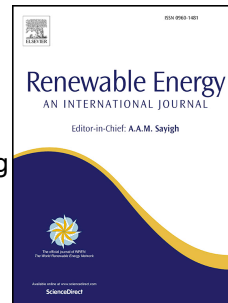


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1 Characterization of a Microfluidic Reactor for CO₂ Conversion with Electrolyte Recycling

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8 Abstract

9 Microfluidic fuel cells and flow batteries are free from the static physical barrier that separated
10 the anodic and cathodic compartments, introducing the advantages of low cost and feasible
11 miniaturized application. Recently, the concept of dual electrolyte stream proves itself an
12 effective strategy to enhance the reactor performance by pairing catholyte and anolyte with
13 thermodynamically favored pHs. Being able to be implemented in both fuel cell and electrolyzer
14 modes, the dual electrolyte strategy demonstrates superior peak power density, low
15 overpotentials, high reactivity, and high efficiency. However, keeping the characteristics of
16 laminar flow requires continuous electrolyte flowing in the microchannel. Besides, neutralization
17 reaction would occur within the mixing layer between the catholyte and the anolyte, requiring
18 higher flow rate to control the layer thickness. These lead to considerable electrolyte wastage
19 that will significantly weaken the economical aspect and electrolyte utilization efficiency. To
20 tackle this issue, this study investigated the electrolyte degradation process and proposed an
21 operation scheme for electrolyte recycling. Key parameters of electrolytes were tracked and
22 monitored by mimicking different reactor situations. Results indicated that with appropriately
23 adjusted operating conditions, electrolyte recycling would be feasible in a microfluidic pH-

24 differential network. Accordingly, an pH indicator for electrolyte recycling was proposed for
25 potential practical application.

26 **Keywords**

27 Dual electrolyte, Electrochemistry, Microfluidics, Electrolyte recycling, pH/conductivity
28 degradation

29 **1. Introduction**

30 Notwithstanding the merits of low cost, high interphasial contact area, and controlled flooding
31 problem, low electrolyte utilization efficiency has long been a problem of flow batteries and
32 microfluidic fuel cells. To drive the electrolyte streams and retain them within laminar
33 characteristics, considerable amount of electrolytes is used, which, in most cases, is disposed.
34 Many researchers have conceived the renewal or reuse of electrolytes. In the research of a
35 quinone-bromide flow battery based on metal-free materials, Huskinson *et al.* proposed that the
36 economical hydroxy-substituted anthraquinones could be utilized to regenerate anthraquinone-
37 based electrolyte solutions for reuse[1]. The undesired cross contamination of anolyte and
38 catholyte through the cell separator always occurs in a flow battery. With four different oxidation
39 states, vanadium redox flow batteries could be used to tackle this issue as they enabled the fuel
40 and oxidant regeneration[2]. Qiu *et al.* established a model that could help investigate and
41 characterize the key parameters of electrolyte utilization, aiming at figuring out the electrode
42 structures and conditions for an optimized operation[3]. However, although reducing agents
43 could be added to recover the electrolyte, vanadium redox based flow batteries still suffered from
44 various losses, especially electrode transport losses and electrolyte wastage. To our best
45 knowledge, no concrete literatures could be found to firmly address this issue.

46 Currently, most researches on electrochemical reduction of CO₂ are based on a proton-
47 exchange membrane, which conducts protons whilst insulates electrons and separates reactants.
48 The high membrane cost, water management, and degradation problems, have hindered its
49 further advancement and miniaturization. In this study, a microfluidic design was implemented,
50 where two fluids flow co-laminarily in a micro-scale channel and perform distinctive behaviors
51 with high surface-to-volume ratios and super-fast mass transfer rates. Microfluidics is a powerful
52 technique to enhance the performance of reaction systems and offers a virtual but effective layer
53 to replace conventional membrane, providing an ultimate solution towards some of the
54 limitations of macroscale devices. The function of this virtual layer has not been fully explored
55 until the concept of dual electrolyte was raised[4]. By coupling electrodes with corresponding
56 thermodynamically favored pHs, not only the fuel cell performance (that is, output power
57 density), but also the electrolysis process (that is, on-set voltage, efficiency, reactivity) could be
58 enhanced significantly. This technique can be, and has been validated in multiple applications by
59 many research groups[5], including the present research team[6]. Yet, the co-laminar flows of
60 acid and alkaline would bring up an unavoidable problem, neutralization losses. The acid-
61 alkaline neutralization reaction is a superfast reaction with a rate constant of $\sim 10^{11} \text{ M}^{-1} \text{ s}^{-1}$ and
62 would intensify the electrolyte crossover contamination phenomenon. Therefore, identifying the
63 degradation mechanism is the key to facilitate electrolyte recycling in the multi-dimensional
64 electrochemistry scenario. Recently, our research group has developed a membraneless dual
65 electrolyte reactor as a regenerative H₂/O₂ fuel cell[6] and a CO₂ conversion system[7]. By
66 pairing electrodes with electrolytes at different pHs, the thermodynamic limitations of water
67 window was relieved and the electrochemical performance was significantly enhanced with high
68 output power density, round-trip efficiency and low on-set voltage. Electrode potentials were

