

Letter

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A pH-Gradient Flow Cell for Converting Waste CO₂ into Electricity

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Abstract

The CO₂ concentration difference between ambient air and exhaust gases created by combusting fossil fuels is an untapped energy source for producing electricity. One method to capture this energy is to dissolve CO₂ gas into water, then convert the produced chemical potential energy into electrical power using an electrochemical system. Previous efforts using this method found that electricity can be generated, but electrical power densities were low and expensive ion-exchange membranes were needed. Here, we overcame these challenges by developing a new approach to capture electrical power from CO₂ dissolved in water: the pH-gradient flow cell. In this approach, two identical supercapacitive manganese oxide electrodes were separated by a non-selective membrane and exposed to an aqueous buffer solution sparged with either CO₂ gas or air. This pH-gradient flow cell produced an average power density of 0.82 W/m², which was nearly 200 times higher than values reported using previous approaches.

27 Introduction

28 Carbon dioxide (CO₂) is produced and released into the atmosphere when fossil fuels are
29 combusted, contributing to global climate change. While there is a clear long-term need to
30 transition to energy producing technologies that do not generate CO₂, there is also a critical
31 short-term need to reduce overall CO₂ emissions by harvesting the potential energy contained
32 in CO₂ exhaust. Previous work has estimated that the theoretical total amount of potential
33 energy that is produced from CO₂ emissions annually is approximately 1,570 TWh,¹ which is
34 more than a third of the total U.S. electricity generated in 2015 (4,078 TWh).² The most
35 extensively studied approach for capturing this energy is to use catalytic processes to convert
36 emitted CO₂ into a fuel, such as hydrocarbons and syngas, which can subsequently be fed
37 into a fuel cell along with other energy dense fuels, such as H₂, to generate electrical power.^{3,}
38 ⁴ Here, we examine an alternative strategy that has been investigated to a lesser degree, which
39 is based on recently developed approaches to produce electrical power from differences in
40 salt concentrations between two waters using electrochemical cells.^{e.g., 5-15} In this study, we
41 used the CO₂ concentration difference between exhaust gas and atmospheric air¹⁶ to create
42 pH differences between two waters, which could subsequently be used to generate
43 electricity.^{1, 17, 18}

44 When CO₂ is dissolved in water, it forms carbonic acid (H₂CO₃), which disproportionates
45 into bicarbonate (HCO₃⁻) and protons (H⁺) at neutral and basic pHs. Prior work has shown
46 that flowing solutions containing dissolved CO₂ and industrial alkaline wastes through
47 different compartments in a fuel cell divided by ion-exchange membranes can be used to
48 generate a voltage across the membranes while mineralizing CO₂.¹⁷ This approach yielded a
49 power density of 5.5 W/m², but it required chemical inputs (i.e., N₂, H₂, and Ca(OH)₂) that

would make the process difficult to implement universally. Carbon dioxide can also be used to generate electrical power without the need for additional resources by creating differences in pH values or bicarbonate concentrations between two solutions. Recently, this approach was shown to produce electricity from CO₂- and air-sparged solutions using solid film and flow capacitive electrodes.^{1, 18} While this approach produced electricity, there were two practical challenges that would limit its practical use. First, reported power densities were low (0.0045 W/m²).^{1, 18} Second, these systems required ion-exchange membranes that would be prohibitively expensive relative to the achievable power densities.^{1, 17-19} Therefore, new technological advances are necessary to increase power densities and reduce material costs to make the proposed approach economically viable.

