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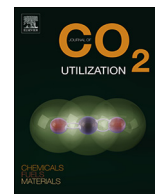
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# Enhanced selectivity of carbonaceous products from electrochemical reduction of CO<sub>2</sub> in aqueous media

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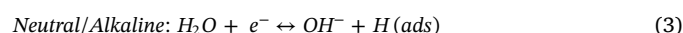
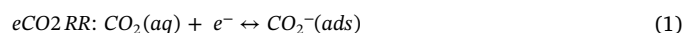
## ABSTRACT

This study highlights the importance of CO<sub>2</sub> supply method and impact of electrolyte alkalinity in aqueous electrochemical CO<sub>2</sub> reduction using Cu<sub>x</sub>O catalyst. Two different CO<sub>2</sub> supply methods using a two-chamber (2C) cell with CO<sub>2</sub> purging into catholyte and a CO<sub>2</sub> gas diffusion electrode (GDE) cell were compared. Faradaic efficiency (FE) of carbonaceous products in GDE cell was more than 3-folds higher than the 2C cell due to improved CO<sub>2</sub> mass transfer. From the investigation of alkaline catholyte in GDE cell, the higher catholyte alkalinity led to higher current density and higher FE of carbonaceous products with a better selectivity of C<sub>2</sub> (ethanol and ethylene). The reason lies in the OH groups around catalyst surface which improve the reaction kinetics and moreover stabilize the catalyst surface oxygen during the reduction process. With the potential of −1.17 V (RHE) in 2.0 M KOH, C<sub>2</sub> FE of 40% and current density of −234 mA cm<sup>−2</sup> were achieved. The production rate of ethylene and ethanol was respectively 0.105 mg min<sup>−1</sup> and 0.035 mg min<sup>−1</sup> on 2 cm<sup>2</sup> electrode with CO<sub>2</sub> flow rate 15 ml min<sup>−1</sup>, which are promising for further development and scale-up.

## 1. Introduction

The increasing demand for energy and challenges from environmental issues and climate change has led to numerous researches on sustainability and carbon recycling. CO<sub>2</sub> concentration in the atmosphere has reached 427 ppm causing environmental concerns and climate change [1]. Increasing production of renewable energy results in demands on energy storage materials and devices. Effectively utilising and directly converting carbon dioxide (CO<sub>2</sub>) into fuels as energy storage media and other valuable chemicals could provide a solution. Among the approaches of CO<sub>2</sub> conversion, electrochemical CO<sub>2</sub> reduction reaction (eCO<sub>2</sub>RR) attracted large interests as it only consumes water and electricity as the inputs to build hydrocarbons and oxygenates (i.e., alcohols and carboxylic acids) and to release pure O<sub>2</sub> as a by-product on the anodic side. However, hydrogen evolution reaction (HER) shares similar reaction potential (0.0 V vs. RHE) with eCO<sub>2</sub>RR and takes place simultaneously. Due to the big energy barrier of CO<sub>2</sub> activation [2], H<sub>2</sub> is theoretically much easier to be produced than carbonaceous products under aqueous eCO<sub>2</sub>RR conditions [3,4].

The rate-determining steps for eCO<sub>2</sub>RR and HER in the competitive charge transfer are both one-electron reversible process as illustrated in Equation (1) and Equation (2 or 3) respectively [2–4].



The reaction rate of the one-electron reversible electrode process is generally defined as Equation (4) [5].

$$R = \frac{j}{nF} = \frac{j_0 \left[ \frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right]}{nF} \quad (4)$$

Where:  $j$ : local current density (A m<sup>−2</sup>)

$n$ : number of electron transfer, here it is 1

$F$ : faradaic constant (96,485 C mol<sup>−1</sup>)

$j_0$ : exchange current density (A m<sup>−2</sup>)

$C_O(0,t)/C_R(0,t)$ : the surface concentration of oxidant/reduced product at time  $t$

$C_O^*/C_R^*$ : the bulk concentration of oxidant/reduced product

$\alpha$ : transfer coefficient (= 0–1)

$f$ : a constant (=  $F/RT$ )

$\eta$ : overpotential (V)

