The massive increase in waste CO₂ has aroused widespread social concern because of its intense impacts on the global environment and climate. Incessant combustion of carbon-based fuels, as the primary energy sources, produce relentless CO₂ and ubiquitous waste heat; a majority of this waste heat is regarded as low-grade heat (<100 °C) and is usually dumped to the environment without use. To reduce the CO₂ level and alleviate the global warming issue, numerous research efforts have been made to develop carbon capture and storage (CCS) technologies which require external input energy or mass to extract and store the waste without efficient utilization, this study proposes a thermally regenerative CO₂-induced pH-gradient cell (TRCPC) that simultaneously utilizes CO₂ and low-grade heat for waste-to-electricity conversion. CO₂ is absorbed in one side of the symmetric electrolyte and causes a change in pH of the cell to induce voltage generation, achieving a peak power density of 0.578 W m⁻². After discharging, the system can be regenerated using low-grade heat while the CO₂ can then be stored and transported. This research proposes a promising method with economic and environmental benefits that converts CO₂ and waste heat into electricity before further CO₂ storage.
The catholyte side is established to build a potential difference through two pH-sensitive MnO₂/MnOOH electrodes. When discharging, the protons in the catholyte intercalate into the manganese dioxide while the anode experiences a reverse reaction. The pH gradient gradually decreases during the process until a CO₂ saturation state is reached. Afterward, NaHCO₃ can be thermally regenerated to Na₂CO₃; the CO₂ can then be further stored. Finally, the two electrodes can be swapped to fully exploit their ratio of oxidation and reduction states.

To generate electricity from TRCPC, the electrode potential is established by the pH change of the electrolyte with an increasing amount of CO₂ absorbed, and then the system is reversible when heat is utilized. Hence, there are three basic requirements for the proposed system to be technically feasible: (1) the cell potential difference can be built by CO₂ absorption; (2) the electrode redox reactions can be driven by the cell potential; and (3) the electrolyte can be thermally regenerated. Figure 2a illustrates the design concept of TRCPC. The red curve is the change of NaHCO₃ percentage with respect to the cell constituent CO₂ injection level, where the pH decreases after CO₂ is absorbed until the electrolyte in the catholyte reaches its saturated condition. The black curve represents the trend of cell open-circuit voltage (OCV) versus pH change between the two sides. Upon heating, NaHCO₃ is decomposed to Na₂CO₃, and a decrease in NaHCO₃ percentage results in the decrease of OCV.

Figure 2b shows that the cell OCV raised rapidly until it reached a peak value of approximately 0.18 V. The OCV can be sustained with a constant CO₂ supply; once the supply is interrupted, the voltage gradually decays (i.e., about 2 h) because of the ion diffusion (e.g., HCO₃⁻) through the membrane from catholyte to anolyte (Figure S2). The slope and peak value of OCV are mainly determined by the CO₂ flow rate, inlet CO₂ concentration, and absorbent concentration. Figure S2a shows the OCV change corresponding to...
different inlet CO₂ percentages with different flow rates. At a fixed flow rate of 2 mL min⁻¹, the pure CO₂ provided 0.16 V while the 10% CO₂ delivered only 0.05 V because of a lower chance of contact between the CO₂ and the electrolyte. Hence, in practical applications, the working fluid with a higher concentration of CO₂ is preferred. As shown in Figures 2c and S2b, a higher flow rate and a higher electrolyte concentration will accelerate the process. According to \( \Delta \text{pH} = \text{pH}_{\text{initial}} - \text{pH}_{\text{equilibrium}} \) and \( \frac{\text{d} \text{pH}}{\text{d} t} \), both the pH change and the rate of pH change increase with increasing concentration of Na₂CO₃, benefiting a higher peak OCV, a shorter equilibrium time, and a larger amount of CO₂ absorption. Taking all these factors into account, the 0.5 M Na₂CO₃ electrolyte and the total amount of 20 mL CO₂ for each cycle with flow rate of 2 mL min⁻¹ were chosen as the standard conditions in all experiments if not otherwise stated. As shown in Figure 2c,d, the three-electrode system, using MnO₂/MnOOH electrode, platinum wire, and Ag/AgCl electrode as the working, counter,
and reference electrode, respectively, was used to measure the relationship between the potential change of MnO2/MnOOH electrode and the pH value of electrolyte in the various NaHCO3/Na2CO3 mixtures. As noted, the electrolytes were prepared by mixing 1 M NaHCO3 and 0.5 M Na2CO3 to maintain the overall c(Na+) in 1 M. Additional discussion on the influence of Na+ in the electrolyte can be found in Supplementary Notes 1. The maximum potential between pure NaHCO3 and Na2CO3 is approximately 0.18 V. In the operation, only part of Na2CO3 was converted to NaHCO3, but the measured voltage also reached close to 0.18 V. Here, the membrane may contribute to the increase in the cell potential. Figure 2d expresses a good linearity between the potential and pH with a slope of 78.8 mV pH−1 in a pH range from 8.4 to 10.5.

