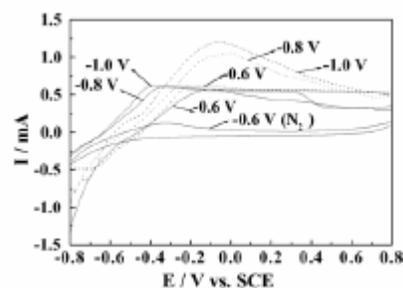
Reaction temperature, 25°C; electrolyte, 0.1 mol dm⁻³ KHCO₃; charge passed, 300 C.

the major products of the reduction were formic acid and/or CO at low pressure while the group 8-10 metals gave these products at the 30 atm pressure. The group 8-10 metals gave hydrogen formation as the major low-pressure product. Significant methane production was seen on the group 5-8 elements and Cu, Co, Al and n-Si and major ethylene production was seen on Fe at 30 atm. For the elements at 30 atm in which methane production was high, the hydrogen formation was also significant.⁷

The result of the electrochemical reduction of CO₂ in a mixed supercritical solution, again high-pressure system, was a successful reduction. However, the products that formed were CO, formic acid, and (COOH)₂.⁸ These were not found with great efficiency and are not considered useful in fuel production applications.

Modified NT/NP Electrodes. Comparing the voltammograms from the NTs and NPs, the reduction occurs much greater in the presence of a CO₂-saturated solution than in the presence of N₂ (Fig. 7).⁹ From the GC/MS analysis of the products from the NTs and NPs, the product of the electrolysis in the N₂-saturated solution was only hydrogen. In the CO₂-saturated solution, GC/MS showed methanol as the main product. RuO₂/TiO₂ NP composite modified electrode had the Faradaic efficiency increase to 60.5% from 30.5% methanol. No other products were mentioned.⁹

Fig. 7. Voltammetric curves of RuO₂/TiO₂ NPs (-) and RuO₂/TiO₂ NTs composite modified electrode (---) in 0.5 M NaHCO₃ saturated with CO₂. Sweep rate: 10 mV s⁻¹.⁹



Discussion

Finding a better CO₂ reduction process is essential for a possible manned mission to Mars. The Martian atmosphere has a composition of 95.3% CO₂, as opposed to the 0.03% composition here on Earth.⁶ Accounting only for the gaseous CO₂ on Mars, this is enough carbon dioxide to

make sustainable human life possible if breathable air, water, and especially fuel can be generated *in situ*. Considering only the fuel production, there are three categories of propellants that could be used: C-free fuels (such as H₂ or SiH₄), H-free fuels (CO), or C,H-fuels (CH₄, CH₃OH, C₂H₂ etc).⁶ The electrochemical reduction of CO₂ produces a variety of these fuels, especially the hydrocarbon fuel methane.

The necessity of a better process stems directly from the fact that all three methods, Sabatier, Fischer-Tropsch, and electrochemical reduction all require that hydrogen be present in some step of the reaction. Since the atmosphere of Mars contains only a trace of water, subterranean water must be used as an *in situ* source of hydrogen.⁶ This subterranean Martian water can be seen in Figures 8 and 9.^{10,11} The *in situ* fuel production on Mars requires both

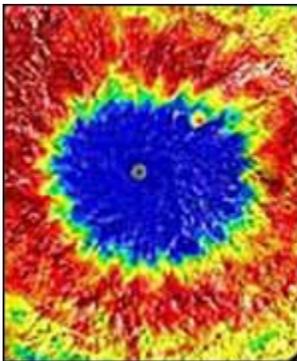


Fig. 8. A gamma-ray spectrometer image of ice (blue) on Mars.¹⁰



Fig. 9. Ice formations on the south pole of the Martian planet.¹¹

atmospheric (CO₂) and subterranean (ice) extraction to produce the methane and methanol fuels. Pioneer Astronautics has determined that Martian raw materials will derive 95% of the reactants for *in-situ* fuel production, leaving less than five percent of the hydrogen required to come from Earth in the form of liquid hydrogen.¹² According to NASA, approximately 0.5 tonnes of hydrogen could be recycled this way as opposed to none with the Sabatier reaction.¹³

Another consideration is again related to the Martian atmosphere. The Martian atmosphere has a mean temperature of 210 K and a high of 293 K.¹⁴ As seen in the first three experimental

considerations at 1 atm, the formation of methane is extremely efficient at low temperatures consistent with Martian-like surface temperatures.^{3,4,5} At 243 K, the Faradaic efficiency, of methane production was as high as 42.5% in methanol, with no side products forming at close to that efficiency.^{3,15} Again, at 243 K, the efficiency was upwards of 63% Faradaic efficient if the methanol solution was treated with LiOH.⁵ Further, the stepwise reduction of the temperature to low temperatures gave increasing electrochemical reduction and better efficiencies in NaHCO₃.⁴ Extending the plot (Fig. 6.) to the mean temperature of the Martian atmosphere would lend rise to efficiencies of approximately 80%.