69 closer to corresponding equilibrium status and hence less Joule heat loss was dissipated,
70 facilitating the possibility of an efficient zero-carbon energy storage platform. The catholyte-
71 anolyte interface and its associated reactant loss have also been demonstrated[8]. The impact of
72 micro-channel thicknesses (that is, inter-electrode distances) and fluid supply rates on the fluid
73 properties have been revealed. The electrochemical performance of the reactor dropped gradually
74 with increasing channel thickness and the drop became significant at the channel thicknesses
75 beyond 1000 μm . It turns out that lowering the micro-channel thickness would shorten the
76 pathway traveled by protons, hence limiting the resistance and potential loss. The fluid supply
77 rate has similar influence as the channel thickness. The higher the fluid supply rate is, the
78 narrower the catholyte-anolyte interface would be. This would lead to less cross-electrolyte
79 contamination and enhance the reactor performance. However, experimental observations
80 suggested that when the flow rates are beyond 500 $\mu\text{L}/\text{min}$, the mixing layer perturbation could
81 lead to instability and the excessive waste electrolytes would cause uneconomical operations.

82 Microfluidic electrochemistry is not only applicable for energy conversion, but also widely
83 implemented in various fields. For instance, Fang et al. has proposed a high-sensitivity
84 electrochemistry-based *in situ* detection methods by a microfluidic flow-through device[9].
85 Scialdone et al. has also achieved significant improvement of COD abatement in a
86 microdevice[10], while Marken group has reported clean organic electrosynthetic processes
87 based on microflow electrolysis reactions[11]. These progresses have all been benefited from the
88 elimination of membrane constraint in a microfluidic network.

89 With the advantageous microfluidic technology, this study aims at improving the electrolyte
90 utilization rate and enhancing the economical aspect by an electrolyte recycling scheme.
91 Experimental observations and quantitative analysis implied good controllability of interface

92 thickness and high possibility of electrolyte reuse. With appropriate conditions, the portion of
93 neutralized acid/alkaline, as can be quantitated and monitored by the mixing layer thickness,
94 could be well suppressed, so does pH and conductivity as key indicators. Technically and
95 economically, electrolyte renewal and regeneration strategy could be developed to revert the exit
96 electrolyte streams to a qualified level for recycling operation. A prediction model was also
97 established based on the pH degradation rate for future practical applications.

98 **2. Methodology**

99 ***2.1 Catalyst preparation***

100 Electrodes were commercially available catalysts (Johnson Matthey) binded with carbon paper
101 by Nafion (DuPont) solution. Pb and Pt black were used as the cathode catalyst and anode
102 catalyst, respectively, with catalyst to Nafion ratio as 30:1. The catalyst loading was 5 mg/cm².

103 ***2.2 Cell fabrication***

104 The electrodes were mounted at the bottom of the flow channels where co-laminar anolyte and
105 catholyte flow. The sizes of the channels were 0.2 cm (W) × 7.5 cm (L), between which another
106 0.01-cm-thick PVC sheet with a 0.2 cm (W) × 0.5 cm (L) window was sandwiched to form the
107 electrolyte contact area. The final distance between electrode surfaces was ~0.05 cm, which is an
108 optimized value as reported in our previous parametric study[8]. A 5 cm (L) × 1 cm (W) × 0.5
109 cm (H) chamber was machined to be the CO₂ reservoir for the cathode side. All layered
110 components were fabricated using a CO₂ laser ablation system (VLS 2.30, Universal Laser
111 System) and clamped together by binder clips (Highmark).

112 ***2.3 Electrochemistry***

113 An electrochemical station (CHI600E, CHI Instruments, Inc) with a sampling frequency of 250
114 Hz was used to hold the cell at constant potentials. Polarization curves were obtained by

115 averaging the integration of a 100-second steady-state data to eliminate transient artifacts.
116 Electrolytes were fed at a controlled flow rate, for example 500 $\mu\text{L}/\text{min}$, by syringe pumps
117 (LSP02-1B, Longer Pump). Polarization curves of anode and cathode were recorded with digital
118 multi-meters connected between each electrode and an external Ag/AgCl reference electrode,
119 which was dipped in a beaker collecting the exit electrolytes. Current and power densities were
120 normalized by the active electrode area (that is, 0.1 cm^2) and with compensated iR drop. It
121 should be noted that unlike a typical 3-electrode system, the reference electrode for the
122 microfluidic reactor is placed in an exit electrolyte collection beaker, which is apart from the
123 main body. The reference electrode is linked with the working and counter electrodes by a
124 central electrochemical station. Repetitiveness test suggested a highly repeatable experiment as
125 has been mentioned in our previous publication[8], where the variation of measured current
126 densities was within 10% and the range of peak Faradaic efficiencies was within 0.7%.