The discharging ability of TRCPC relies on the pseudocapacitance behavior of the MnOOH/MnO2 electrodes. In Figure 3a, the cyclic voltammetry curve of MnOOH/MnO2 electrode (50%/50%, molar fraction) in 0.5 M Na2CO3 electrolyte indicates a capacitance of 26.24 F g−1. The synthesized MnO2 particles were approximately 500 nm as illustrated in Figure 3b. As shown in Figure 3c–e, the X-ray photoelectron spectroscopy (XPS) spectrum provided evidence that MnO2 and MnOOH coexisted. Figure 3e demonstrates the transformation from MnO2 to MnOOH during the controlled discharging process. Additional discussion on XPS results can be found in Supplementary Note 2.

After the CO2-induced voltage generation and electrode discharging capability were investigated, the charge–discharge cycles were conducted in a single cell (Figure S5) to study the system performance. In Figure 4a, the peak power density of TRCPC was calculated to be 0.578 W m−2. Figure 4b shows the constant current discharging performance of our standard 20 mL CO2 system as compared with the 60 mL CO2 system, where the discharging times were 360 and 720.4 s under 1 mA discharging current, respectively. Although the initial potential of the 60 mL CO2 system (0.1601 V) was slightly higher than that of the 20 mL CO2 system (0.1404 V), there was a quick potential drop at the beginning, and both systems had a similar level of average discharging potential (0.0425 and 0.0428 V). The overall energy densities were calculated to be 153.05 and 70.614 J m−2 for 60 and 20 mL, respectively (Supplementary Note 3). Unifying to 1 mol CO2, energy density values of 15.871 Wh m−2 mol−1 (60 mL) and 21.972 Wh m−2 mol−1 (20 mL) were obtained. In principle, under the same discharging conditions, the discharging time of a 60 mL CO2 system should be 3 times that of a 20 mL CO2 system; however, a 60 mL CO2 system showed only a 2.17-fold increase. This difference was mainly caused by two reasons. First, in a limited electrolyte volume (1.6 mL), the CO2 absorption rate decreased with increasing the proportion of NaHCO3, leading to a nonlinear relationship between CO2 absorption capability and CO2 supply. In the late absorption period of the 60 mL system, the same amount of CO2 supply provided a relatively short discharging time. Second, more ions (e.g., HCO3−) would diffuse across the membrane from catholyte to anolyte during the longer operation time of the 60 mL CO2 system, resulting in a larger potential drop. Therefore, the energy density of the 60 mL CO2 system was less than that of the 20 mL CO2 system.

Before cycling experiments were conducted, the cutoff point was determined. The theoretical calculation method of ion concentration at different conditions is shown in Supplementary Note 4, which indicates that only little CO2 can be
further dissolved in the electrolyte after the conversion from 0.5 M Na₂CO₃ to 1 M NaHCO₃. Thus, a control system with pure 1 M NaHCO₃ in both anolyte and catholyte was investigated, where CO₂ was supplied to the catholyte. This control system represented the saturated condition, so its potential plateau of 50 mV can be used as the cutoff point when Na₂CO₃ was fully converted to NaHCO₃ in TRCPC, as seen in the dashed lines in Figures 4c and S7.

Once the voltage is lower than the cutoff point, it is time to regenerate the electrolyte by heat. Under this circumstance, the overall 30 cycles were performed from the initial state to the cutoff point with the final built-in potential of approximately 55 mV (Figures 4c and S8). The total energy of these 30 cycles was counted by integrating the discharging energy of every cycle when discharge time decreased from 322.2 s for the first cycle to 48.78 s for the last cycle; the total energy produced is computed to be 0.05646 J, corresponding to the 0.02679 mol of CO₂ inlet and the generation of 0.0016 mol of NaHCO₃ (Supplementary Note 3 and Table S1). The built-in voltages decreased because the CO₂ absorption capability gradually declined as the solution became a mixture of Na₂CO₃ and NaHCO₃. It is important to note that the potential does not start from 0 V except for the first charge-discharge cycle because of the membrane potential being built by the concentration difference between anolyte and catholyte. It takes a long time for ions to completely diffuse across the membrane to remove these residual charges. After several charging-discharging cycles, the cathode was in the reduced state with more MnOOH while the anode was in the oxidized state with more MnO₂. It is worth noting that the two state with more MnOOH while the anode was in the oxidized charging-discharging cycles, the cathode was in the reduced membrane to remove these residual charges. After several cycles, the origin of the voltage difference between anolyte and catholyte. It

