

HYDROGEN AS A CARRIER OF ENERGY AND WATER

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ABSTRACT

Water and energy are inextricably linked. Water is required by nearly all-living organisms as well many modern industrial processes including the generation of energy. Energy is used to treat and transport water and water is produced from hydrogen and fossil fuel reactions as well as used for cooling for thermoelectric power generation. In this way, energy contains embedded water and water contains embedded energy. Fuel cells are devices capable of producing both energy and clean water. Here the concept of using hydrogen as a carrier of water and energy is explored by studying the quality of water produced by two types of fuel cells. Water is recovered from a lab-scale (10 W) polymer electrolyte membrane fuel cell (PEMFC), a commercial alternative power unit (1 kW) PEMFC, and a commercial scale (300 kW) molten carbonate fuel cell (MCFC).

The results indicate that water produced by PEM fuel cells needs some treatment to be potable, according to the Environmental Protection Agency (US EPA) standards and the World Health Organization (WHO) guidelines for drinking water, to reduce nickel and aluminum content.

1. Introduction

Water and energy production and demand are interconnected [1]. About 4% of US electricity is employed for transporting and treating water [2], and 80% of water processing costs are due to electricity [3]. The thermoelectric, hydroelectric, and nuclear generation of energy also requires considerable water. According to the US Department of the Interior, thermoelectric power plants use 48% of the total (fresh and saline) water withdrawals in the US [4]. In this way, energy contains embedded water and water contains embedded energy. The US Department of Energy (DOE) reports that hydrogen could play an important role in America's energy future to provide electricity [5]. Hydrogen has the potential for reducing the dependence on petroleum and reducing air pollution [5]. The DOE also forecasts that a hydrogen economy will take at least two more decades to develop. In such a scenario the water generated by the fuel cells may play an important role. In a typical hydrogen fuel cell each kilogram of fuel used produces 9 kilograms of water, thus hydrogen can be considered as an energy and water carrier. In this way, the production water could be used as by-product of on-site power generation. For instance, the average daily household electricity consumption in the US is approximately 31 kWh per day [6]. If this demand of electricity were replaced by a hydrogen fuel cell, it would produce about 15 L of water of unknown quality. If this water is of high purity and sufficient quantity, it could offset costs and consumption of energy in the current mode of centralized water treatment and distribution.

Herein, we present a detailed study of the water quality and quantity produced by a 25 cm² lab-scale PEMFC that is designed as a controlled, monitored and closed system that is flexible to a wide range of materials, membranes, and humidification strategies. Our experiments vary the membrane chemical composition, fuel cell operating temperature, fuel cell operating current density, humidification system water quality, and fuel cell bipolar plate material. Additionally we present the water quality and yield obtained from two commercial units, a PEMFC and a MCFC. For the fuel cells studied we describe the water recovery setup used to collect the water samples and present the most relevant results obtained in terms of water quality to determine whether the water produced by the three systems complies with USEPA and WHO recommendations for drinking water [7, 8]. The

commercial fuel cell systems are evaluated in order to establish the quality and quantity of the water generated by a fuel cell operating under realistic conditions.

2. Experimental approach

2.1 Lab-scale PEMFC

We use a 25 cm² active area lab-scale PEMFC that was designed and constructed in house. The anode and cathode each consist of a base, current collector plate, bipolar plate and gaskets. The bases, constructed of aluminum 6061, are the main structure used to fasten the fuel cell together and house electrical heaters that maintain the operation temperature between 30°C and 100°C. The current collectors are made of copper to ensure high electrical conductivity and coated with a layer of nickel and a layer of gold to prevent corrosion and improve electrical conductivity. The bipolar plates are fabricated from graphite. We also fabricated second set of bipolar plates made of stainless steel 316 L coated with gold and nickel to evaluate the impact of bipolar plate material on water quality. This second set of bipolar plates also acts as current collector plates.