The initial rate of either eCO<sub>2</sub>RR or HER accords with Equation (4) which is mainly co-determined by the exchange current density  $j_0$ , the surface concentration of reactant, and overpotential. The  $j_0$  is primarily

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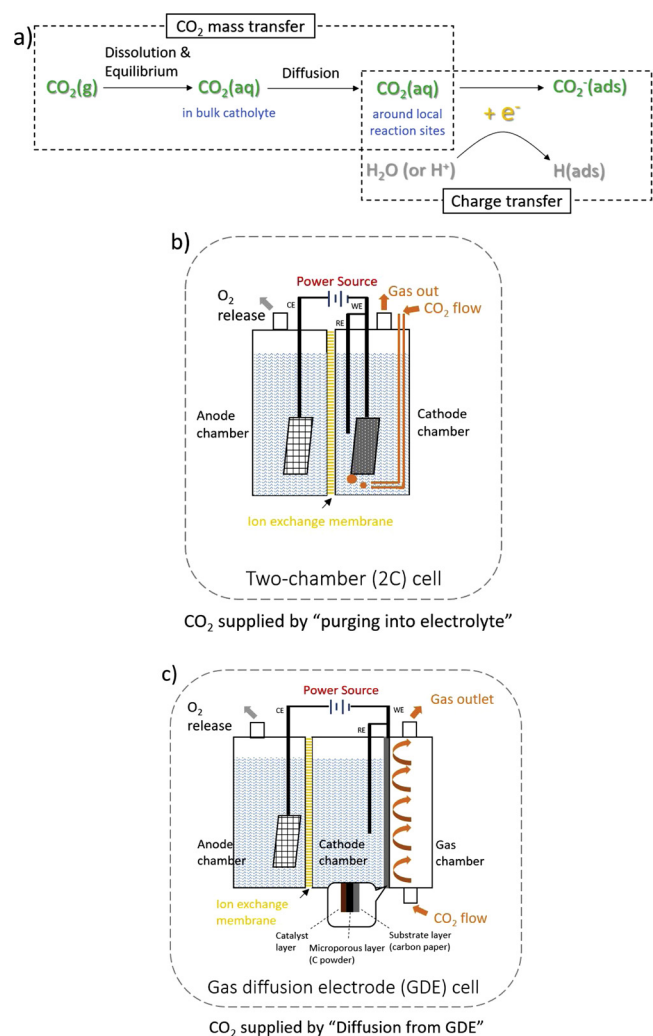


Fig. 1. a) Mass transfer and charge transfer in aqueous eCO<sub>2</sub>RR system. Schematic diagrams of aqueous eCO<sub>2</sub>RR system using b) 2C cell and c) GDE cell.

related to the adsorption energy of the active species (CO<sub>2</sub><sup>-</sup>(ads) and H(ads)) on the electrode material [6]. A suitable catalyst [7] can change the adsorption energy to those species, intending to control the selectivity between carbonaceous products and H<sub>2</sub>. In the aqueous eCO<sub>2</sub>RR system, the inherent competitive advantage for HER is mass transfer, in another word, the surface concentration of H<sub>2</sub>O (or H<sup>+</sup>) is always sufficient. However, the mass transfer of heterogeneous CO<sub>2</sub> gas is a more complicated process as illustrated in Fig. 1a.

Table 1  
Summary of eCO<sub>2</sub>RR performance with GDE working electrode from literature.

Cathode	Anode	Electrolyte	Cell voltage/cathode potential (V)	<i>j</i> (mA cm <sup>-2</sup> )	FE for main products
Sn-GDE [19]	Pt/C coated membrane pressed GDE	0.1 M KHCO <sub>3</sub> (C) 1 M KOH (A)	Cell: -2.75 V	-26	65% Formate
Ag-GDE [20]	Pt/C-GDE	1 M KCl	Cell: -3 V	-90	92% CO
Ag-GDE [21]	Pt/C-GDE	1 M CsOH	Cathode: -1.62 V (vs. Ag/AgCl)	-80	89.8% CO
Cu <sub>x</sub> O-GDE [22]	IrO <sub>2</sub> -GDE	1 M KOH	Cathode: -0.8 V (vs. RHE)	-400	> 50% C <sub>2</sub>
N-doped graphene quantum dots-GDE [23]	IrO <sub>2</sub> -GDE	1 M KOH	-1.0 V (vs. RHE)	-240	60% C <sub>2</sub> 5% C <sub>3</sub>
Pb-GDE [24]	PtRu-GDE	0.5 M K <sub>2</sub> SO <sub>4</sub> + 0.5 M H <sub>2</sub> SO <sub>4</sub> (C) 1 M KOH (A)	-2 V (vs. SHE)	-330	90% Formate

C: catholyte; A: anolyte.