127 During the experiment of catholyte $\text{pH} = 2$ and anolyte $\text{pH} = 14$, on top of the above-
128 mentioned experimental conditions, gaseous CO_2 ($\geq 99.5\%$ purity, Linde) was supplied at a
129 constant flow rate of 50 sccm controlled by a mass flow controller (GFC17, Aalborg).

130 ***2.4 Formic acid determination method***

131 To determine the concentration of the formic acid generated, the measurement method adopted a
132 non-enzymatic allochroic reaction upon the mixture of formate and several chemicals[12]. The
133 absorption maximum of the destination color is at 510 nm, which could be obtained by a
134 spectrophotometer (6105 U.V./Vis. Jenway) to determine the formate concentration. 0.25 mL of
135 collected exit electrolyte sample was extracted and diluted by 0.25 mL deionized water and 0.05
136 g citric acid was mixed with 1 g acetamide. Ultrasonic dispersion was then conducted in 10 mL
137 2-propanol, 0.5 mL of which was dissolved in a mixture of 0.5 mL of the sample, including

138 0.025mL 30% w/v sodium acetate and 1.75mL acetic anhydride for 1.5 hr. Before each set of
 139 experiment, standard formate solutions were prepared at concentrations of 2.5, 5, 7.5, 10, 12.5,
 140 15, 17.5 and 20 mmol/L, whose corresponding color absorption was quantitatively determined as
 141 benchmarks by a correlative equation:

$$142 \quad 0.0588 \times \text{Concentration of HCOO}^- + 0.0562 = \text{Absorbance} \dots\dots\dots \text{Equ. (1)}$$

143 **2.5 pH & conductivity measurement**

144 The measurement of pH/conductivity was conducted by a pH/conductivity meter (Orion Star
 145 A215, Thermo Scientific). Before each set of measurements, calibration was done by dipping the
 146 pH probe into buffering solutions with pH=4.01, 7, 10.01 and conductivity probe into solutions
 147 of $12.9 \text{ mS} \cdot \text{cm}^{-1}$ and $1413 \mu\text{S} \cdot \text{cm}^{-1}$. The pH/conductivity probe was dipped into the collected
 148 sample solutions until the readings stabilized and recorded.

149 **2.6 Efficiency calculation**

150 Under appropriate conditions where the electrochemical reduction reaction of CO_2 occurs,
 151 Faradaic efficiencies would be calculated to reveal the fraction of the electrons transferred for
 152 formic acid production. The measured current indicates the total electrons passing through the
 153 reaction sites and the electrons used for generating formic acid is obtained by the
 154 spectrophotometer detection. Denote the flow rate as $M \text{ L/s}$, the applied current as $N \text{ ampere}$, and
 155 HCOO^- concentration as $Y \text{ mol/L}$. The amount of electrons used for forming formic acid is
 156 $2 \times Y \times M \text{ mol/s}$. On the other hand, the total number of electrons passing through the electrode
 157 surface is $N \times K \text{ mol/s}$, where $K = 1.04 \times 10^{-5} \text{ mol/A}$ stands for the mole of electrons per
 158 ampere, concluding the equation for Faradaic efficiency as shown below:

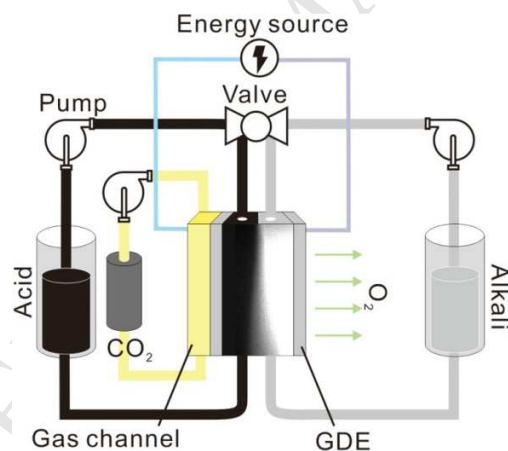
$$159 \quad \text{FE} = \frac{2 \times Y \times M}{N \times K} \times 100\% \dots\dots\dots \text{Equ. (2)}$$

160

161 3. Results and discussion

162 3.1 Working principle

163 A microfluidic reactor with electrolyte recycling was designed as shown in Figure 1. The ion
164 concentration gradient across the microchannel, as marked and visualized by fluorescent dye,
165 was also demonstrated. The microfluidic structure could effectively control the catholyte-anolyte
166 interface and suppress the cross-contamination. When in need, the gaseous feed was supplied
167 into the gas reservoir chamber on the cathode side and migrated through the gas diffusion layers
168 (GDLs) to the catalyst surfaces. Catholyte and anolyte solutions were driven into corresponding
169 channels by individual syringe pump, followed by collection and recirculation. As predicted, exit
170 catholyte and anolyte were evenly distributed, validating the effective reactor design and
171 fabrication.