The ancillary equipment that delivers the conditioned reactants, collects the product water, and controls and monitors the fuel cell is shown in Figure 1.

The product water from the lab-scale PEMFC is recovered from the cathode using a glass condenser, which cools and condenses the water exiting the fuel cell as vapor, and a flask for water collection. The cooling water is cooled to 10°C by a recirculating chiller (Julabo FE 500). The cooling system was selected based on the dew point temperature of the reaction by-products and the chiller capability. This condensing system is not optimized for water collection yield because the primary focus of our work is the water quality.

We use a Nafion N-111 (Ion Power, New Castle, DE) and two different N-212 (BCS Fuel Cells, Bryan, TX) membranes. The N-111 membrane has an impregnated catalyst and requires an external GDL. The N-212 membranes are obtained as complete 5-layer MEAs, one of which requires humidification and one of which is self-humidified (denoted as N212 SH) and was tested without external humidification. The catalyst layers of all membranes are made of carbon with a loading of 0.3 mg Pt/cm²/side.

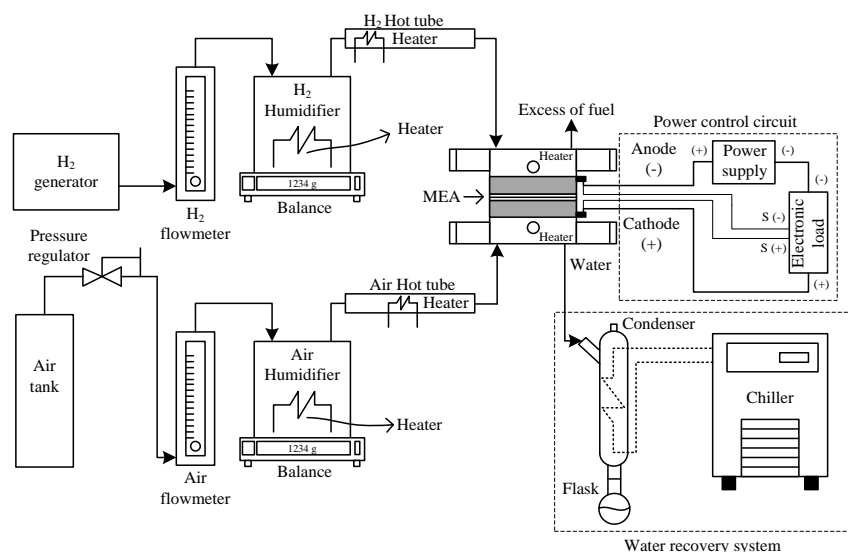


Figure 1. Experimental setup used to determine the water quality and quantity from a lab-scale PEMFC. When self-humidified membranes are tested, humidifiers are not used.

The lab-scale PEMFC was operated with external humidification (DI water filled) and graphite bipolar plates at a temperature of 60°C when membranes N-111 and N-212 were used. We compared these two membranes at this baseline condition over a range of current densities (0.1 to 1.0 A/cm², stepping every 0.1 A/cm²). We also investigated the role of humidification water quality by filling the sparging units with tap water (N-212 membrane and current of 0.7 A/cm²). The fuel cell was operated several times at these conditions to conduct a long term analysis to determine if membrane degradation affects the quality of the product water. For all experiments with membrane N-212, two balances (Ohaus[®] Trooper[™] Industrial Bench Scales, 120 VAC, 15 kg) were employed to quantify accurately the humidifier water used. In some experiments with membrane N-212, the condensing unit was not employed to compare the water recovery efficiency with and without a condensing system. When the condensing system was not used, the cathode fuel cell outlet was connected directly to a water collection flask.