Majority of publications [8,9] applied a traditional two-chamber (2C) cell where the reactant CO<sub>2</sub> gas was supplied by “purging into electrolyte”, as shown in Fig. 1b. CO<sub>2</sub> mass transport is determined by CO<sub>2</sub> solubility. Different approaches have been carried out to increase CO<sub>2</sub> solubility in the electrolytes, such as altering the reaction environment with high pressure [10–12] and low temperature [13], and using alcoholic base [14,15] or ionic liquid [16] as the electrolyte. However, comparing with the ambient pressure, room temperature and aqueous electrolytes, those approaches carry their own set of cost and sustainability issues.

The use of a gas diffusion electrode (GDE) changes the CO<sub>2</sub> supply way from “purging into electrolyte” to “diffusion from GDE” as shown in Fig. 1c, which can directly feed CO<sub>2</sub> gas flow to the reaction interface which has been used by fuel cells for a long time [17]. An increasing number of GDE-based studies in aqueous eCO<sub>2</sub>RR were published in recent years, commonly achieving a remarkable current density (*j*) and reasonable faradaic efficiency (FE) towards C-products at ambient temperature and pressure, as summarised in Table 1. In the aqueous system with 2C cells, satisfying FE (> 50%) of carbonaceous products have also been reported but the current densities were averagely low (< 10 mA cm<sup>-2</sup> at moderate potentials around -1.0 V (vs. RHE) [18]) which is about 10-folds less than GDE cells. The application of GDE should be a reliable approach to transition this bench-scale research to industry. For the further optimisation, the real effect of GDE on eCO<sub>2</sub>RR and the factors for the high current density achieved in GDE-related studies still need to be explicit.

J. Albo et al. [25] compared the GDE performances with Cu<sub>2</sub>O catalyst when CO<sub>2</sub> supplied as gas and when CO<sub>2</sub> supplied in saturated aqueous catholyte. The direct CO<sub>2</sub> gas feeding showed ~ 3 mA cm<sup>-2</sup> higher current density and ~ 9% FE increase in methanol production. However, the reactor dimensions, electrolytes, membrane, applied potential, supply rate of reactants, etc. all have impacts on eCO<sub>2</sub>RR performances, an univariate comparison is needed to examine the effect of CO<sub>2</sub> supply method on eCO<sub>2</sub>RR. In this work, a 2C cell and a GDE cell were designed in the same dimension and fabricated by 3D printing. Their eCO<sub>2</sub>RR performances were compared using the same Cu<sub>x</sub>O catalyst, KHCO<sub>3</sub> catholyte with various concentrations at a wide range of potentials. The big difference of product distribution disclosed the crucial role of CO<sub>2</sub> mass transfer in the selectivity of carbonaceous products. Compared to the 2C cell, GDE cell with efficient CO<sub>2</sub> mass transfer showed more than 3-folds improvement of FE for carbonaceous products. eCO<sub>2</sub>RR performances in GDE cell with KHCO<sub>3</sub> and KOH with various concentrations were also investigated.

## 2. Experimental

### 2.1. Cell fabrication and set up

The CO<sub>2</sub> supply methods of “purging into electrolyte” and “diffusion

from GDE” were carried out by two different electrochemical cells respectively: a 2C cell and a GDE cell were designed with the same dimension of the cathodic and anodic chambers, and fabricated by 3D printer (Form 2, Formlabs) using the photoreactive resin (Form 2 Clear Resin, Formlabs). Cell parts were screwed together using metal bolts. The cathodic and anodic chambers were separated by a cation exchange membrane (CEM) (F-950, Fumapem). The cathode used in both cells was Cu<sub>x</sub>O painted GDE with the geometric surface area 2 cm<sup>2</sup> and the anode was Platinum plated Titanium mesh with a dimension of 4 cm<sup>2</sup>. The schematics of the two cells are as described in Fig. 1b and c. Figure S1 shows the 3D drawings of the two cells set-up, with the design information given below in the Supplementary Data.

