High-Energy Density, Room-Temperature Carbonate Fuel Cell

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A room-temperature carbonate fuel cell has been constructed by modifying anion exchange membranes to transport carbonate. The cells were operated with hydrogen, 1 M methanol, and pure methanol fuels, and dry O2 and CO2 as the cathode gases. CO2 was produced at the anode, and O2 and CO2 were necessary at the cathode for operation, indicating that carbonate was the conducting ion. Using pure methanol as the fuel with no need for dilution significantly raises the energy density.

Fuel cells have several potential advantages over other energy conversion and storage devices.1 High-temperature cells, such as solid oxide fuel cells, have high power and energy conversion efficiency.2 Low-temperature fuel cells (i.e., near room temperature), such as proton exchange membrane (PEM) fuel cells, are more convenient to use, however the power and conversion efficiency are lower because of kinetic limitations.3 PEM cells using liquid fuels, such as methanol or formic acid,4 can have high-energy density compared to batteries, if concentrated liquid fuels can be used. Dilute methanol or formic acid are often used to increase the power density at the expense of energy density.

PEM cells use a polymeric membrane to transport protons from the anode to the cathode, converting the fuel (e.g., hydrogen, methanol, formic acid) and oxygen into water. Equation 1 shows the half reaction for the oxidation of methanol and water

CH3OH + H2O → CO2 + 6H+ + 6e− [1]

Expensive, precious metal catalysts, such as platinum, are required at the cathode due to the production of hydrogen peroxide under acidic conditions.1 Alkaline fuel cells can use nonprecious metal catalysts (e.g., nickel) due to a more facile mechanism for oxygen reduction and the higher operating temperature.1,5,6 However, alkaline cells with hydroxide electrolytes are intolerant to air because of the formation and precipitation of carbonate salts. Molten carbonate cells are tolerant to carbon dioxide and can be operated in air, although their operating temperature and liquid electrolyte are technologically challenging to deal with.1

Small fuel cells, where high-energy density and convenience are at a premium, are generally operated at ambient temperature with little or no auxiliary hardware (such as pumps or water recycling equipment) because of the lack of insulation and the need for low cost. The critical aspect of low power fuel cells, such as for low power wireless sensors, is the ability to store and use highly concentrated fuels in the smallest possible form factor.

In this work, we examine the feasibility of a room-temperature carbonate (RTC) fuel cell system. A RTC cell offers carbon monoxide tolerance, as well as the potential to use nonprecious metal catalysts (e.g., nickel), especially at the air cathode.1 Another significant advantage of the carbonate cycle is that when methanol is used as the fuel at the anode, water is not necessary to oxidize methanol (as in PEM cells). Thus, the anode does not consume water and it may not need to be carried with the fuel, which would significantly increase the energy density of the fuel. Equations 2 and 3 show the proposed half-reaction for an ambient temperature carbonate conducting fuel cell using hydrogen or methanol as the fuel

CH3OH + 3CO32− → 2H2O + 4CO2 + 6e− [2]

H2 + CO32− → H2O + CO2 + 2e− [3]

Carbonate fuel cells recycle the carbon dioxide produced at the anode to the cathode, Eq. 3, so as to increase its concentration and the fuel efficiency

2CO2 + O2 + 4e− → 2CO32− [4]

In this study, the viability of a high-energy density, low-power, room-temperature carbonate fuel cell has been investigated. A solid carbonate conducting electrolyte based anion exchange membrane was used. The pH sensitivity of the membrane was addressed by converting it to the bicarbonate/carbonate form. The resistivity of the membranes was measured and chemical stability in methanol evaluated. Hydrogen, 1M, and pure methanol have been shown to be viable anode fuels. Carbon dioxide was observed at the anode exhaust when operating on hydrogen.

Experimental

Calcium hydroxide (>99.5%, Fisher Scientific) and methanol (99.9%, Fisher Scientific) were used as-received or diluted with deionized (DI) water. 1-butyl-3-methylimidazolium tetrfluoroborate (BMIBF4, >97%, Fluka) was used as-received. Carbon dioxide, hydrogen, oxygen, and nitrogen gases were obtained from Air Products. Carbonate anion exchange membranes were prepared by soaking chloride containing AFN anion exchange membranes (AFN, Somerset, New Jersey) in aqueous solutions of sodium bicarbonate (>99.9%, Fisher Scientific) and sodium carbonate (>99.5%, EMD Chemicals). Upon soaking in 1 M sodium carbonate, the membranes darkened from a light brown to near black and were found to be unusable as carbonate exchange membranes due to the high pH. The aqueous solution also changed from clear to yellow. In an attempt to prevent damage to the membranes, sodium bicarbonate was added to lower the pH of the solution (resulting in green transparent membranes). The resulting membrane was measured to be 150 μm thick. Fuel cells were constructed in two ways. The cells used for the hydrogen tests were formed by sandwiching the carbonate anion exchange membrane between two carbon electrodes coated on one side with platinum [20 wt % Pt/Vulcan XC-72 (1 mg/cm2 Pt), ElectroChem, Inc.] and hot-pressed together. The cells used in the methanol tests were constructed using epoxy to attach a rubber gasket (with a hole of known area punched out) to the electrode and membrane. An EG&G Princeton Applied Research model 263A potentiostat was used for the electrochemical measurements.