Membrane N-212 SH was tested at four different current densities from 0.4 to 0.8 A/cm², stepping every 0.1 A/cm². The operating range for the fuel cell using this membrane was limited due to the lack of external humidification, and the fuel cell heaters were not utilized

to avoid membrane dehydration. We tested this type of membrane to establish the impact of humidification water on the quality and quantity of product water. Furthermore, we utilized membrane N-212 SH to test the effect of changing the bipolar plate material on water quality. Thus, the SS 316L bipolar plates were mounted in the fuel cell and tested at a fixed current of 0.7 A/cm^2 for approximately 600 h. In addition, the external condensing system was not employed during any experiments performed with membrane N-212 SH; water was recovered directly from the fuel cell exit with a flask. A total of 105 samples were collected and analyzed from all experiments. Once an experiment finished, the water collected was stored in a 60 mL precleaned vial and refrigerated at 5°C .

2.2 Commercial fuel cells

We used a 1 kW PEMFC (I-1000, ReliOn[®]) that was operated for six months in Phoenix, AZ at a hydrogen storage/filling facility. It uses hydrogen and air at atmospheric conditions as reactants. Figure 2 depicts the experimental setup utilized to operate the system and recover the water produced. Once a week a sample of water was collected, the volume of generated water measured, and time recorded to determine water yield rate. In total, 23 samples were collected. We recorded the power generated from the fuel cell at each measurement interval.

We also studied the water product from a 300 kW MCFC unit (FuelCell Energy[®], DFC300[™]). This MCFC system uses the natural gas produced from the anaerobic digestion of sludge generated during wastewater treatment process.

The Figure 3 presents a simplified flow diagram of the MCFC. In this figure the values inside the squares represent the mole fraction for each component at one specific point in the system as supplied by the manufacturer [9]. The temperature of the mixture of gases leaving the heat recovery unit (HRU) is about 350°C which makes difficult to recover the total of water generated. The water samples were collected from the bottom of the HRU of the fuel cell. The water which is exiting from the bottom of the HRU is condensate from the exhaust gases of the MCFC. We collected about 2 L of water divided in three different samples for analytical tests.

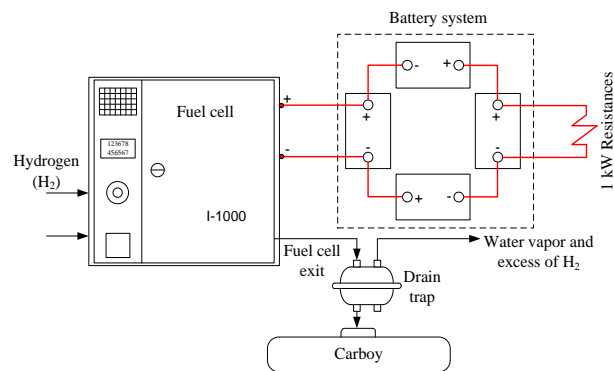


Figure 2 PEMFC I-1000 experimental setup. Battery storage system buffers the power generated by the PEMFC. Water product is collected directly in the HDPE carboy.

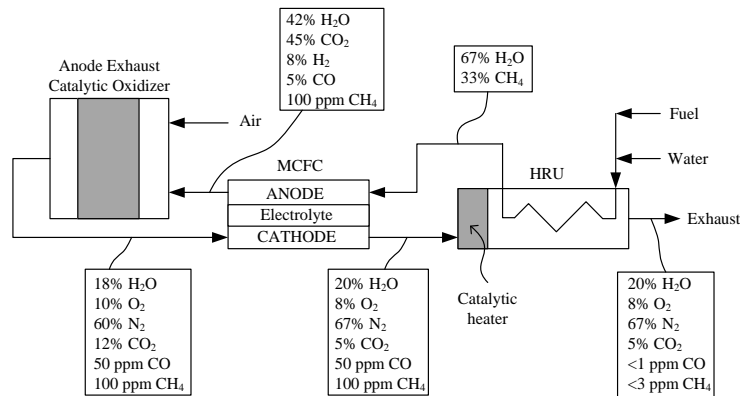


Figure 3 Flow diagram of the MCFC system studied.

