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A Switchable pH-differential Reactor with High Reactivity and Efficiency for CO₂ Utilization

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Abstract

CO₂ can be converted to useful fuels by electrochemistry method. As an effective strategy to address greenhouse effect and energy storage shortage, electrochemical reduction of CO₂ still needs major improvements on its efficiency and reactivity. This work demonstrates a switchable pH-differential dual electrolyte microfluidic reactor (DEMR) that enhances the thermodynamic property and raises the electrochemical performance based on a laminar flow membrane-less architecture. It is the first time that the CO₂ electrochemical reduction reaction is freed from the hindrances of thermodynamic limitation. DEMR has also achieved a high reactivity and Faradaic efficiency, revealing the potential for larger-scale applications in future urban energy network, such as a carbon-neutral energy conversion system.

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Nomenclature

DEMR	Dual Electrolyte Microfluidic Reactor
PTFE	Polytetrafluoroethylene
NHE	Normal Hydrogen Electrode
E	Electrical potential

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R	Universal gas constant (8.314 JK ⁻¹ mol ⁻¹)
T	Temperature (298K)
F	Faraday constant (96485 Cmol ⁻¹)
K _i	Equilibrium constant

1. Introduction

Electrochemical conversion of CO₂ into usable fuels has drawn more and more attention, which can provide a solution towards a carbon-neutral energy conversion system. We found that individual electrode potentials can be altered by altering pH for better CO₂ electrochemical reduction. This can be achieved by pairing the cathode with acid and the anode with alkaline electrolytes. Yet, most electrochemical reactors have been designed and developed based on polymer membrane structure [1, 2], which suffers from high cost, flooding problem, and poor durability as an acid-alkaline separator.

To address this issue, a state-of-the-art microfluidic structure [3, 4] is constructed for the implementation of pH adjustment technique. In this work, a switchable pH-differential dual electrolyte microfluidic reactor (DEMUR) achieves the conversion of CO₂ into formic acid with improved thermodynamic characteristics. Our research covers catalyst preparation, and pH optimization for anolyte & catholyte. By breaking the thermodynamic barrier, both reactivity and Faradaic efficiency of the system are enhanced.

2. Methodology

2.1 Material and methods

2.1.1 Catalyst preparation

Commercially available catalysts (i.e. Pb as cathode, Pt black as anode; Johnson Matthey) supported by carbon paper were used as electrodes and Nafion (DuPont) solution was used as catalyst binder. The catalyst ink was scattered onto a PTFE-hydrophobized gas diffusion carbon paper (HCP120, Hesen) to achieve a carbon loading of 5 mg/cm².

2.1.2 Cell fabrication

The electrodes were housed between two 0.05-cm-thick Poly(vinyl chloride) (PVC) sheets as embedding plates. Two silver plates were used as current collectors. Each of the embedding plates were machined with a 0.2 cm (W) × 0.5 cm (L) window as reaction area. Two 0.01-cm-thick PVC sheets were used to separate the electrodes and create identical anolyte and catholyte channels of 0.2 cm (W) × 7.5 cm (L), between which another 0.01-cm-thick PVC sheet with a 0.2 cm (W) × 0.5 cm (L) window was sandwiched to form the electrolyte contact area. A 5 cm (L) × 1 cm (W) × 0.5 cm (H) chamber was machined to act as the CO₂ reservoir for the cathode side. All layered components were fabricated using a carbon dioxide laser ablation system (VLS 2.30, Universal Laser System).

2.1.3 Electrochemistry

Electrochemical tests were conducted by holding the cell at constant potentials by an electrochemical station (CHI600E, CHInstruments, Inc). Each data point was collected by averaging the integration of a 100-second steady-state data to eliminate transient artifacts. Individual potentials of anode and cathode were recorded with digital multi-meters (Fluke) connected between each electrode and an external Ag/AgCl reference electrode in the exit electrolyte stream.

2.1.4 Formic acid determination method

The determination of formic acid adopted the method proposed by Sleat et al. [5], which was based on a non-enzymatic specific reaction forming a red color with an absorption maximum at 510 nm when formate and several chemicals were mixed. Calibration was conducted by quantitatively determining corresponding color formation in the presence of formate at 2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20 mmol/L.