Here we developed and tested a novel electrochemical pH-gradient flow cell for producing electricity from the pH difference generated from CO₂- and air-sparged aqueous solutions. We hypothesized that manganese oxide (MnO₂) electrodes could be used to rapidly develop pH-dependent electrode potentials and hence produce electricity (Fig. 1a). While MnO₂ has been extensively studied in the past due to its use as a catalyst, supercapacitor in energy storage devices, and electrode material in salinity gradient energy technologies,^{9, 20-23} no work has previously investigated if MnO₂ electrodes could be used to generate electricity from pH-dependent electrode potentials. In the flow cell, the MnO₂ electrodes were separated by an inexpensive, non-selective membrane and were each exposed to two different aqueous solutions containing sodium bicarbonate buffer: one sparged with CO₂ gas, the other sparged with air. Here we demonstrated the feasibility of this approach by showing power production as a function of external resistance over multiple cycles, compared the measured cell voltage with the predicted value from the Nernst equation, and outlined how this cell could be

improved for increased power production.

Materials and Methods

MnO₂ was synthesized by following a previously reported co-precipitation method.^{24, 25} Briefly, a 0.2 M MnSO₄ solution (120 ml, Alfa Aesar) was poured into a 0.2 M KMnO₄ solution (80 ml, Alfa Aesar) under vigorous stirring at room temperature. The resulting MnO₂ precipitates were washed and collected by centrifugation, followed by overnight drying in a vacuum oven at 70°C. To prepare composite electrodes, MnO₂ powder (70 wt%), carbon black (20 wt%, Vulcan XC72R, Cabot) and polyvinylidene fluoride (10 wt%, kynar HSV 900, Arkema Inc.) were mixed homogeneously in 1-methyl-2-pyrrolidinone (2 mL per 0.1 g MnO₂, Sigma Aldrich). The resulting slurry was loaded dropwise onto carbon cloth (1071HCB, AvCarb Material Solutions), where the mass loading of the composite electrode was approximately 4 – 5 mg/cm², which was chosen as an optimal condition for the power production (data not shown). Afterwards, the electrodes were dried overnight in a vacuum oven at 70°C. Additional details regarding the characterizations of the MnO₂, flow cell construction, and the electrode potential of MnO₂ as a function pH are in sections A and B of the SI.

To convert the CO₂ concentration difference between exhaust gas and ambient air into electricity using MnO₂ electrodes in a flow cell, two 1 M NaHCO₃ solutions were sparged using a gas diffuser stone and stirring using either pure CO₂ (final pH=7.7) or air (final pH=9.4) to produce a pH difference between the solutions (Δ pH = 1.7). Each solution was simultaneously injected into one of the two channels in the flow cell using a peristaltic pump (Cole-Parmer) at a flow rate of 15 mL/min that was large enough to keep the pH difference

between two channels and hence to develop the pseudo-equilibrium cell voltage.²⁶ Electricity produced by connecting two electrodes was measured at different external resistances ($R_{\text{ext}} = 4, 6, 10, 16, 22 \Omega$). During electricity production, the cell voltage (ΔE_{cell}) was recorded using a potentiostat (VMP3, Bio-Logic). A cycle was completed when the cell voltage decreased below ± 30 mV, and a new cycle was initiated by switching the solutions to the alternate channels.

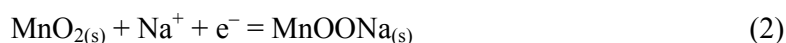
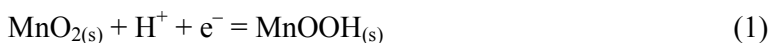
The power density of a cycle was calculated using the cell voltage and the external resistance ($P = \Delta E_{\text{cell}}^2 / R_{\text{ext}}$) divided by the membrane area ($\sim 3 \text{ cm}^2$). The average power density (P_{avg}) was calculated over the complete cycle, which produced the energy density (W) when multiplied by time. Note that a conventional method (i.e., constant current discharging) can also be used to produce electricity, but the power density calculated using this method would only account for the discharging process. The method for recording the cell voltage while connecting the external resistance during the entire process provides a power density that includes the time taken for switching solutions and developing the cell voltage (i.e., the charging process).

