FE/CO_2 FUEL CELLS FOR CO_2 CAPTURE AND SEQUESTRATION PLUS H_2 AND ELECTRICITY PRODUCTION

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Introduction

Satisfying an increasing global demand for energy while stabilizing the atmospheric CO_2 concentration may be the greatest societal and technological challenge of the 21rst century.[1] In this context a range of potential CO_2 capture/sequestration technologies have been proposed[2], yet their capacity, economics, practicality, and/or environmental impacts have thus far proven to be impediments to large-scale application. Because of their abundance and important role in the global carbon cycle, carbonates (inorganic compounds containing the -CO_3 moiety) have been studied as possible long-term storage forms for CO_2.[3] The conversion of CO_2 into solid carbonates via reactions such as: $XO + CO_2 \rightarrow XCO_3$ (X=divalent metal) present one such mechanism, but reaction rates with CO_2 are exceedingly slow unless additional energy (heat and/or pressure) is introduced. The conversion of metal oxides to hydroxides and subsequent reaction with CO_2 has also been considered, but the cost of chemically forming such hydroxides (rare in nature) appear to be prohibitive. Thus, despite their desirability as stable CO_2 reservoirs, cost and other factors have proven to be impediments to the formation of solid carbonates as a CO_2 capture/ sequestration strategy.

However, it has been recognized in the geologic CO_2 sequestration field (i.e., subterranean injection of CO_2) that certain geochemical conditions can exist where the formation of $FeCO_3$ would be favored and could provide a stable trap for CO_2 injected underground.[4] Also, the oxidation of iron metal in the presence of CO_2 is well known.[5,6] This proceeds by the reaction:

$$Fe^0 + 2CO_2 + 2H_2O \rightarrow Fe^{2+} + 2HCO_3^- + \uparrow H_2 \qquad (1)$$

which can further lead to the precipitation of a solid carbonate via pH elevation (e.g., removal of excess CO_2):

$$Fe^{2+} + 2HCO_3^- \rightarrow \downarrow FeCO_{3(s)} + \uparrow CO_{2(g)} + H_2O. \qquad (2)$$

The net reaction is then:

$$Fe^0 + CO_2 + H_2O \rightarrow \downarrow FeCO_{3(s)} + \uparrow H_2. \qquad (3)$$

Given the abundance of Fe in nature (globally, 4rth most abundant element) and as a waste metal (US scrap iron production = 10^7 tones/year, ref. 7), it is worth considering purposeful, aboveground iron carbonate formation as a CO_2 sequestration tool. Additionally two valuable by-products can be produced from reaction 1, electricity and hydrogen. Because 2 moles of electrons are transferred per mole of Fe reacted and H_2 formed, electricity could be made to flow between a reactive anode (Fe^0) and a non-reactive cathode (e.g. graphite); the anodic reaction being $Fe^o \rightarrow Fe^{2+} + 2e^-$ and the cathodic reaction being $2CO_2 + 2H_2O + 2e^- \rightarrow H_2 + 2HCO_3^-$. Assuming a conservative Fe reaction rate of 10^{-5} moles m^{-2} s^{-1}, a cell current density of 1.9 A m^{-2} is calculated. The cell potential of 0.44V leads to a power generation of 85kW per mole Fe reacted s^{-1}, or about 421 kWh_e per tonne Fe reacted hr^{-1}. Such energy production is confirmed by voltage and current densities generated in experimental iron corrosion studies (**Figure 1**).

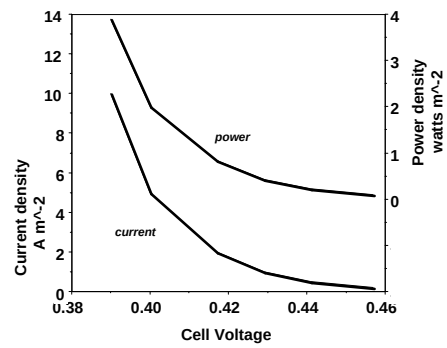

Figure 1. Trends in voltage vs current and power densities in a galvanic cell composed of an unalloyed steel anode in an oxygen-free electrolyte solution saturated with CO_2 at 298˚K (ref. 5).