172

173 Figure 1 Schematic diagram of the microfluidic reactor with electrolyte recycling.

174 3.2 Benchmarks

175 Single electrolyte modes were regarded as benchmarks. To identify their characteristics, both
176 single acid (catholyte pH = anolyte pH = 0) and single alkaline (catholyte pH = anolyte pH = 14)
177 modes were established and tested as shown in Figure S1 and Figure S2, respectively.

178 As can be seen in Table 1, Figure S1a and Figure S2a, beyond the on-set electrolysis voltages,
 179 that is, ~2 V, the reactivity was statistically multiplied for several times in either single acid or
 180 single alkaline, and the former one increased faster. This could be explained by the fact that the
 181 acidic electrolyte conductivity was twice as much as that of its alkaline counterpart (see Table
 182 S1), enhancing the chemical kinetics.

183 Table 1 Comparison of reactor reactivity between single acid and single alkaline modes.

| Cell voltage (V) | Current density in single acid (mA/cm ²) | Current density in single alkaline (mA/cm ²) |
|---------------------|--|--|
| | Catholyte pH = Anolyte pH = 0 | Catholyte pH = Anolyte pH = 14 |
| | Electrolyte flow rate = 500 μ L/min | Electrolyte flow rate = 500 μ L/min |
| 4.0 | 694.2 | 354.8 |
| 3.7 | 452.3 | 253.3 |
| 3.4 | 283.4 | 167.1 |
| 3.1 | 187.8 | 72.2 |
| 2.8 | 130.0 | 27.7 |
| 2.5 | 72.4 | 12.1 |

184
 185 Table S1, Figure S1d and Figure S2d suggested that during the 10-cycle operation, the
 186 electrolyte conductivity remained highly stable in single electrolyte mode, with coefficient of
 187 variation (CV) no more than 0.03. On top of the high steadiness, the small fluctuations of
 188 electrolyte conductivity were still observable, due to the balance between the ion consumption of
 189 electrochemical reactions and the productions of new species. Another key factor to evaluate the

190 electrolyte properties during long-term operation is the change in pH values. As shown in Table
 191 S2, Figure S1c and Figure S2c, the pH variation remained small with a CV less than 0.09,
 192 implying its high stability and low degradation rate. The low degradation of pHs and
 193 conductivity demonstrated the high feasibility of electrolyte recycling in practical applications,
 194 where not only electrolyte production and disposal costs are crucial, the number of recycling
 195 cycles is also important.

196 The variation of current density, however, was considerably large as can be seen from both the
 197 graphic plots (Figure S1e and Figure S2e) and the statistical results (Table 2). Comparison of CV
 198 indicated that current densities in single alkaline mode appeared relatively steady than those in
 199 single acid mode, which is due to the suppressive nature of hydroxy radical towards formate
 200 generation.

201 Table 2 Statistical results of current densities during the 10-cycle operation in single acid and
 202 single alkaline modes at applied potentials of 2.8, 3.4 and 4 V.

| Catholyte pH = Anolyte pH = 0 | | | |
|---|--------------------------------|-----------------------------------|------|
| Electrolyte flow rate = 500 μ L/min | | | |
| Applied potential (V) | μ (mA/cm ²) | σ (mA/cm ²) | CV |
| 4.0 | 735.3 | 82.5 | 0.11 |
| 3.4 | 232.5 | 36.6 | 0.16 |
| 2.8 | 72.9 | 19.3 | 0.26 |
| Catholyte pH = Anolyte pH = 14 | | | |
| Electrolyte flow rate = 500 μ L/min | | | |
| Applied potential | μ | σ | CV |

| (V) | (mA/cm ²) | (mA/cm ²) | |
|-----|-----------------------|-----------------------|------|
| 4.0 | 364.3 | 15.6 | 0.04 |
| 3.4 | 168.3 | 16.9 | 0.10 |
| 2.8 | 34.0 | 10.5 | 0.31 |

203

204 **3.3 Effects of flow rate**

205 With single electrolyte as the benchmark, dual electrolyte modes were tested. The catholyte and
 206 anolyte were prepared by 1 mol/L sulfuric acid and 1 mol/L potassium hydroxide, respectively.
 207 The neutralization reaction that occurred in the acid-base mixing layer brought in more
 208 complexity to the system. As shown in Figure S3a and Figure S3b, while the catholyte pHs
 209 gradually increased, cliff falls could be observed on the anolyte pHs. Afterwards, the alkaline
 210 anolyte was completely acidified. This could be explained by the fact that a sulfuric acid
 211 molecule possesses two ionizable hydrogen with a low second ionization rate[13, 14]. Upon the
 212 depletion of the first ionizable hydrogen ion, the second would be released to dominate the
 213 electrolyte solution.