## 2.2. Catalyst synthesis and working electrode preparation

Cu<sub>x</sub>O catalyst was synthesized using the hydrothermal method by reduction of Cu acetate (Sigma-Aldrich, 98%) in the solvent of water and ethanol (Sigma-Aldrich, > 99.8%) mixture reported previously [26]. The volume ratio of water and ethanol was controlled as 1:7, i.e., 10 ml water and 70 ml ethanol. The catalyst was dried at 60 °C in an oven (Oven-30S, SciQuip) in air for 8 h.

15 mg catalyst (Cu<sub>x</sub>O) was weighed and dispersed in 200 μl isopropanol and 33 μl Nafion suspension (Sigma-Aldrich, 5 wt.%) to prepare the catalyst ink. The ink was sonicated for 20 min before painting onto the surface of carbon paper with gas diffusion layer (GDL) (H2315 I2 C6, Freudenberg). Drying (45 °C, 1–3 min) was applied between each layer. Painting and drying were repeated until the desired Cu<sub>x</sub>O catalyst loading of 4.5 mg cm<sup>-2</sup> was achieved.

## 2.3. eCO<sub>2</sub>RR electrochemical analysis

All the electrochemical reactions and measurements were carried out at ambient temperature and pressure using a potentiostat (Metrohm Autolab PGSTAT128 N). The flow rate of CO<sub>2</sub> (BOC 99.99%) was controlled at 15 ml min<sup>-1</sup> by a flow meter (Cole-Parmer TMR1-010462). 5 M KOH solution was employed as the anolyte in all the tests. KHCO<sub>3</sub> (Alfa Aesar, 99%) and KOH (Emsure®, 85%) solution with different concentrations of 0.1, 0.5, 1.0, and 2.0 M (only in KOH) were used as the catholyte, and the comparison was carried out. Ag/AgCl (RE-5B, BASI, 3 M NaCl, 0.197 V vs. SHE) was used as the reference electrode, and a luggin capillary was applied to prevent it from being damaged in alkaline electrolyte. The applied potentials (vs. Ag/AgCl) in the three-electrode system were all converted to the reversible hydrogen electrode (RHE), thus the potentials stated in this study are referred to RHE unless otherwise stated.

In the 2C cell, CO<sub>2</sub> was purged into catholyte 1 h before electrochemical tests.

In the GDE cell, a peristaltic pump (120U/DM2, Watson Marlow) was used to supply fresh catholyte to maintain the local pH and to remove liquid product for reaction equilibrium. The flow rate was controlled at 0.25 ml min<sup>-1</sup> under the applied potential -0.17~-0.77 V and at 0.5 ml min<sup>-1</sup> under the applied potential -0.77~-1.17 V.

Electrochemical characterisations were made by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). CV was carried out three cycles between 1.4 to -1.0 V with the scan rate 50 mV s<sup>-1</sup> to initially explore the cathode electrochemical behaviour. The FRA32 M module on the Autolab potentiostat was operated for EIS measurement, which was recorded with an ac-amplitude of 10 mV over the frequency range from 10k Hz to 0.1 Hz either at open circuit voltage (OCV) or at -0.77 V cathodic potential. The impedance spectra were analysed and fitted using NOVA 2.0 software.

eCO<sub>2</sub>RR was carried out by chronoamperometry (CA) recording the current at a particular applied potential for 30 min. The current density (*j*) was calculated based on the geometric surface area 2 cm<sup>2</sup> of the working electrode.