Results and Discussion

Hydrogen provides the more facile electrochemical fuel for testing the operation of the carbonate fuel cell and was first used in the anode compartment. Carbon dioxide and oxygen, in a roughly 2:1 ratio, were used as the feed to the cathode. Figure 1 shows the polarization curve for a cell operated at four temperatures. The maximum power and current increased from 0.54 mW/cm2 and 5.4 mA/cm2 to 0.68 mW/cm2 and 6.2 mA/cm2, as the temperature increased from 26 to 44°C. However, when the temperature was increased to 55°C, the performance deteriorated significantly with
the maximum current, 4.8 mA/cm², falling below that measured at 26°C. When discharged across a 74.4 Ω resistor, a stable 0.3 V (±2 mV) was measured for more than 6.5 h, after which the experiment was terminated.

The performance drop at 55°C is likely due to drying of the polymer membrane. The effect of humidification was tested by soaking two membranes in the same 0.5 M sodium bicarbonate/0.5 M sodium carbonate (0.5B/0.5C) solution. One membrane was then removed from the solution and used while the other was dried under vacuum at ambient temperature for 18 h. The resistivity of each membrane was measured in a 0.5B/0.5C solution. The “area resistivity” of the dried membrane was found to be 101.4 cm², which was nearly three times higher than the measured 36.2 cm² for the membrane that was not dried. It is known that the membranes swell when exposed to moisture, resulting in an increase in conductivity. The dried membrane was then resoaked in a 0.5B/0.5C solution for 48 h. After soaking, the area resistivity dropped below 5 Ω cm². It is believed that this reduction in resistivity is related to the contraction and swelling that occurs on drying and wetting of the membranes. Upon drying, the membrane contracts, potentially forming larger pores or pinholes that allow carbonate ions to more easily pass from one side of the cell to the other. As the treatment with carbonate solution impacts the structure of the membrane, these defects are more likely to occur in the treated membranes than the untreated membranes. Also, upon drying, the membrane contracts and pulls away from the Pt on the carbon electrode, resulting in poorer interfacial contact between the electrode and membrane, reducing the performance of the system.

In an attempt to retain moisture in the membrane, a new fuel cell was constructed and characterized. BMIBF₄, a hydrophobic ionic liquid (IL), was applied first to the surface of the anode and then to the surface of the cathode. The polarization and power curves from the initial test and after the addition of IL to the surfaces are shown in Fig. 2a and b. Application of the IL to one side of the cell increased the current nearly 30%. However, when the cell was retested 3 days later (Fig. 2a and b) with IL on both electrodes, the performance returned to the initial level. It is believed that the hydrophobic IL will slow water loss from the surface of the membrane and impact the diffusion of CO₂, H₂, and O₂ to the surface of the membrane. Also, the IL may trap the gases, retaining them at the surface for reaction while improving the wetting between the electrode and electrolyte. Studies to optimize the contact area between electrode and electrolyte are underway.

Verification of carbonate ion transport is an important issue. This involves consumption of carbon dioxide at the cathode, transport of carbonate ions in the membrane, and production of carbon dioxide at the anode. To verify carbonate transport and carbon dioxide consumption and production, two tests were carried out. Each of the inlets and outlets was properly sealed and/or purged to prevent atmospheric CO₂ from interfering. In the first test, hydrogen was used as the fuel and the anode exhaust was first passed through a gas trap cooled with liquid nitrogen and then bubbled through an oil bubbler to prevent air from back-diffusing into the cell. The cell was operated under a 50 Ω load for approximately 10 h (potential 0.190 ± 10 mV) and a thick white solid accumulated at the bottom of the trap during the run. After completion of the run, the stopcocks
at the inlet and outlet of the gas trap were closed. A tube was then connected to one side, with the other side immersed in a calcium hydroxide solution. If the precipitate were carbon dioxide, produced at the anode according to Eq. 2, calcium carbonate would participate. When the stopcock was opened, the solution immediately turned milky due to reaction between CaOH and CO$_2$. As the white solid warmed, it evaporated increasing the pressure in the gas trap. When directly injected into the gas trap, the CaOH solution became white. These tests indicate that a large amount of carbon dioxide was present in the anode exhaust during the operation of the cell, consistent with the production of CO$_2$ at the anode, which could only occur if carbonate/bicarbonate were the conductive ions.