214 Nevertheless, behind the superficial ‘cliff drop’, there actually existed a linear decrease trend
 215 in the concentration of ions (see Table 3) as could be deduced from the pH results in Table S3 by
 216 the equation $\text{pH} = -\lg[\text{H}_3\text{O}^+]$. The degradation rate dropped from 0.16 to 0.089 and then 0.06
 217 mol/L per cycle when increasing the flow rate from 200 to 300 to 400 $\mu\text{L}/\text{min}$. The degradation
 218 rate finally stabilized at around 0.035 mol/L per cycle at flow rates of 500 $\mu\text{L}/\text{min}$ and above. In
 219 terms of number of cycles before complete acidification, it increased from 4 cycles at 200
 220 $\mu\text{L}/\text{min}$ to 9 cycles at $\geq 500 \mu\text{L}/\text{min}$. This statistical observation implied that 500 $\mu\text{L}/\text{min}$ was the
 221 threshold of the electrolyte flow rate. At the same time, it was experimentally observed that

222 further increasing the flow rate would disturb the acid-alkaline interface, hence lowering the
 223 reactor performance and stability.

224 In Table 3, the threshold pH values, after which the anolyte pHs would drop to acid range,
 225 were extracted from Table S3 as underlined. With the CV as low as 0.005, the mean value of
 226 13.8 could be regarded as the threshold value, upon which the electrolyte recovery should be
 227 conducted in potential practical applications.

228 Table 3 Statistical results of OH^- concentration degradation rate during the 10-cycle operation
 229 and threshold pH values before complete neutralization in dual electrolyte modes at flow rates
 230 from 200 to 700 $\mu\text{L}/\text{min}$. Initial catholyte $\text{pH}=0$ and anolyte $\text{pH}=14$ under zero applied voltage.

| Flow rate ($\mu\text{L}/\text{min}$) | Degradation rate of OH^- concentration (mol/L per cycle) | Threshold pH before complete neutralization |
|---|--|--|
| 200 | 0.160 | 13.71 |
| 300 | 0.089 | 13.74 |
| 400 | 0.060 | 13.74 |
| 500 | 0.040 | 13.89 |
| 600 | 0.037 | 13.85 |
| 700 | 0.035 | 13.84 |
| | | $\mu = 13.80$ |
| | | $\sigma = 0.07$ |
| | | CV = 0.005 |

231
 232 Meanwhile, Figure S3b indicated that the electrolyte conductivity would experience a sudden
 233 change before the neutralization reaction was completed. This phenomenon was caused by two

234 mechanisms. Firstly, no more ions were sunk in neutralization reaction and both electrolytes
 235 were acidified. Secondly, the second ionization of sulfuric acid was massively triggered upon the
 236 threshold, supplying plenty of hydrogen ions and boosting the catholyte conductivity.