## 2.4. Product analysis

A gas chromatography (Shimadzu Tracer GC-2010) equipped with Barrier Discharge Ionization (BID) detector was used to analyse gas products and alcoholic liquid products. The ShinCarbon ST micro-packed column 80/100 (Restek) was used to quantitatively analyse permanent gases and light hydrocarbons, while the Zebron ZB-WAXplus capillary column (Phenomenex) was used for alcoholic liquids. An ion chromatography (Eco IC, Metrohm) equipped with the “METROHM 6.1005.200” column was used for quantifying volatile fatty acids (VFA) including formic acid. The faradaic efficiency (FE) for each product was calculated based on Faraday’s law (5)<sup>3</sup>, where *z* is the number of electrons transferred for per mole of reactant (e.g., *z* = 2 for reduction of CO<sub>2</sub> to CO), *n* is mass of the product from the electrode in moles, *F* is Faraday’s constant (96,500 C mol<sup>-1</sup>), *Q* represents the total charge passed.

$$FE = \frac{z n F}{Q} \quad (5)$$

## 2.5. Material characterisation of Cu<sub>x</sub>O catalyst

X-ray diffraction (XRD) spectrum which showing the crystal structure of the catalyst were obtained by a Philips X-ray diffractometer PW 1730 diffractometer equipped with a Cu X-ray tube (Cu-Kα; λ = 0.154 nm) operated at 40 kV and 40 mA. To determine the elemental compositions and valence states of the electrode surface (~10 nm depth), X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Nova XPS spectrometer using a K-Alpha line X-Ray source (225 W) over an area of approximately 300 × 700 μm. Microstructural characterisation of the catalyst was performed by scanning electron microscopy (SEM, Hitachi SU-70) coupled with an energy dispersive X-ray detector (EDX, Bruker Quantax 400).

## 3. Results and discussion

### 3.1. Effect of CO<sub>2</sub> supply method

The two CO<sub>2</sub> supply methods of “purging into electrolyte” and “diffusion from GDE” implemented by 2C cell and GDE cell respectively, were compared through eCO<sub>2</sub>RR using the same Cu<sub>x</sub>O-painted GDE as the cathode and same KHCO<sub>3</sub> catholyte. The catalyst morphology before and after 3 h eCO<sub>2</sub>RR in 1.0 M KHCO<sub>3</sub> was analysed by SEM and EDX as shown in Figure S2. The fresh catalyst consisted of spherical particles (100 ~ 1000 nm) which became finer after reaction. The EDX analysis (Figure S2) indicated that Cu<sub>x</sub>O catalyst was reduced during eCO<sub>2</sub>RR since the atomic ratio of copper to oxygen (Cu/O) was increased from 2.81 (before reaction) to 8.13 (after reaction). Since the substance composition and morphology of Cu<sub>x</sub>O catalyst changed over the eCO<sub>2</sub>RR duration, fresh Cu<sub>x</sub>O catalyst was used in each eCO<sub>2</sub>RR, with CV measurements in N<sub>2</sub> and CO<sub>2</sub> atmosphere respectively at the beginning. CV results which preliminarily evaluated the reaction behaviour are shown in Figure S3. After CV, eCO<sub>2</sub>RRs were carried out by CA at specific fixed potentials (30 min for each potential), the raw data of CAs are given in Figure S4. The normalized FEs for carbonaceous products and H<sub>2</sub>, and the average current density of eCO<sub>2</sub>RRs in the 2C and GDE cell were calculated and are shown in Table S1. FE sum of all the carbonaceous products and current density (*j*) taken from Table S1 are presented in Fig. 2.

It can be observed from the comparison between Fig. 2a and b that:

Within the potential range from -0.17 to -1.17 V, the GDE cell produced carbonaceous products with higher FE than the 2C cell. Although the current densities of the two cells were similar at the same catholyte and potential, the current in the 2C cell was mostly associated with HER. Only a small amount of formate and CO were produced when potentials were more negative than -0.37 V in the 2C cell, whereas CO