Results and Discussion

In this flow cell system, we created a pH gradient between two aqueous solutions by sparging 1 M NaHCO_3 with either air (pH = 9.4) or CO_2 (pH = 7.7). These two solutions were then pumped through the two channels in the flow cell, with each contained an identical electrode composed of amorphous MnO_2 (Fig. 1b). The difference in pH between the two solutions created a voltage difference between the two electrodes of $0.196 \pm 0.001 \text{ V}$ (Fig. 2a) when the circuit was open. Periodically alternating which solution flowed through each

channel yielded a reversal in the cell voltage that developed within 60 seconds.

To examine the relationship between the solution pH and the MnO₂ electrode potential, we measured open circuit potentials of an MnO₂ electrode in several sodium bicarbonate/carbonate solutions with pH values ranging from 7.7 and 11.9 and a constant Na⁺ concentration of 1 M. The MnO₂ electrode potential decreased as the solution pH increased, with the potential being linearly proportional to the pH with a slope of –0.059 V/pH unit (Fig. 2b). Previous work has found that structural Mn³⁺ and Mn⁴⁺ in MnO₂ can undergo a reversible redox reaction through the intercalation/deintercalation and/or adsorption/desorption of protons or cations (i.e., Na⁺ in this system) according to the following half reactions:^{21, 27-30}



In our system, the Na⁺ concentrations (and activities) were the same in all the solutions, and therefore the relative potential difference between the electrodes was due to the pH difference according to Eq 1. The Nernst equation for Eq. 1 can be written as:

$$E = E^0 + \frac{RT}{F} \ln a_{\text{H}^+} \quad (3)$$

where E is the electrode potential, E^0 is the standard electrode potential, R is the gas constant (8.314 J mol^{–1} K^{–1}), T is absolute temperature (K), F is the Faraday constant (96,485 C mol^{–1}), a is activity, and the activity of each solid is assumed to be 1. At room temperature (25°C), the Nernst equation can be re-written as:

$$E = E^0 - 0.059 \times \text{pH} \quad (4)$$

The predicted pH-dependency from Eq. 4 (–0.059 V/pH unit) was in excellent agreement with experimental data shown in Fig. 2b (–0.059 V/pH unit). In addition, the theoretical

estimation made by applying the pH difference between CO₂- and air-sparged solutions ($\Delta\text{pH} = 1.7$) shown in Fig. 2a to Eq. 4 (0.201 V) also resulted in good agreement with the cell voltage achieved in the flow cell (0.196 V).

To convert the cell voltage that was developed in the flow cell into electricity, the circuit was closed using an external resistor ($R_{\text{ext}} = 22 \Omega$) while flowing the CO₂-sparged and air-sparged solutions through each channel. Upon closing the circuit, the cell voltage rapidly increased over the first five seconds, then gradually decreased as the cell discharged (Fig. 3a). The reason that the voltage initially increased then decreased was that two competing factors were affecting it: (1) the cell voltage increased because the MnO₂ electrodes were developing pH-dependent potentials when exposed to the solutions (Eqs. 3 and 4), resulting in charging of the cell, and (2) electrical power was being produced as a result of the potential difference between the electrodes (i.e., the cell voltage), which decreased the cell voltage as a result of discharging of the cell through redox reactions (Eqs. 1 and 2). Based on the cell voltage and current flow, we calculated an average power density of 0.52 W/m²-membrane area. After the first discharge, additional electricity could be produced by switching the solutions that flowed over each electrode, resulting in a similar average power density of 0.51 W/m² in the opposite direction. Switching the flow path between the low and high pH solutions altered the electrode potentials and reversed the cell charging/discharging mechanism, allowing the discharged electrodes to re-charge.