2.2 Formulae for potential and efficiency calculations

2.2.1 Thermodynamics

The equilibrium potentials of cathode reaction E_{cathode}^0 can be calculated from the Nernst equation[6]:

$$E_{\text{cathode}}^0 = E_{\text{cathode @ pH=0}}^0 - \frac{RT}{2F} \cdot \ln\left(\frac{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2}}{1 + \frac{K_3}{[\text{H}^+]}} \cdot \frac{1}{[\text{H}^+]^2}\right) \quad (1)$$

where $K_i = e^{-pK_i}$, $pK_1 = 6.39$, $pK_2 = 10.32$, $pK_3 = 3.75$, $E_{\text{cathode @ pH=0}}^0 = -0.042 \text{ V}$, $[\text{H}^+] = 10^{-\text{pH}}$. [6, 7]

2.2.2 Efficiency calculation

Faradaic and energetic efficiencies are two key benchmarks for a CO_2 electrochemical reduction system. The former is the fraction of the electrons used for formic acid formation and the latter is to measure the portion of energy converted & stored in formic acid. Equations are shown as below:

$$\text{Faradaic efficiency} = \frac{2 \times Y \times \frac{M}{10^6 \times 60}}{N \times 1.04 \times 10^{-5}} \times 100\% \quad (2)$$

$$\text{Energetic efficiency} = \frac{\text{Standard potential}}{\text{Standard potential} + \text{Overpotential}} \times \text{FE} \quad (3)$$

3. Results and discussion

3.1 Catholyte pH optimization

A DEMR was fabricated to construct a microchannel network (Fig. 1). As explained, pH is found to be an important factor that affects the performance of the DEMR. The anolyte was kept as commonly used aqueous 0.5 mol/L K_2SO_4 solution while the catholytes at different pHs were prepared by adjusting 0.5 mol/L K_2SO_4 with 0.5 mol/L H_2SO_4 . This preparation process could preclude the effect of conductivity and focus the performance comparison on pH.

As quantitated by current density, the whole cell reactivity at pH=0 catholyte was five times as much as that of pH=1, whose reactivity was more than twice as much as those of pH=2. From pH=2 onwards,

slight degradation of reactivity was observed. In terms of efficiencies, no formic acid was detected in pH=0 and 1 because HER is dominated at such high H^+ concentration. The situation changed at pH=2, where a Faradaic efficiency of 90.8% and energetic efficiency of 46.4% were obtained at 2.8V. From pH=3 onwards, the figures were gradually diminishing. Considering both reactivity and efficiency, pH=2 was selected as catholyte condition of our DEMR.

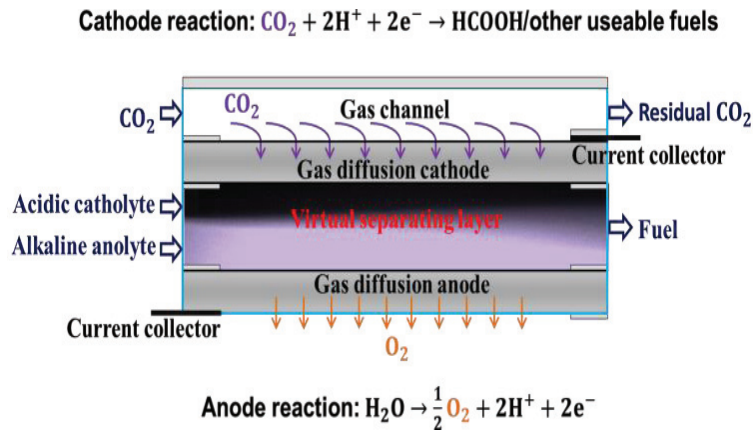


Fig. 1 Schematic diagram of a DEMR (N.B. the virtual separating layer is identified by fluorescein microscopy)

3.2 Anolyte pH optimization

With catholyte pH set to 2, the effect of anolyte pH was studied from pH=7 to pH=14, where the latter showed overwhelming advantage over others in terms of reactivity, i.e. four times more than pH=3 as quantitated by current density. Individual electrode polarization curves demonstrated that pH=14 gave impetus to anode performance, which did not affect the cathode side and hence corroborating that the microfluidics in our DEMR could effectively separate electrolytes and create distinguished conditions for electrodes. Efficiencies were found in accordance with reactivity. When anolyte pH was 14 the peak Faradaic efficiency and energetic efficiency were as high as 94.9% and 48.5%, respectively. With decreasing pH, efficiencies dropped. It should be noted that further increasing the pH would lead to catalyst poisoning and instability. Thus, pH=14 was selected as anolyte pH for our DEMR.