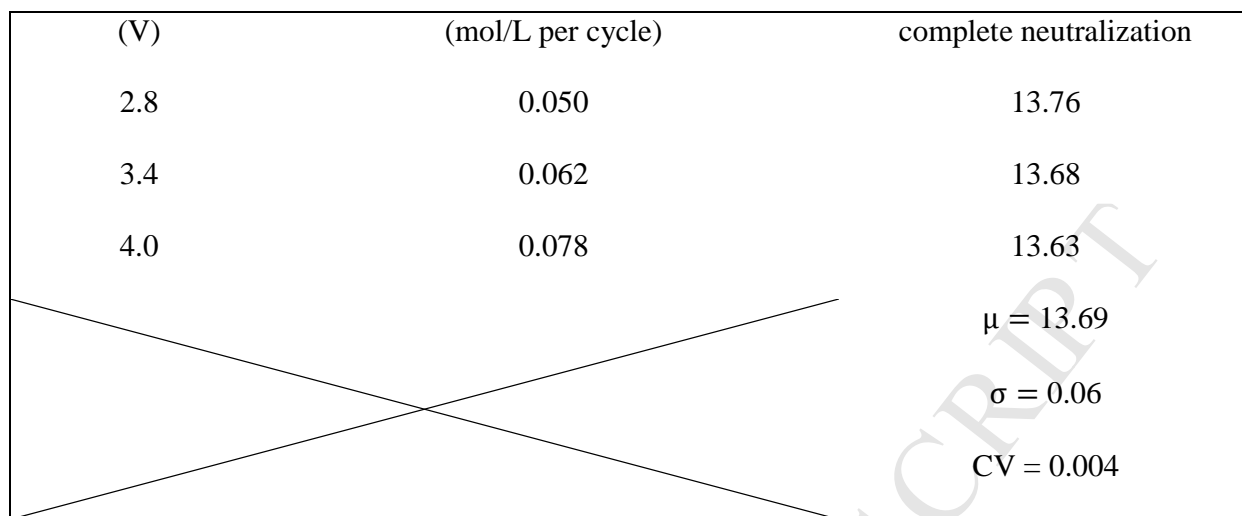
237 **3.4 Effect of applied potential**

238 Figure S4 demonstrated the degradation mechanism at applied potentials of 2.8, 3.4 and 4 V. The
 239 numbers of cycles which the cliff falls of pHs occurred are different for different applied
 240 potentials. The anolyte pH was acidified after 8 cycles at 4 V and 9 cycles at lower voltages. The
 241 crossover of acid-base was fiercer at elevated potentials because more ions and gaseous side
 242 products were generated, interfering the interface and accelerating the neutralization reaction.
 243 This phenomenon could be corroborated statistically. Deduced from the pHs (see Table S4), the
 244 degradation of ion concentrations (see Table 4) was observed to be linear and the degradation
 245 rate descended from 0.078 mol/L per cycle at 4 V to 0.05 mol/L per cycle at 2.8 V. The threshold
 246 pH values, as underlined in Table S4 and extracted in Table 4, were at a mean of 13.69 with a
 247 CV of 0.004.

248 Similar to those single electrolyte modes, sudden changes of catholyte conductivity could also
 249 be found beyond the threshold. On top of the two rationales mentioned in Section 3.3, one more
 250 ion source should not be neglected, that is, ongoing formate generation reaction at applied
 251 potentials above the on-set voltage.

252 Table 4 Statistical results of OH⁻ concentration degradation rate during the 10-cycle operation
 253 and threshold pH values before complete neutralization in dual electrolyte modes at applied
 254 potentials of 2.8, 3.4 and 4 V. Initial catholyte pH=0 and anolyte pH=14, both supplied at a flow
 255 rate of 500 μL/min.

| Applied potential | Degradation rate of OH ⁻ concentration | Threshold pH before |
|-------------------|---|---------------------|
|-------------------|---|---------------------|



256

257 As shown in Figure S4c, the influence of voltages on pH variation was insignificant, but
 258 current densities were deeply affected. With the cliff falls of pHs, anolyte was acidified and the
 259 dual electrolyte mode was transformed into single acid mode. The depletion of the affiliated
 260 thermodynamic dividend of dual electrolyte mode caused sudden drops of current densities (see
 261 Figure S4e). The CV of current densities at 2.8, 3.4 and 4 V were low and close to one another
 262 (see Table 5), validating the previous finding of their corresponding threshold pHs.

263 Table 5 Statistical results of current densities during the 10-cycle operation at applied potentials
 264 of 2.8, 3.4 and 4 V. Initial catholyte pH=0 and anolyte pH=14, both were supplied at a flow rate
 265 of 500 $\mu\text{L}/\text{min}$.

| Catholyte pH = 0 & Anolyte pH = 14 | | | |
|------------------------------------|-----------------------|-----------------------|------|
| Applied potential | μ | σ | CV |
| (V) | (mA/cm ²) | (mA/cm ²) | |
| 4.0 | 1010.1 | 202.8 | 0.20 |
| 3.4 | 643.6 | 138.2 | 0.21 |
| 2.8 | 429.8 | 141.2 | 0.33 |

266 *3.5 Effect of electrolyte ion concentration*

267 As the thermodynamic properties of an electrochemical reactor could be adjusted by altering
268 variables in the Nernst equation, tuning the OH^-/H^+ concentrations, that is, pHs, inevitably
269 becomes an important strategy. In order to investigate the impact and feasibility in practical
270 applications, three representative combinations were tested, that is, H_2SO_4 solution as catholyte
271 and KOH solution as anolyte at the same concentrations of 1, 2, and 3 mol/L. It could be
272 observed from Figure S5b that the limiting current density was raised from $\sim 1000 \text{ mA/cm}^2$ at 1
273 mol/L to $\sim 1600 \text{ mA/cm}^2$ at 3 mol/L and the reactivity was the highest at 2 mol/L (Figure S5a).
274 The reason that 3 mol/L did not show superior reactivity was that the enhanced thermodynamic
275 properties would promote allied side reactions and products at the same time, which were
276 disruptive to the laminar nature of the acid-base layer.