To optimize the power production of the pH-gradient flow cell, we measured cell voltage profiles as a function of external resistance. Decreasing the external resistance from 22 Ω to 4 Ω led to an increase in current flow between the electrodes and a decrease in cell voltage, due to an increase in ohmic drop (Fig. 3b). For each resistance, we calculated the energy and

average power densities. We achieved the highest average power density ($0.82 \pm 0.01 \text{ W/m}^2$) and energy density ($15.00 \pm 1.74 \text{ J/m}^2$) when R_{ext} was 6Ω (Fig. 3c). Note that the average power density increased up to 1.70 W/m^2 using the highest achievable pH difference between pure CO_2 and ambient air (i.e., $\text{pH}_1 = 7.6$, $\text{pH}_2 = 10.0$; see section D, SI). To examine the power production of the flow cell over prolonged periods, we tested the performance over 50 cycles at $R_{\text{ext}} = 16 \Omega$ by periodically alternating the solutions that flowed into each channel. We observed stable average power densities for 50 cycles (Fig. 3d), indicating that the electrodes underwent reversible reactions. The average power density was approximately $0.66 \pm 0.01 \text{ W/m}^2$ for the first 10 cycles, which decreased to $0.64 \pm 0.01 \text{ W/m}^2$ for the last 10 cycles (2% decrease).

To produce the high average power and energy densities demonstrated here, the cell design and solution chemistry played important roles. The MnO_2 electrodes developed pH-dependent potentials that could be constantly discharged, thus electricity was continually produced without the need for an additional step for charging using a secondary device (e.g., a potentiostat). The use of NaHCO_3 solutions also benefited electricity production in multiple ways. First, it kept the pH above 7, which was important because the MnO_2 electrodes could destabilize in acidic solutions.³¹ Second, the ability of bicarbonate to buffer the pH provided a source of protons at the electrode surface, which yielded an achievable charge storage capacity that was more than double of what was achieved using NaCl as an electrolyte (Fig. S5). Third, the use of NaHCO_3 solutions allowed for the rapid cell voltage development for the faradaic reaction. The quick equilibration time was due in part to the pH buffering of the bicarbonate in solution. In a control experiment conducted with 1 M NaCl solutions ($\Delta\text{pH} = 1.7$), the voltage difference only reached approximately 0.08 V after 250 sec (Fig. S6),

suggesting that the bicarbonate ions served as proton donors/acceptors near the electrode surface. Forth, the NaHCO_3 solutions did not require additional inputs other than CO_2 gas, and can likely be combined with non-precious salt solutions such as brackish water.

The pH-gradient flow cell demonstrated that high power densities could be achieved when converting waste CO_2 into electricity using the pH difference between CO_2 - and air-sparged solutions. The use of MnO_2 electrodes that developed pH-dependent potential allowed for producing an average power density (0.82 W/m^2) that was nearly 200 times higher than what has previously been reported.^{1, 18} This power density was comparable to those produced in salinity gradient technologies ($0.1\text{--}10 \text{ W/m}^2$) that use similar cell designs to produce electricity from seawater and river water.^{9, 32-34} The power densities were relatively low, however, compared to other fuel cells systems that use CO_2 ($1\text{--}10 \text{ kW/m}^2$).^{3, 4} There are two reasons for this: (1) the fuel cell systems require other energy dense fuels, such as H_2 , and elevated temperatures, which increase the amount of potential energy available, and (2) fuel cell technologies have been studied far more extensively than the technology discussed here, and therefore are further along in development and optimization. The cell described here has advantages over these technologies in that it uses only inexpensive materials and can be operated at room temperature. In addition, operating our system was focused on maximizing power density, thus the amount of energy harvested would be only a portion of the available energy between two solutions due to the inherent tradeoff between maximum power and energy recovery efficiency.⁵ Our calculations indicated that the amount of harvestable energy normalized the volume of mixed solution (0.295 kJ/L) or mass of CO_2 (76.8 kJ/kg) was more than twice as larger as the energy inputs needed for sparging and pumping (see SI, section E). Note, however, that the relative values would certainly change