3.3 Discussion

Thermodynamically, acid condition on the cathode side and alkaline on the anode side can lower the potential difference. When applying acidic catholyte, a lower equilibrium potential of cathode reaction can be obtained (-0.199V in acid vs. -1.02V in alkaline, vs. NHE). More desired product, formic acid, can be generated with lower pH, especially when pH is less than 3 [8], and hence increasing the Faradaic efficiency. Lower pH also favors the current density enhancement by reducing polarization losses, i.e. improves the reaction kinetics. On the anode side, alkaline environment ensures the oxygen formation at low equilibrium potential. It should be noted that under neutral or alkaline conditions, unwanted HCO_2^- would be generated and pH>9 does not favor HCO_2^- formation as the reactive $CO_2(aq)$ is sequestered as bicarbonate/ carbonate.

Heat visualization in our previous study showed that acid-base interfacial heat is dominant in a DEMR, whose ohmic Joule heat is much less than a single electrolyte system. Our previous study has utilized fluorescence microscopy to demonstrate that raising the flow rate could enhanced the heat removal and formed a thinner interfacial mixing layer, hence controlling the reactor temperature and suppressing the heat loss.

The implementation of the pH differential technique on microfluidic reactors is only one approach to enhance the electrode thermodynamic property. Further study could be conducted on the performance improvement in other types of fuel cells, such as H₂/O₂ solid oxide fuel cells (SOFCs). Nernst equation,

$E = \frac{RT}{2F} \ln \frac{K p_{H_2} p_{O_2}^{\frac{1}{2}}}{p_{H_2O}}$, tells that the operation temperature and partial pressure of gaseous reactants would affect the electrode thermodynamics. Here, K is the equilibrium constant of the reaction of hydrogen oxidation, p is the partial pressure in the electrode compartment [9]. Pourbaix diagram, as plotted in Fig. 2, demonstrates a voltage adjustment of only 0.02V for 100°C, indicating the insignificant effect on microfluidic or polymer exchange membrane fuel cells operating below 200°C. However, for SOFCs, whose temperature range could be 500-1000°C, the influence of temperature is critical and could bring a voltage difference of 0.1V to the hydrogen electrode potential.

Concentration is another key impact factor of the thermodynamics. In general, for a reaction:



$$E = E^0 - \frac{RT}{zF} \ln \frac{c_G^g c_H^h}{c_A^a c_B^b} \quad (5)$$

In case of H₂/O₂ regenerative fuel cell, the reduction reaction:



corresponds to the Nernst equation:

$$E_{H^+/H_2} = E_{H^+/H_2}^0 + \frac{RT}{nF} \ln \left(\frac{[H^+]^2}{p_{H_2}} \right) \quad (7)$$

The oxidation of water



corresponds to:

$$E_{O_2/H_2O} = E_{O_2/H_2O}^0 + \frac{RT}{nF} \ln (P_{O_2} [H^+]^4) \quad (9)$$

Under unit pressure of gaseous H₂/O₂, the influence of reactant concentrations could only fall in the ion, i.e. pH, instead of gas, because of the particularity of H⁺. This can be explained by the working principle of concentration cells, where the transition from a concentrated solute to its dilute form would be accompanied by a fall in free energy.