277 Cliff falls of pHs appeared earlier in higher electrolyte concentration (see Figure S5c) because
278 the neutralization reaction was much fiercer at elevated thermodynamic activity. The
279 neutralization reaction was completed at the 6th cycle at 3 mol/L, 7th cycle at 2 mol/L and 9th
280 cycle at 1 mol/L, followed by homogenization towards single acid mode. Higher electrolyte
281 concentrations would quicken the ion concentration degradation and intensify the catholyte-
282 anolyte crossover. Statistically, 1 mol/L electrolyte concentration showed significantly lower
283 degradation rate, that is, 0.05 mol/L per cycle, compared with 2 and 3 mol/L, whose rates are
284 0.27 and 0.29 mol/L per cycle (see Table 6).

285 Different from the impact of flow rates or applied potentials, threshold pH values before
286 complete neutralization varied with different ion concentrations, that is, 13.76 at 1 mol/L, 12.96
287 at 2 mol/L, and 14.18 at 3 mol/L, at a relatively high CV, that is, 0.005 (see Table 6 and S5). The
288 reason behind was that the intrinsic nature of the electrolyte was changed and the critical points

289 where the OH^- would be completely depleted by H^+ were shifted as well. However, as the
 290 variation was still within the acceptable range, the mean value of the threshold pHs, that is, 13.63,
 291 was applicable as the criterion of electrolyte recovery.

292 Summarizing all the threshold pH values in the above-mentioned scenarios, a value of 13.7
 293 was determined as a general threshold pH to identify the kickoff of electrolyte recovery.

294 Table 6 Statistical results of OH^- concentration degradation rate during the 10-cycle operation
 295 and threshold pH values before complete neutralization in dual electrolyte modes at different
 296 concentrations. Both anolyte and catholyte were supplied at a flow rate of 500 $\mu\text{L}/\text{min}$ at an
 297 applied voltage of 2.8 V.

| Electrolyte pH | | Degradation rate of OH^- concentration (mol/L per cycle) | Threshold pH before complete neutralization |
|----------------|---------|--|--|
| Catholyte | Anolyte | | |
| 0.00 | 14.00 | 0.050 | 13.76 |
| -0.30 | 14.30 | 0.270 | 12.96 |
| -0.47 | 14.47 | 0.290 | 14.18 |
| | | | $\mu = 13.63$ |
| | | | $\sigma = 0.62$ |
| | | | $\text{CV} = 0.005$ |

298
 299 Surprisingly, the reactivity did not increase with more favorable thermodynamic settings as
 300 shown in Figure S5e and Table 7. The mean current densities and their affiliated standard
 301 deviations even dropped at high electrolyte concentrations. This was caused by the fact that more
 302 side products were generated to disturb the microfluidic characteristics as explained earlier in
 303 this section.

304 Table 7 Statistical results of current densities during the 10-cycle operation at different
 305 electrolyte concentrations. Both anolyte and catholyte were supplied at a flow rate of 500
 306 $\mu\text{L}/\text{min}$ at an applied voltage of 2.8 V.

| Catholyte pH | Anolyte pH | μ (mA/cm^2) | σ (mA/cm^2) | CV |
|--------------|------------|--------------------------------------|---|------|
| 0.00 | 14.00 | 429.8 | 141.2 | 0.33 |
| -0.30 | 14.30 | 346.1 | 180.6 | 0.52 |
| -0.47 | 14.47 | 368.7 | 121.0 | 0.33 |

307
 308 Our previous parametric study has reported that for a CO_2 electrochemical reduction reactor, a
 309 catholyte pH = 2 and anolyte pH=14 gave the optimal performance, including reactivity and
 310 conversion efficiency[7]. The electrode potentials were closer to the equilibrium status because
 311 of the reduced electrode overpotentials. Connected to CO_2 supply, experiment was conducted on
 312 the feasibility of electrolyte recycling for this type of pH combinations, that is, unbalanced acid-
 313 base concentration.

314 As shown in Figure S6a and Figure S6b, with an on-set voltage reduced to ~ 1.8 V, the peak
 315 Faradaic and energetic efficiencies were recorded as high as 95.6% at $143 \text{ mA}/\text{cm}^2$ and 48.5% at
 316 $62 \text{ mA}/\text{cm}^2$, respectively. Although the reactor performance was raised, the pH degradation rate
 317 precluded the possibility of electrolyte recycling because the relatively weak acid catholyte was
 318 rapidly alkalinized after the first cycle as indicated by the electrolyte pHs shown in Table S6.
 319 The catholyte and anolyte pHs gradually approached each other from the 2nd cycle and are
 320 completely neutralized at the end of the 10th cycle. The whole cell was then transformed into a
 321 single alkaline mode, where the current densities and Faradaic efficiencies tended to be smooth

322 (see Figure S6e and Table 8). In this work, five operation scenarios, including single acid, single
 323 alkaline, dual-pH at different flow rates, dual-pH at different applied potentials and dual-pH at
 324 different ion concentrations, were tested. The electrolyte recycling scheme was successfully
 325 realized in four of them at acid-base equilibrium states, which could be used for regenerative fuel
 326 cell applications. The last scenario, that is, acid-base imbalance for CO₂ electrolysis, indicated its
 327 incompatibility with electrolyte reutilization due to the dominant ion crossover. The final formic
 328 acid concentration was recorded as 30 mmol/L, below the practical throughput requirements.