when scaling up the technology for real-world applications due to variations in the flue gas physical properties and chemistry, specifically the CO₂ concentration (typical values are approximately 10%, but they can vary depending on the source)³⁵, the flue gas temperature after cooling (40 – 60°C)³⁶, and the impurities present in the gas stream (e.g., sulfur). Additional energy would also be consumed for separating CO₂ from a flue gas and constructing reactor components. We note, however, that determining if this process would be economically viable when scaled up would require a full energy return on investment. At this stage, the results demonstrated here indicate that the pH-gradient flow could represent a promising approach for converting CO₂ into electricity, but further investigations on optimizing performance and assessing energy balance are needed.

Acknowledgements

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Associated content

Supporting information available: detailed information on the electrode material characterizations, reactor construction, electrochemical characterizations, and energy calculations is provided in the supporting information. This material is available free of charge via the internet at <http://pubs.acs.org>.

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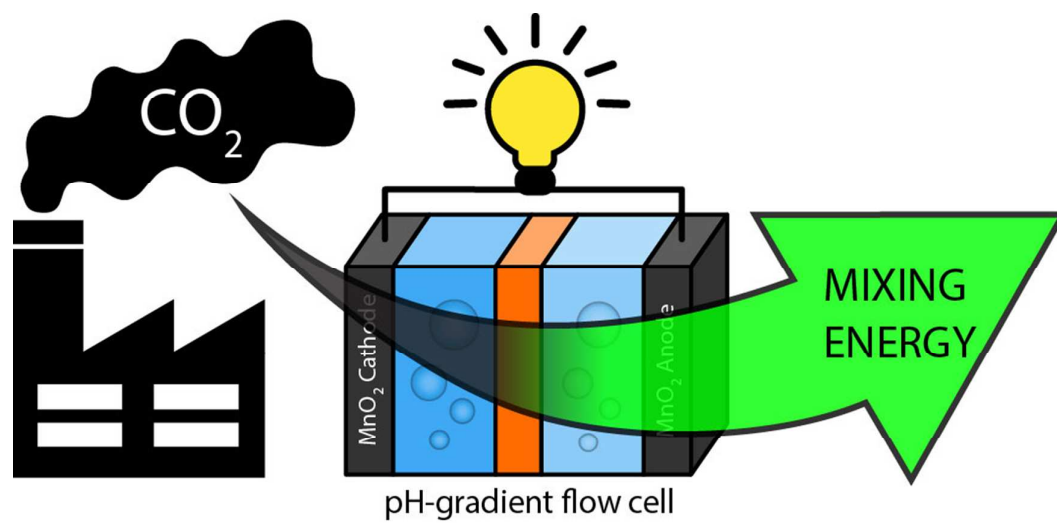
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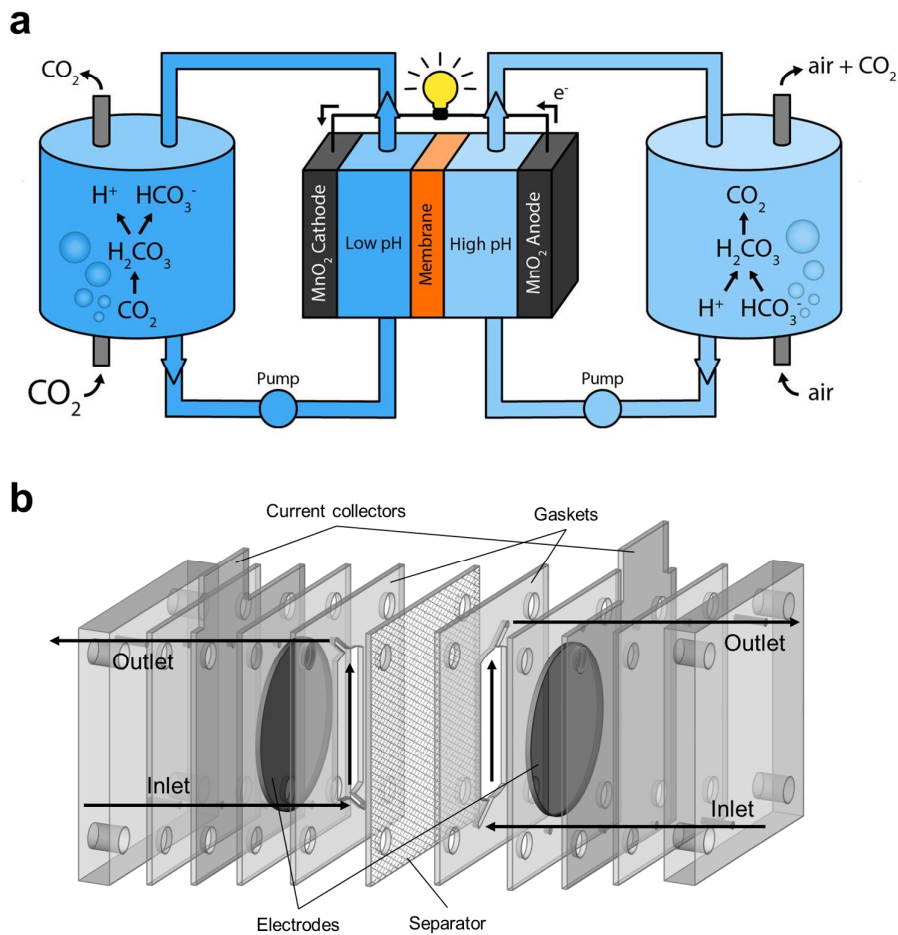
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329