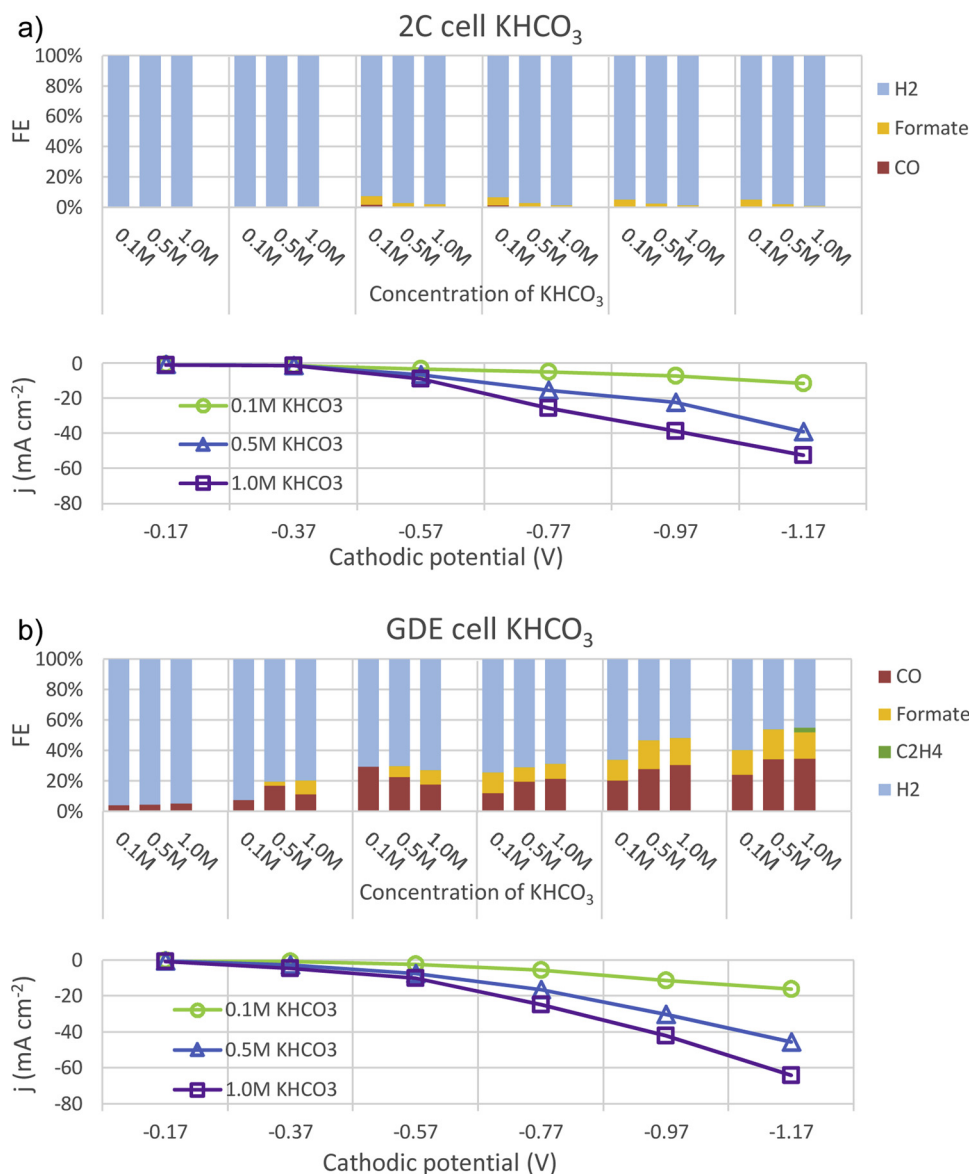


Fig. 2. eCO<sub>2</sub>RRs catalysed by Cu<sub>x</sub>O at a wide range of applied potentials in a) 2C cell with different concentrations of KHCO<sub>3</sub> and b) GDE cell with different concentrations of KHCO<sub>3</sub>.

was observed from  $-0.17$  V in all KHCO<sub>3</sub> electrolytes from GDE cell. The FE of carbonaceous products in GDE cell increased with more negative potential, 5% at  $-0.17$  V to 54% at  $-1.17$  V.

The relationship between total FE of carbonaceous products and KHCO<sub>3</sub> catholyte concentration in 2C cell and GDE cell were opposite. In the 2C cell, FE of carbonaceous products decreased with an increase in KHCO<sub>3</sub> concentration (a similar result was reported by Hori [27]). However, the GDE cell showed the carbonaceous FE increased with the increasing KHCO<sub>3</sub> concentration.