Fuel Cell Scenarios, Issues, and Concerns

It is envisioned[8] that reaction 1 would occur in vessels or cells in which anodes produced from waste iron and cathodes composed of an appropriate conducting material (e.g., graphite) are submerged in a carbonic acid electrolyte formed by the continuous hydration of waste CO_2 with water. Hydrogen gas and electricity would be produced from such cells while the electrolyte would be continuously or sporadically bled off and the iron carbonates, $Fe(HCO_3)_2$ or $FeCO_3$, concentrated or removed. Possible fuel cell design considerations and operating procedures are further considered below.

The electrodes. Due to cost and the carbon intensity of production, scrap rather than new iron or steel would be preferred as anode material.[8] Waste car bodies might be appropriate given their relatively uniform size, metallurgical composition, and abundance.[9] However, the use of anti-corrosion coatings and non-Fe components in automobiles would require preparation of the scrap bodies via sanding, chemical treatments, or other processes, as well as forming the scrap into useable anodes. The cathodes need only be conductive to electricity and are not consumed in the fuel cell. However, the performance of the cathodes could degrade over time due to ancillary chemical reactions or fouling. The use of graphite is suggested here, but the performance and cost/benefit of using other materials need to be evaluated.

The electrolyte. The electrolyte would be formed by contacting waste CO_2 with water by bubbling the gas stream through the water, by spraying water in the gas stream, or by some other means that is energetically efficient and cost-effective in hydrating CO_2, thus forming a carbonic acid solution. This acid formation could occur within the fuel cell or upstream from it. The higher the CO_2 content in the gas the higher the equilibrium carbonic acid concentration in electrolyte and hence the higher reaction rates. It may be cost-effective to pressurize the gas stream or electrolyte head space in order to increase carbonic acid concentration, reaction rates, and hence the volume density of H_2 and electricity generation and CO_2 mitigation. The purity of the CO_2 waste gas stream could also be an issue, where contaminants such as SO_x, NO_x, heavy metals, etc., common in the gas effluent from coal and oil combustion, could interfere with (or enhance?) reactions 1-3. These contaminants could also affect the quality of the downstream H_2 and liquid and solid wastes from the fuel cell. Use of relatively clean CO_2 waste gas streams from natural gas combustion or gasification could avoid these potential problems. Waste gas from gasification/steam reforming plants and power generators would be especially attractive

because of its high CO_2 content and very low or no O_2, features that would depress electrolyte pH and Eh in equilibrium with such gas, thus maximizing Fe solubilization and minimizing the formation of iron oxides.

With at least 0.3 tonnes of H_2O consumed per tonne Fe reacted, the source, quality, and cost of water are issues for fuel cell operation. Sources of water might include municipal, industrial, or recycled supplies, provided that the contaminants or additives they contain, such as chlorine, do not impede reactions 1-3. On the other hand, the addition of chemicals to the electrolyte such as acids and salts (or use of seawater), known to increase Fe solubility and to reduce anode passivation by $FeCO_3$ deposition[5,6], might enhance fuel cell performance and prove cost effective.

Products, carbon sequestration, and waste streams. The H_2 generated at the cathode could be harvested and stored by employing conventional methods used in the production of H_2 via electrolysis. It is unknown what purity and concentration of H_2 might be achievable, and these issues could affect the end-use and marketability of the hydrogen.

The electricity produced per cell would be low-voltage direct current, requiring multiple cells in series as well as current inversion in order to conform to conventional electrical grid requirements of high voltage AC. An attainable cell power density of about 20 kW m^{-3} is crudely estimated based on that of possibly analogous Fe/air electrochemical cells (40 kW m^{-3}, ref. 10), reduced by 50% considering the likely volume and packing inefficiencies posed by the unconventional anode material proposed. Thus, a battery composed of a minimum of 250 cells in series, each 2 m x 2 m x 2 m (1000 m^2 total battery area) would be needed to generate 40,000 kW at 110 VDC. Inverting this to AC would probably reduce power output by some 20%. Also, varying the load or resistance across the electrodes could modulate the flow of electrons and thus reaction rates within the cells. In the extreme case, close-circuiting the electrodes would forego electricity use, but maximize $Fe(HCO_3)_2$ and H_2 production rates.