331 **Figures**



332
333 **Figure 1.** (a) Schematic of the pH-gradient flow cell for converting CO_2 into electricity. The
334 flow cell consisted of two identical MnO_2 electrodes (black) divided by a non-selective
335 membrane (orange) placed between channels. The channels were simultaneous fed by 1 M
336 NaHCO_3 solutions with a low pH value (7.7, dark blue) and high pH value (9.4, light blue)
337 that were generated by sparging the solutions with CO_2 (pH = 7.7) or air (pH = 9.4). (b)
338 Detailed diagram illustrating the components of the flow cell.
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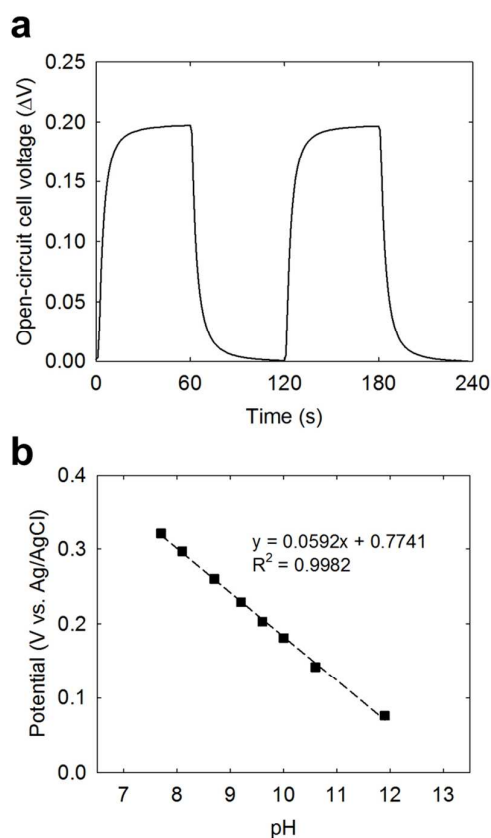


Figure 2. (a) Open-circuit cell voltage profile of a full cell measured by switching the injection of CO_2 - and air-sparged 1 M NaHCO_3 solutions ($\Delta\text{pH} = 1.7$) every 60 s at the flow rate of 15 ml/min. (b) Open-circuit potential of MnO_2 electrode as a function of pH measured in a half cell consisting of a platinum counter electrode and Ag/AgCl reference electrode. Solutions with pH 7.7 to 11.9 was prepared by mixing 1 M NaHCO_3 and 0.5 M Na_2CO_3 solutions in different ratios.