2.3 Water Quality and Analytical Methods

All the samples collected from the three fuel cell systems were transported and stored in accordance with procedures described in *Standard Methods for Examination of Water and Wastewater* [10]. The pH and conductivity were measured using a combined pH conductivity meter (Corning Pinnacle 542). The total organic carbon (TOC) was measured using combustion/non-dispersive infrared gas analysis method (Shimadzu 5050A TOC and TDN, MDL 0.5 mg TOC/L and 0.1 mg TDN/L). The concentrations of the major salts and metals were measured using ion chromatography (Dionex DX-120, MDL 50 $\mu\text{g/L}$) with 150 μL loop and bicarbonate as eluent, and inductively coupled plasma mass spectroscopy (Thermo Fisher - Element 2, MDL <1 $\mu\text{g/L}$). For the commercial PEMFC and the MCFC the concentration of semi-volatile organic compounds in water samples was analyzed by

gas chromatography/mass spectrometry (GC/MS) at commercial analytical lab in accordance to the EPA method SW8270c [11]. The results were compared with US EPA maximum contaminant levels (MCLs) and secondary maximum contaminant levels (SMCLs). US EPA does not regulate nickel concentration, so we report WHO drinking water guidelines.

3. Results and discussion

3.1 pH and conductivity

The pH values of the water collected from the lab-scale PEMFC are shown in Figure 3 and compared with the pH range recommended by US EPA, which is between 6.5 and 8.5. Our measurements show no relationship between pH and current density or membrane age. Although nearly all of the averages (except for N-111) fall within the acceptable values, the N-111 and N-212 using DI water as the humidification source show that in several cases the water does not comply with the US EPA standard for pH (shown as large RMS values). The pH variation is large for all membranes. This variability and the low pH in the N-111 and N-212 membranes are common in very pure waters, which exhibit low buffering capacity. This suggests that in some cases the water generated by the fuel cell would need pH adjustment.

All conductivity values for water collected from the lab-scale PEMFC operating at different conditions were between 1.6 and 23.1 $\mu\text{S}/\text{cm}$. These low conductivity values imply high purity of the water (the conductivity of ultrapure water (18.2 M Ω MiliQ system) is typically between 1 and 2 $\mu\text{S}/\text{cm}$ when exposed to atmospheric air). For membranes N-111 and N-212, the low conductivity values are related to the fact that low-conductivity DI water was used in the humidifiers. When tap water is used in the humidifiers with membrane N-212, the average conductivity is slightly higher. The conductivity of the Tempe, Arizona, tap water is about 1000 $\mu\text{S}/\text{cm}$, but because of the distillation process that occurs inside the humidifiers, the water delivered to the fuel cell has a conductivity of approximately 20 $\mu\text{S}/\text{cm}$. For this reason, using tap water for humidification does not strongly impact the conductivity of the collected water. When stainless steel bipolar plates were used instead of graphite bipolar plates, the conductivity was less than 16 $\mu\text{S}/\text{cm}$. This suggests that use of

these two materials in the bipolar plates has no effect on the conductivity of the water. Furthermore, these low conductivity values suggest a lack of ion contamination from the materials that comprise the fuel cell system.

The pH of the 23 samples of water collected from the commercial PEMFC unit ranged from 6.3 to 8.5 (average= 7.0 ± 0.7). The conductivity values of the collected samples were in the range between 3.7 and 11.6 $\mu\text{S}/\text{cm}$ (average= $5.9 \pm 1.8 \mu\text{S}/\text{cm}$). Only three samples exhibited higher conductivity than 7 $\mu\text{S}/\text{cm}$. No apparent temporal trends existed for pH or for conductivity. The pH fluctuation in this very low conductivity, poorly buffered water, can be associated with low alkalinity and gradual equilibration with atmospheric carbon dioxide. While these water samples fall within this pH range, their low conductivity and alkalinity could make them fairly corrosive to household plumbing.