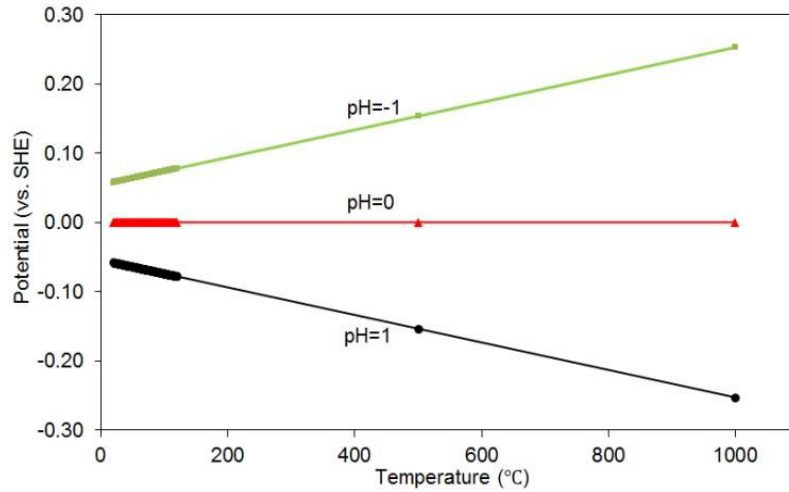


Fig. 2 Pourbaix diagram of the hydrogen electrode

In case of other commonly used fuels and oxidants combinations e.g. H₂/Cl₂, whose standard reduction potential in acidic solution at 25°C is 1.358V to reference hydrogen electrode. The electrolyte of a H₂/Cl₂ fuel cell is usually HCl [10]. The Nernst equation of the hydrogen side reaction is:

$$E_{H^+/H_2} = E_{H^+/H_2}^0 + \frac{RT}{nF} \ln\left(\frac{[H^+]^2}{P_{H_2}}\right) \tag{10}$$

and the chlorine side reaction corresponds to:

$$E_{Cl^-/Cl_2} = E_{Cl^-/Cl_2}^0 + \frac{RT}{nF} \ln\left(\frac{[Cl^-]^2}{P_{Cl_2}}\right) = 1.358 + 0.0257 \ln[Cl^-] \tag{11}$$

The increase of Cl⁻ concentration and decrease of H⁺ concentration, such as the addition of NaCl or KCl, would raise the whole cell output potential. The conductivity should not be sacrificed in all circumstances by means such as salt addition. Also, unlike H⁺ with H₂O as donor, the reduction of Cl⁻ could not lower the electrode potential because of the lack of reactants. It should be noted from the stability diagram of chlorine in water, Cl₂ is unstable in water except at very low pH; it decomposes into HOCl and Cl⁻. Acidic condition is necessary for the stable existence of Cl⁻ species in water [11].

Fig. 3 shows the Pourbaix diagram of H₂/Cl₂ and another similar example, H₂/Br₂ fuel cell, whose standard reduction potential in acidic solution at 25°C is 1.066V to reference hydrogen electrode. As can be seen, by coupling low concentration of H⁺ and high concentration of anions, the theoretical open-circuit voltage of a H₂/Cl₂ fuel cell could be improved from 1.36V to 1.82V and that of a H₂/Br₂ fuel cell could be raised from 1.07V to 1.53V.

Besides, cathode alkalization and anode acidification are observed in microbial fuel cell as reported by some literatures [12, 13]. Hence, coupling microbial fuel cell with the pH-differential technique could achieve the dual electrolyte configuration while saving the consumption of raw electrolyte materials.

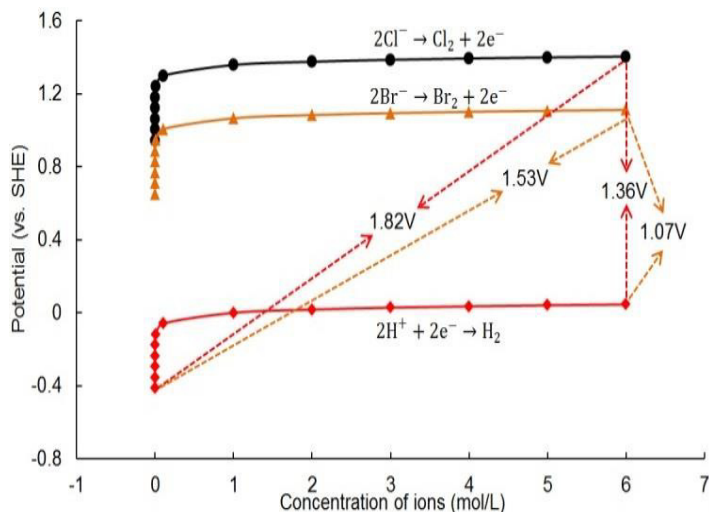


Fig. 3 Pourbaix diagram of H_2 , Cl_2 and Br_2 electrode reactions at room temperature

4. Conclusions

This study is the first systematic investigation and analysis to apply pH-differential and microfluidic techniques on CO_2 reduction. The results indicated that catholyte of pH=2 and anolyte of pH=14 has the optimal whole cell performance. In a dual electrolyte system, the reactivity was raised for ~3 times compared with a single neutral electrolyte arrangement and the peak Faradaic efficiency was improved from 81.6% to 95.6%. This design not only provides a solution towards the improvement of current CO_2 utilization system, but also offers a sustainable prospect for a powerful and efficient energy conversion system with multiple thermodynamic enhancement strategies in various applications.