329 On the other hand, the trend of conductivity was smooth. Catholyte conductivity gradually
 330 increased from 82.81 to 137.5 mS/cm and that of anolyte dropped from 214.6 to 178 mS/cm.
 331 Different from other dual electrolyte modes as reported above, no sudden changes were observed
 332 because of their different dominant ion transfer mechanisms, that is, diffusion vs. neutralization.
 333 It should be noted that during the process, the CO₂ formed dissolved into the electrolytes and the
 334 generation of CO₂ conversion products would result in small fluctuations of pH and conductivity.
 335 Table 8 Statistical results of current densities during the 10-cycle operation. Initial catholyte pH
 336 = 2 and anolyte pH = 14. Both anolyte and catholyte were supplied at a flow rate of 500 μ L/min
 337 at an applied voltage of 2.8 V.

| | Current density (mA/cm ²) | Faradaic efficiency (%) |
|----------|--|----------------------------|
| μ | 29.8 | 89.3 |
| σ | 9.8 | 4.9 |
| CV | 0.33 | 0.06 |

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339

340 **3.6 Summary and discussion**

341 Single electrolyte mode demonstrated superior recyclability with low pH/conductivity
342 degradation. At the same time, single acid mode illustrated higher ion transfer rate because of its
343 higher conductivity compared with single alkaline mode. Phenomena in dual electrolyte modes,
344 where neutralization reaction dominated, were different and the electrolyte degradation
345 mechanism became essential. Flow rates played a major role in influencing the pH/conductivity
346 degradation rate and the electrolyte could be recycled for 9 times at or above 500 $\mu\text{L}/\text{min}$.
347 Another key factor was the electrolyte concentration, which could raise the neutralization rate
348 and decrease recycling cycles. The impact of applied potentials was not significant at a voltage
349 of 3.4 V or below, which would not quicken the electrolyte crossover. A threshold pH value of
350 13.7 was recommended to trigger the electrolyte recovery. It was also observed that the
351 prerequisite of electrolyte recycling was to create an acid-base equilibrium state and the
352 imbalance would lead to instant electrolyte cross-contamination.

353 **4. Conclusions**

354 Microfluidics provided a useful matrix for electrochemical devices and revealed a low cost
355 solution towards membrane-based architecture. Exploiting the function of the virtual layer
356 created by the microfluidic network, the pHs of electrolytes could be altered to adjust their
357 affiliated electrode thermodynamic positions, hence improving the reactor performance.
358 However, maintaining the laminar flow nature and controlling the virtual layer thickness
359 required high electrolyte flow rates, leading to considerable electrolyte wastage.

360 This study is the first systematic investigation and demonstration of enhancing the economical
361 aspect of a microfluidic reactor by recycling electrolytes. A deeper understanding of the reactor
362 performance and fluid dynamic behavior was obtained, as well as the electrolyte degradation

363 mechanism under different operation conditions. It was observed that in a single electrolyte
364 modes where no neutralization loss existed, electrolyte recycling was feasible and durable. In
365 dual electrolyte modes, ion concentrations were found to degrade linearly with time and pHs
366 would experience sudden changes. The rationale was revealed as the synergistic effects of ion
367 sink into acid-base neutralization, ion generation from electrochemical reactions, and the second
368 ionization of the sulfuric acid.

369 Higher flow rates showed positive impact on the duration of electrolyte recycling operation;
370 yet, there existed a threshold value of 500 $\mu\text{L}/\text{min}$ and its operation duration of 27,000 seconds,
371 beyond which the virtual layer stabilization would be disturbed. On the contrary, lower applied
372 potentials were preferable to slow down the electrolyte cross-contamination because of the
373 suppression of side reactions. An ion concentration degradation rate of 0.05 mol/L per cycle was
374 observed at 2.8 V. Similar trend occurred on the initial concentrations of electrolytes. Not only
375 the operation durations were lowered at higher electrolyte concentrations, the reactivity was also
376 sacrificed because of the accelerated electrolyte crossover and subsequent mixing layer
377 disruption. A threshold pH value of 13.7 was recommended as the indicator for followed-up
378 processes, that is, electrolyte recovery. On the other hand, electrolyte recycling under the optimal
379 pH combination for CO_2 reduction, that is, catholyte pH = 2 and anolyte pH = 14, appeared to be
380 infeasible because of the species unbalance and consequent alkalization.

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Highlights

- Electrolyte recycling feasible on dual electrolyte microfluidic networks
- Key operation conditions optimized for better recycling operation
- pH degradation predictable for practical applications
- Reactor performance can be controlled within a stable range