The water recovered from the commercial MCFC fuel cell exhibited a pH between 6.9 and 7.7 (average= 7.2 ± 0.4). The conductivity values of these samples varied between 109 $\mu\text{S}/\text{cm}$ and 628 $\mu\text{S}/\text{cm}$ (average= $306 \pm 281 \mu\text{S}/\text{cm}$). Conductivity in the commercial MCFC is one order of magnitude higher than in the PEMFC (discussed below), but is still much lower than the average tap water in the US.

3.2 Total organic carbon (TOC)

Figure 4 shows the measured TOC concentrations of the water produced by the lab-scale fuel cell when operated at the different experimental conditions tested. The TOC concentrations in the product water from membrane N-111 are greater than 2 mg/L. For membranes N-212 and N-212 SH, the TOC concentrations are lower than 2 mg/L. The figure also presents the measured TOC value of the Tempe, Arizona, tap water for comparison.

The results obtained with membrane N-212 operating with tap water in the humidifiers and with membrane N 212 SH operating with stainless steel bipolar plates suggested that neither the water used for humidification nor the bipolar plate material affect the TOC content in the product water. The amount of TOC present in the product water is thought to be related to the chemical degradation of the membrane assembly components and bipolar

plates as well as organic compounds from the GDL (made mainly of carbon) and CL (noble metals on carbon support).

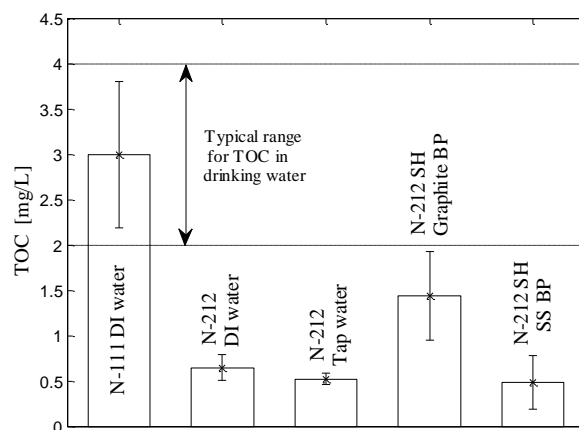


Figure 4. Total organic carbon (TOC) concentrations in the water produced by the lab-scale PEMFC operating under different conditions.

The data shows that the TOC in the water samples from the commercial PEMFC decreases sharply with increasing sample number and time. On average, the PEMFC water exhibited TOC < 0.8 mg/L with the exception of four samples from the initial period. This trend suggests that during the initial operating period, the contaminants present in the fuel cell were flushed from the cell into the collected water. If the fuel cell water is going to be used for potable purposes, it should be run for some time before the water is collected.

The average TOC of the three samples of water obtained from the MCFC is 3.0 mg/L. The release of organic matter from the MCFC could be related to the fact that methane is utilized as the fuel to produce the hydrogen in the reforming process and some remaining hydrocarbons could be present in the gases leaving the fuel cell. Concentration of all semi-volatile organic compounds from water product of the PEMFC and MCFC were below the MDL of the instrument. A complete list of the measured semi-volatile organic compounds is available in the supplemental information.

3.3 Major anions and cations

In all the samples from the three systems we measured the concentration of the following anions: fluoride, chloride, nitrite, nitrate, sulfate and phosphate. The concentrations of all of

the samples from the were well below the US EPA maximum contaminant level (MCL) or the secondary maximum contaminant level (SCML) [12] for drinking water. Except for the nitrite in the commercial MCFC, which concentration was higher than the US EPA MCL. The discharge of nitrite are likely due to the combustion process that occurs in the catalytic heater as well as the reactions that occur at high temperatures in the presence of nitrogen.

Figure 5 shows how the commercial PEMFC fluoride concentration and the power generated by the unit evolve with respect to time of the sample collection. This plot shows that as the fluoride concentration (lower than US EPA recommendation for drinking water) slowly increases over time the power generated decreases. We attribute the release of fluoride to membrane decomposition since typically PEMFCs use perfluorosulfonic acid membranes. We expect that as the membrane degrades it releases fluoride and the PEMFC performance diminishes. In our previous work a Fenton's reagent leaching test was conducted in a Nafion membrane (N-111) [13].