The atmospheric pressure on Mars ranges between 6-10 hPa ($\sim 7.895 \times 10^{-3}$ atm), considerably lower than that on Earth.⁶ The formation of methane with good efficiency was achieved at high pressures, 30 atm, and 298K.^{7,8} None of the electrodes used from Table I gave methane, a primary fuel source, or C₂H₂ formation at high-pressure with high efficiency.⁷ Also, the reduction, which was attempted at 1 atm for all the Table I electrodes, did not result in high hydrocarbon efficiencies. The groups 5-10 and Au and C electrodes did however give H₂ with high efficiency at 30 atm. This is the competing reaction and should have low efficiencies if successful fuel production is to occur. Thus high pressures and even Earth-like pressures would be good for recyclable hydrogen formation, but not fuel production.¹² Low Martian-like temperatures have not been explored.

A secondary consideration for high-pressures was reduction in a mixed supercritical fluid.⁸ This was the first demonstration that this could be done, achieving CO₂ reduction in aprotic mixtures in supercritical phase. Once again, the high-pressure system led to the formation, at high efficiencies, of an “undesirable” product, or non-propellant. The oxalate product, (COOH)₂, formed and is presently of no use in terms of exochemical applications.

Considering that most fuel sources, methanol and methane included, need oxygen as an oxidizer, they need to be compared on another basis. The performance of these fuels are measured by their Specific Impulse (I_{sp}), the amount force integrated over a period of time or propulsive impulse which can be produced by a unit mass of the propellant.⁶ Methane has an I_{sp} of 3700 m s^{-1} and methanol an I_{sp} of 3050 m s^{-1} .⁶ Although methanol has a lower specific impulse than methane, it is still a much better rocket fuel than propellants, such as cold gas (nitrogen) or hydrogen peroxide monopropellant with I_{sp} s of 780 and 1600 m s^{-1} , respectively.⁶ Nanotubes and nanoparticles provide viable electrode options for the electrochemical reduction of CO_2 .

Methanol was used as a electrolyte solution in the low temperature considerations, but also is a viable fuel.^{3,4,5,6} Under “Earth” conditions, the use of modified nanotubes and nanoparticles gave excellent methanol efficiency. With Faradaic efficiency between 40 and 60%, the production of methanol via reduction on NTs and NPs leads to another fuel source, other than methane, that can be achieved effectively. The benefits of the nano-composites are no by-products formed in the electrochemical reduction of CO_2 and accompanying the increased efficiency, increased catalytic activity can be achieved.⁹

With electrochemical reduction, there is also a chemical efficiency desired in producing rocket fuels along with the high Faradaic efficiency. The best method for avoiding by-products is the use of modified nanotubes or nanoparticles as Pt electrodes. No significant by-products are reported when this method is used.⁹ In low temperature electrochemical reductions, there is a tendency to have unavoidable by-products, including a mixture of hydrocarbons and hydrogen gas.^{3,4,5} These by-products average a total of 10% of the total Faradaic efficiency. This is a significant amount considering the methane or methanol product efficiency is between 40% and 78% depending on the temperature, electrodes used, and the electrolyte solution.^{3,4,5} The NTs and

NPs gave approximately the same efficiencies and the paramount goal of a pure rocket fuel from *in situ* production.^{6,9}

In addition to the uses for possible Mars missions, the electrochemical reduction of carbon dioxide could have possible uses here on Earth. With the reduction of fossil fuels occurring at an increasing rate, methane and methanol could serve as possible alternative fuels to crude oil around the world.² In addition to fuel production, the electrolysis of carbon dioxide could be extremely important for the lessening of the concentration of green-house gases in the atmosphere.⁹ These are possible uses that are proposed.

Conclusions

The electrochemical reduction of CO₂ is achieved with high efficiencies at low temperatures and with modified NT/NPs as Pt electrodes. These conditions are favorable for the *in-situ* fuel production on Mars. The high-pressure reduction results in a mix of electrolysis products and therefore does not have a real application without further refining of the process. The electrochemical reduction works best on Pt electrodes or a modification of them. With good Faradaic efficiencies and chemical efficiencies, the electrolysis of CO₂ is a better method of obtaining methane and methanol than the Sabatier or Fischer-Tropsch processes alone because it can be achieved at lower energies.

In 2004, President Bush announced a renewed spirit for the space exploration program in which he mentioned going to the Moon as a “stepping stone for more ambitious missions” and to go beyond there by 2020.¹⁶ The goal of a mission to Mars is seemingly not too far off in the future to President Bush and his vision for NASA.¹⁶ The electrochemical reduction of CO₂ provides for a means to that end in the use of Martian raw materials for fuel power. As mentioned in the Presidential press release, more than 1300 NASA and other space technologies have added to the quality of life and the way industry works here on Earth.¹⁶ Cell phones, satellite networks, CAT

scanners, MRI imaging, and even the chemical process involved in kidney dialysis came from NASA developed ideas.¹⁶ The electrochemical reduction of CO₂ is viable for space, but the home applications are of importance here on Earth and need to be considered in the years to come and could even be used here for fuel before the reaching a land far away.

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