This can be caused by different reaction species from different CO<sub>2</sub> supply method. In the 2C cell, it has been widely accepted that the real reactant in the eCO<sub>2</sub>RR system is the dissolved CO<sub>2</sub> (generally written as CO<sub>2</sub>(aq) or H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>), rather than ionic HCO<sub>3</sub><sup>-</sup> and CO<sub>3</sub><sup>2-</sup> [2–27,1–29]. Although H<sub>2</sub>CO<sub>3</sub><sup>\*</sup> concentration increased from higher CO<sub>2</sub> solubility in higher concentration of KHCO<sub>3</sub>, the CO<sub>2</sub> reduction was determined by the ratio of H<sub>2</sub>CO<sub>3</sub><sup>\*</sup>/Total carbonate, which is higher in lower concentrations of KHCO<sub>3</sub> according to Heng et al.[29] leading to higher selectivity in 0.1 M KHCO<sub>3</sub> than in 1.0 M KHCO<sub>3</sub>.

In aqueous medium, the process of CO<sub>2</sub> mass transfer is composed of two major steps: Step 1. CO<sub>2</sub> gas dissolution and equilibrium to produce

the reactant CO<sub>2</sub>(aq), Step 2. CO<sub>2</sub>(aq) diffusion from bulk catholyte to local reaction sites. The rate of each step and the corresponding influence factors are summarized in Table S2. A brief review related to CO<sub>2</sub> mass transfer process given below Table S2 indicates that KHCO<sub>3</sub> with higher concentration can balance slightly more CO<sub>2</sub>(aq) in the bulk electrolyte [29] in Step 1, but constrains CO<sub>2</sub>(aq) diffusion [30] in Step 2. Moreover, under reduction potential, the K<sup>+</sup> of catholyte would be adsorbed around the double layer that further hinders CO<sub>2</sub>(aq) diffusion [31], in favour of hydrogen evolution.

In the GDE cell, the reactant was more likely activated CO<sub>2</sub> species, CO<sub>2</sub><sup>\*</sup>, which the adsorption mechanism as shown in Equation (6) where gaseous CO<sub>2</sub> or CO<sub>2</sub><sup>\*</sup> can be directly reacting at the catalyst interface. The gas adsorption mechanism in GDE was also reported in oxygen reduction reaction (ORR) related studies [32]. With this mass transfer mechanism in GDE cell, sufficient CO<sub>2</sub> reactant could be provided around reaction sites, which develops the competitiveness of eCO<sub>2</sub>RR against HER, reflected in a significantly enhanced carbonaceous selectivity than 2C cell.