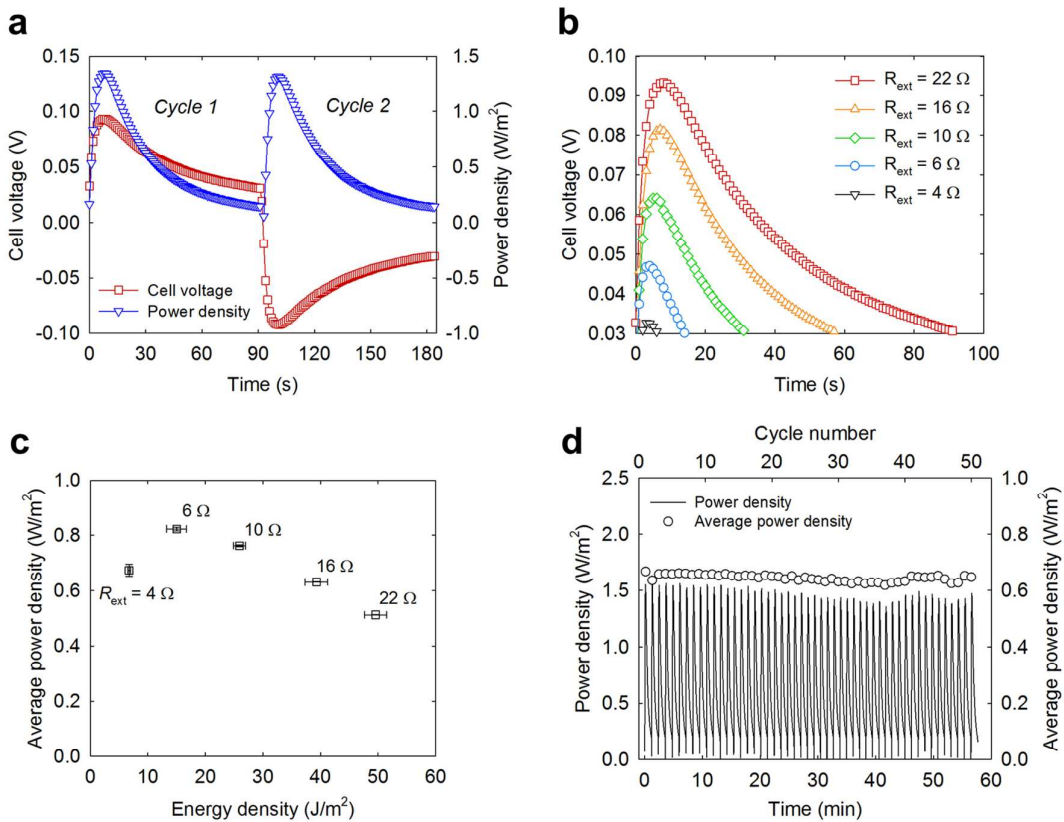


Figure 3. (a) Representative cell voltage and power density profiles for the pH-gradient flow cell ($R_{\text{ext}} = 22 \Omega$). A cycle (cycle 1) started by switching the flow path between CO_2 - and air-sparged 1 M NaHCO_3 solutions, and ended when the cell voltage decreased below ± 30 mV. Switching the flow path produced power in the sequel cycle (cycle 2), and reversed the cell voltage. (b) Representative cell voltage profiles. (c) Average power density vs. energy density plot as a function of load placed between electrodes. The error bars denote the range for duplicated experiments. (d) Long-term cycle performance for 50 cycles ($R_{\text{ext}} = 16 \Omega$).