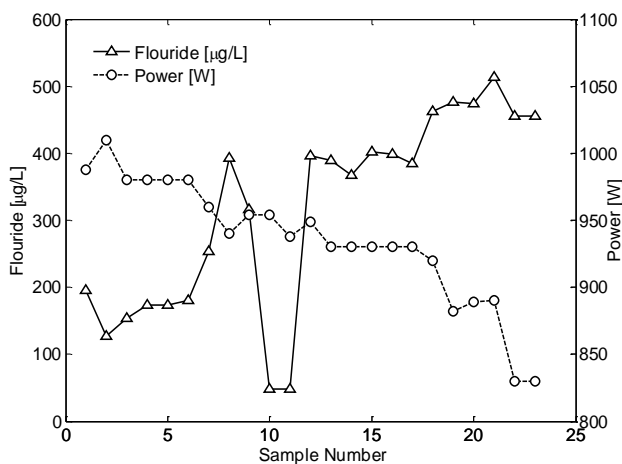


Figure 5 Fluoride concentration and power over the time for commercial scale PEMFC.

The measured cations concentrations are below the US EPA MCL or SCML in nearly all cases. The aluminum concentration was higher than recommended when membranes N-111 and N-212 operating with DI water for humidification were employed in lab-scale PEMFC. The fuel cell bases, which are made of aluminum 6061, are likely releasing the aluminum. The nickel concentration is higher than the WHO guideline value for all experiments

performed with membranes N-212 and N-212 SH. The source of the nickel is likely the collector plates, which are coated with gold and nickel to improve their electrical conductivity. Although the copper concentration is lower than the US EPA recommendation, its release was significantly lower when membrane N-212 SH was used with stainless steel bipolar plates instead of the copper collector plates used for the other tested conditions.

In Table 1 we include the list of all cations measured in water product from the three systems analyzed.

Table 1. List of all metals measured using ICP-MS

Li	Be	B	Rb	Y	Zr	Nb	Mo
Ru	Rh	Pd	Ag	Cd	In	Sn	Sb
Cs	Ba	La	Ce	Pr	Nd	Sm	Eu
Gd	Tb	Dy	Ho	Er	Tm	Yb	Hf
Ta	W	Re	Os	Ir	Pt	Au	Tl
Pb	Bi	Th	U	Na	Mg	Al	V
Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga
Sr	In	K	Ca	Ge	As	Se	

The average concentrations of major metals measured for the commercial PEMFC samples of water were significantly lower than the MCL or SMCL, except for 2 metals. Aluminum is most likely released by an aluminum heat transfer fuel cell component. The nickel average concentration is higher than the WHO's guideline value of 0.07 mg/ but lower than the 0.1 mg/L recommended by USEPA for nickel in 1992 [14, 15]. The high nickel content is observed because the collector plates of the commercial PEMFC are coated with nickel which we determined using energy dispersive spectroscopy (EDS) analysis.

For the commercial MCFC all average metal concentrations, with the exception of manganese, are below the MCL or SMCL. The high content of manganese is likely released from the bipolar plates of the fuel cell made of stainless steel.

4. Conclusions

The water produced by the two PEMFC units needs some treatment to stabilize the pH, increase the salt content, and lower the concentrations of aluminum and nickel when required. The quality of the product water is affected mainly by the materials used to manufacture the unit, whereas the effects of membrane chemical composition and external humidification water are negligible. Water produced by the MCFC does not comply fully with the drinking water standards recommended by EPA and WHO. Nitrite and manganese concentrations are higher than their respective EPA MCL and SCML values. Additionally, the nickel concentration is above the WHO's guidelines. With proper treatment, the water from the MCFC would be potable or could be reused in the methane reforming process.

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