After the system reaches the saturated state, the electrolyte can be thermally regenerated by using low-grade waste heat. The absorbed CO₂ will be released and then stored, allowing TRCPC for the next operation. To efficiently utilize the waste heat, a lower regenerating temperature and a larger built-in potential are expected at the same time. The pH changes of the electrolytes were monitored under different temperatures to estimate the proportion of NaHCO₃ and Na₂CO₃. Calculated from the results in Figures 5a and 2c, approximately 17 L of CO₂ (regenerate ratio = 80%) and 2.912 L of CO₂ (regenerate ratio = 13%) were released from 1 L electrolyte for the regeneration at 90 and 70 °C, respectively. As noted, the CO₂ storage capacity corresponds to not only the regeneration temperature but also the operating temperature; theoretically, the storage capacity will remain the same at each cycle. Thus, a larger temperature difference gives a higher CO₂ storage capacity. Figure 5b further demonstrates the release of CO₂ from the electrolyte at the temperature of 90 °C. It can be estimated that a single cell needs 0.23 kJ of heat for electrolyte regeneration at 90 °C (Supplementary Note 3).

The proof-of-concept implementation of one cell working under 10 Ω load is shown in Figure 5c. After building up the OCV of 0.11 V, the switch was turned on, and then the current was recorded by the ammeter under continuous supply of gas. As seen, the discharging potential was stabilized at 0.047 V with a stable current output of 0.32 mA. Once the CO₂ supply was interrupted, the potential and current quickly decreased within 1000 s. It is suggested that a continuous CO₂ supply can maintain the potential difference and will extend the discharge time. The TRCPC shows great potential to scale up in industry, particularly in a thermal power plant. According to our current design, 14.7 W h of electricity can be produced based on 1 ton CO₂ in a single TRCPC cycle. However, this result was obtained from the single cell while a single cell was not available to absorb all the CO₂. In practical application, it is feasible to construct a cascade system with integrated cells, making full use of CO₂. If all the CO₂ can be fully used, 493 W h of electricity will be generated from 1 ton of CO₂ per cycle. Assuming CO₂ emission of 20 million tons per year from one power plant, 22 9.8 GW h of electricity is able to be produced by one TRCPC cycle.

This work demonstrated the design principle and a proof-of-concept device for TRCPC. There is still plenty of opportunity for system optimization based on our theoretical calculation (Supplementary Note 3). For example, tuning the electrode helps to enlarge the capacity and make the discharge time longer; improving the electrolyte benefits the built-in potential and CO₂ consumption, and modifying the membrane assists to find the best balance between the diffusion and the concentration difference. In addition, engineering optimizations in the flow rate, pipe diameter, and so on are equally important. Other underlying improvements may exist, such as altering the Na₂CO₃ absorbance into an amine.

In summary, we proposed the TRCPC for waste-to-electricity conversion by exploiting CO₂ and low-grade heat. The TRCPC was constructed for practical electricity generation in CCS technologies. The feasibility of the scheme was experimentally confirmed, and the origins of the voltage and current were studied and discussed through electrochemical experiments as well as materials characterization. A pH difference was then examined in the membrane-separated electrolyte, and an OCV difference was established through the pseudocapacitance behavior of the MnOOH/MnO₂ electrode in the Na₂CO₃ electrolyte. The proposed system displayed a competitive power density of 0.578 W m⁻². The regenerative stage was completed by supplying the thermal energy to convert 0.5 M Na₂CO₃ electrolyte into the initial state. Finally, a proof-of-concept demonstration showed promising potential to be applied in large-scale applications when further improved by controlling the working conditions, such as the flow rate, membrane, and pipe diameter. Assuming CO₂ emission of 20 million tons per year from one power plant, 22 9.8 GW h of electricity is able to be produced by one TRCPC cycle. These results have significant implications for continuous energy recovery during the CCS process.

**ASSOCIATED CONTENT**

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c01000.

Experimental methods (synthesis of the MnO₂ powder, preparation of the electrodes, fabrication of the cell, and measurements (electrochemical, XPS, XRD, and EDS)), supplementary notes 1–4 (discussion of the electrolyte influence and the results of XRD and XPS; calculation of efficiency and ion concentration change with pH), Figures S1–S10 (pH-working mechanism, gas and concentration effects, EDS, XRD, fabrication of the cell, charge-discharge performance, cycle performance, and the energy balance diagram), and Table S1 (average
discharging voltage and time in the cycling experiments) (PDF)
Video of experiment (MP4)

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