Based on the DEMR, a carbon-neutral energy supply system can be incorporated into future urban energy network. This system would realize the inter-conversion between CO_2 and various fuels (i.e. methanol, formic acid) boosted by the instantaneous surplus of renewable energy sources such as wind and solar power. The usable fuels can be converted into electricity via fuel cells upon the demand of urban power supply (i.e. electric vehicles). From the mass-balance point of view, no carbon emission is generated in this cycle because CO_2 presents as an intermediate product, revealing a new solution towards CO_2 mitigation and renewable energy utilization.

Acknowledgements

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References

- [1] Li H, Oloman C. The Electro-Reduction of Carbon Dioxide in a Continuous Reactor. *Journal of Applied Electrochemistry*. 2005;35:955-65.
- [2] Köleli F, Atilan T, Palamut N, Gizir AM, Aydin R, Hamann CH. Electrochemical reduction of CO₂ at Pb- and Sn-electrodes in a fixed-bed reactor in aqueous K₂CO₃ and KHCO₃ media. *Journal of Applied Electrochemistry*. 2003;33:447-50.
- [3] Zhang H, Leung MKH, Xuan J, Xu H, Zhang L, Leung DYC, et al. Energy and exergy analysis of microfluidic fuel cell. *International Journal of Hydrogen Energy*. 2013;38:6526-36.
- [4] Wang H, Leung DYC, Xuan J. Modeling of a micro auto-electrolytic cell for hydrogen production. *International Journal of Hydrogen Energy*. 2012;37:10009.
- [5] Sleat R, Mah RA. Quantitative method for colorimetric determination of formate in fermentation media. *Applied and environmental microbiology*. 1984;47:884.
- [6] Reda T, Plugge CM, Abram NJ, Hirst J. Reversible interconversion of carbon dioxide and formate by an electroactive enzyme. *Proceedings of the National Academy of Sciences*. 2008;105:10654-8.
- [7] Lower SK. Acid-base equilibria and calculations. *A Chem*; 2014.
- [8] Oloman C, Li H. Electrochemical processing of carbon dioxide. *Chemsuschem*. 2008;1:385-91.
- [9] Demin A, Tsiakaras P. Thermodynamic analysis of a hydrogen fed solid oxide fuel cell based on a proton conductor. *International Journal of Hydrogen Energy*. 2001;26:1103-8.
- [10] Thomassen M, Børresen B, Hagen G, Tunold R. H₂/Cl₂ fuel cell for co-generation of electricity and HCl. *Journal of applied electrochemistry*. 2003;33:9-13.
- [11] Beverskog B, Puigdomenech I. Pourbaix diagrams for the system copper-chlorine at 5–100 C. *SKI Report*. 1998;98:19.
- [12] Lefebvre O, Shen Y, Tan Z, Uzabiaga A, Chang IS, Ng HY. Full-loop operation and cathodic acidification of a microbial fuel cell operated on domestic wastewater. *Bioresource technology*. 2011;102:5841-8.
- [13] Gil G-C, Chang I-S, Kim BH, Kim M, Jang J-K, Park HS, et al. Operational parameters affecting the performance of a mediator-less microbial fuel cell. *Biosensors and Bioelectronics*. 2003;18:327-34.



Biography

Prof. Dennis Y.C. Leung received his B.Sc. (Eng.) in 1982 and Ph.D. in 1988, both from the Department of Mechanical Engineering at the University of Hong Kong. He joined the same department in 1993 and is now a full professor of the department specializing in renewable energy and energy conservation. He has published more than 400 articles including 210+ peer reviewed SCI journal papers. Prof. Leung is the top 1% highly cited scholars in energy field from 2010 to 2014.