In the second test, we examined the impact of interrupting the flow of carbon dioxide feed to the cathode to see if CO$_2$ is consumed at the cathode. Figure 3 shows that immediately after the CO$_2$ flow was stopped, there was a substantial drop in cell voltage across the load resistor. The voltage then continued to decay more slowly over the next 4 h. However, the system did not reach 0 V by the end of the test, indicating the continued presence or introduction of CO$_2$. These tests indicate that a large amount of carbon dioxide was permeated through the membrane from the anode to the cathode is neutral CO$_2$ through the membrane from the anode to the cathode is desirable for cell operations, it does make it difficult to eliminate CO$_2$ from the cathode compartment for test purposes. In addition, it is difficult to completely purge and seal out all air from the cathode compartment.

While hydrogen provides an efficient method of testing the carbonate conduction mechanism, liquid fuels are of interest for atmospheric pressure operation and fuel storage. Methanol was tested as a fuel in the carbonate fuel cell under a variety of conditions. Figure 4 shows a polarization curve for 1 M methanol fuel after 2 h of operation using dry air and carbon dioxide as the cathode feed. From the current-voltage curve, the maximum power and current were $\sim 2 \mu$W/cm$^2$ and $\sim 16.2 \mu$A/cm$^2$, respectively. After 1 h of operation, the power of the fuel cell increased to 2.5 $\mu$W/cm$^2$ when operating with a 15 $\Omega$ load. After 24 h, the open circuit voltage (OCV) increased to 750 mV. Purging the cathode chamber with nitrogen for several hours resulted in the steady reduction of the cell voltage. When the oxygen flow was reestablished, the cell voltage increased rapidly as O$_2$ and CO$_2$ were available at the cathode for reduction. Cycling the CO$_2$ flow on and off affected the performance of the cell. For example, when operating near OCV (current $< 1$ nA/cm$^2$), the voltage increased more than 40 mV (from 763 to 804 mV) when the CO$_2$ flow was turned on. Stopping the flow would lead to a gradual decline in the voltage of the cell and not a full loss of voltage because CO$_2$ was also supplied from the anode side by permeation through the membrane.

A critical test for the carbonate cell is the ability to operate with pure methanol, according to Eq. 2, maximizing the energy density of the system. In contrast, as shown in Eq. 1, a proton exchange membrane requires water and methanol at the anode for oxidation to CO$_2$. The addition of water lowers the energy density of the system. Measurements were taken while the cell was operated with pure methanol. The polarization curve taken after 5 h of operation under load is shown in Fig. 5. The current under load was higher than with 1M methanol, however OCV was less, $-440$ mV. The maximum current, $-74 \mu$A/cm$^2$, and power, $-8.8 \mu$W/cm$^2$, are more than four times the values measured for the 1 M methanol system. The higher current is due to the increased methanol concentration, from 1M to 24.7 M in pure methanol. The decrease in OCV, from 750 to 440 mV, is likely due to crossover from the anode to the cathode.

The effective diffusion coefficient of pure methanol through the 0.5B/0.5C treated membranes was evaluated by measuring the rate of transport through the membrane. A reservoir of methanol was sealed in a glass container with the membrane as the top enclosure. Based on the weight change with time, the effective diffusion coefficient was found to be $2.26 \times 10^{-7}$ cm$^2$/s. While this value is an order of magnitude lower than that measured for Nafion 117 ($2.38 \times 10^{-6}$ cm$^2$/s), it is sufficient for methanol to pass...
through the membrane and wet the cathode electrode resulting in a lower cell voltage. In the case of 1 M methanol, the concentration of methanol is only 4% of pure methanol, substantially lowering the methanol diffusion through the membrane and its effect on OCV.

Conclusion
A room-temperature carbonate fuel cell has been constructed by modifying anion exchange membranes to transport carbonate. The cells were operated with hydrogen, 1 M methanol, and pure methanol fuels using dry O₂ and CO₂ as the cathode gases. CO₂ was produced at the anode, and O₂ and CO₂ were necessary at the cathode for operation, indicating that carbonate was the conducting ion. Though the initial performance was poor, the feasibility of a RTC fuel cell has been demonstrated. As no water is required for oxidation, this system could be utilized with pure methanol, maximizing the energy density of the system. In an effort to improve the system performance, work is underway to improve the carbonate membrane, its sensitivity to high pH values, and the interface between the electrodes and membranes.

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References