The sequestration of carbon could be achieved either through the formation of dissolved $Fe(HCO_3)_2$ (reaction 1), or dissolved or solid $FeCO_3$ (reaction 2). The former compound captures twice the carbon as does the later carbonate, thus doubling the sequestration benefit per tonne Fe reacted. A further sequestration benefit could result by disposing of the dissolved iron bicarbonate in certain areas of the ocean where photosynthesis and hence CO_2 conversion to biomass is Fe-limited. In such regions the tonnes of CO_2 sequestered per tonne Fe^{2+} added has been observed to exceed 20,000:1 (ref. 11), which if realized would dominate the economics of Fe/CO_2 fuel cell operation if a market/societal value of \$10/tonne CO_2 sequestered (or even if DOE's target of \$2.73/tonne, ref. 2) were in place.

Alternatively, spent electrolyte containing dissolved iron bicarbonate/carbonate could be injected/stored underground or the solid iron carbonate precipitated from it. The latter would occur spontaneously as the excess CO_2 in the solution degassed to the atmosphere, thus increasing the pH and saturating the solution with CO_3^{2-}. Once the $FeCO_3$ had been precipitated some care would be needed in storing this solid in order to avoid its slow oxidation via exposure to air and hence CO_2 loss. Conceivably, the carbonate would be precipitated from the electrolyte downstream from the fuel cell with the water recycled for further electrolyte use. The ultimate storage site for solid carbonates in the context of CO_2 sequestration could include abandoned mines or specially dug burial sites[3], or at the bottom of large water bodies containing low or no O_2 which presumably could preserve the iron carbonate indefinitely.

Economics

To calculate the net cost or income from Fe/CO_2 fuel cells, the following costs (per tonne Fe) were assumed[8]: scrap Fe=\$85, anode finishing=\$15, and other capital, operating and maintenance=\$35, for a total investment of \$135. Gross income would include: hydrogen=\$129, electricity=\$21, and carbon mitigation=\$13, with total income=\$163. This assumes the following product market values: \$3,600/tonne H_2, \$0.05/kWe, and \$10/tonne CO_2 avoided. A net income (total gross income – total costs) of \$28/tonne Fe reacted or \$34/tonne CO_2 mitigated is thus calculated. Such a profit estimate is, however, extremely uncertain given that the performance and operating requirements of Fe/CO_2 fuel cells in the preceding context have not been demonstrated. If accurate, a net profit of >\$30/tonne CO_2 mitigated is significantly better than DOE's 2008-2012 sequestration cost targets of \$2.73/tonne CO_2 for non-point-source methods and "...less than a 10% increase in the cost of energy services..." for direct capture and sequestration approaches.[2] This income could therefore provide an important economic incentive for sequestration, while at the same time generating H_2 and electricity free from new atmospheric CO_2 emissions.

Summary and Conclusions

Fe/CO_2 fuel cells pose several advantages over existing carbon mitigation strategies. They could provide a way of producing H_2 and electricity in a manner that consumes rather than generates CO_2, unlike current commercial methods. At the same time they convert waste CO_2 and iron metal into a relatively inert carbon-containing solute or solid that is amenable to verification, long-term storage, and monitoring, important objectives for any CO_2 sequestration strategy.[2] The estimated market value of the H_2 and electricity produced (>\$180/tonne CO_2) raises the possibility that this economic benefit could help drive the implementation of this process. However, such a profit motive for Fe/CO_2 fuel cell utilization critically hinges on accurately determining its capital and operating costs and the market value of the products produced. Is it possible that Fe/CO_2 fuel cells could provide a means of consuming part of industrial society's waste CO_2 and iron while generating "CO_2-free" H_2 and electricity, motivated by economics rather than or in addition to regulatory taxes/incentives?

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