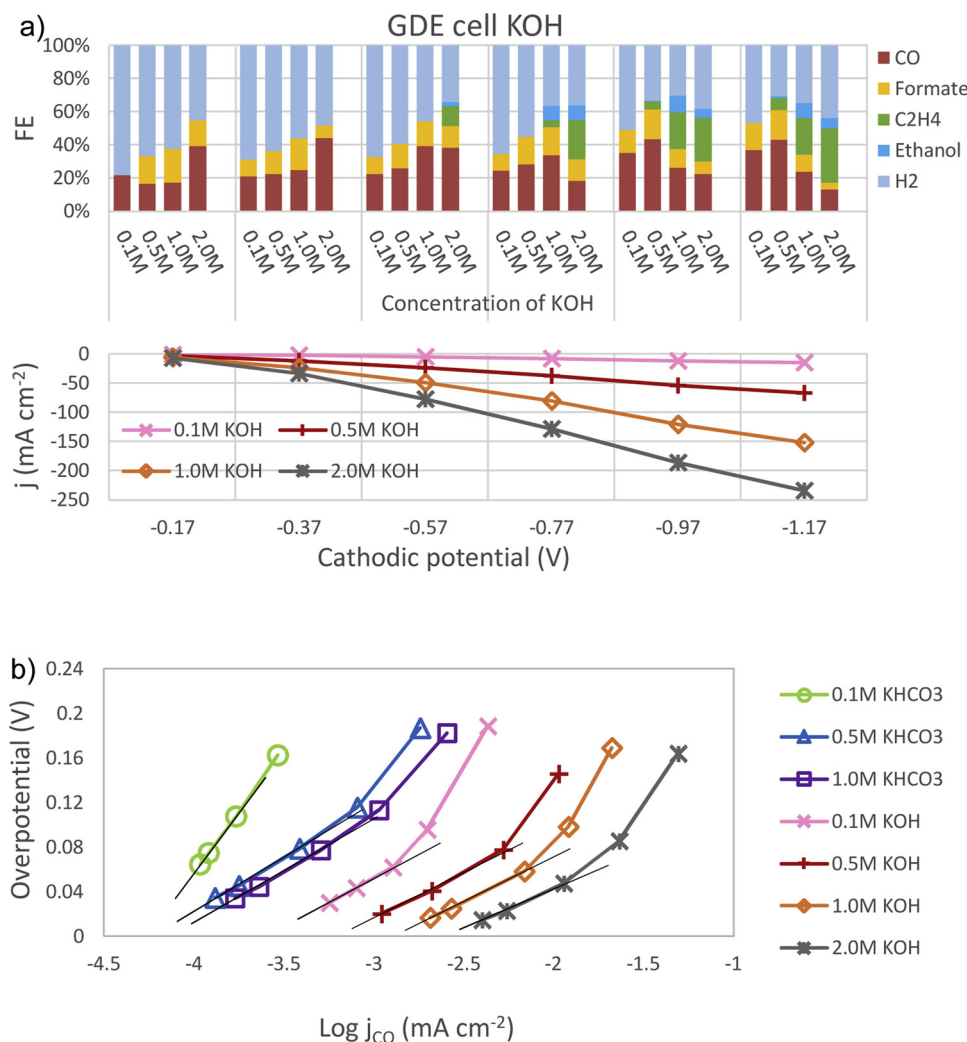


Fig. 3. a) eCO<sub>2</sub>RRs catalysed by Cu<sub>2</sub>O at a wide range of applied potentials in GDE cell with different concentrations of KOH. b) Tafel plots of the partial current density of CO<sub>2</sub> reduced to CO versus overpotential for CO formation in GDE cell with different catholytes.

In GDE cell, FE of carbonaceous products and current density both increased with the KHCO<sub>3</sub> concentration which was probably related to the alkalinity of catholyte. KOH with different concentrations were applied to further study the effect of alkaline catholyte in GDE cell, shown below (Fig. 3a).

### 3.2. Effect of alkaline catholyte in GDE cell

Fig. 3a shows the eCO<sub>2</sub>RR results in GDE cell by applying different concentrations of KOH as the catholyte, Cu<sub>2</sub>O was the catalyst. Tafel plots of CO production from eCO<sub>2</sub>RR are displayed in Fig. 3b to assess the mechanistic pathway of eCO<sub>2</sub>RR in GDE cell with different catholyte since CO was the common product for all the situations and the easiest to be generated at low overpotential. The Tafel slopes show the relationship of IR-corrected overpotential, to eliminate the effect from resistance of the solution, and the log of the partial current density using the actual electrode surface area 108.6 cm<sup>2</sup>, which was determined by measuring the double layer capacitance in 0.1 M HClO<sub>4</sub> [33] (Figure S5 and Table S3).

Table 2 shows the Tafel parameters of different catholytes in GDE cell obtained from Fig. 3b. With the increasing catholyte pH, the Tafel slope decreased, and the exchange current density  $j_0$ (eCO<sub>2</sub>RR) for CO production increased, indicating faster kinetics and higher activity of eCO<sub>2</sub>RR with more alkaline catholyte. Apart from 0.1 M KHCO<sub>3</sub> with lowest [OH<sup>-</sup>], the difference between other Tafel slope values were

Table 2

Tafel parameters obtained from the Tafel plots (Fig. 3b), b represents the Tafel slope for the lower overpotential region.

	KHCO <sub>3</sub>			KOH			
	0.1 M	0.5 M	1.0 M	0.1 M	0.5 M	1.0 M	2.0 M
pH	8.55	9.04	9.67	13.02	13.56	13.96	14.30
b /mV dec <sup>-1</sup>	213	95	92	90	86	81	74
$j_0$ /mA cm <sup>-2</sup>	5.41	5.76	7.30	2.61	5.77	1.30	2.60
	$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-5}$	$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-3}$	$\times 10^{-3}$

small, decreased from 95 mV dec<sup>-1</sup> in 0.5 M KHCO<sub>3</sub> to 74 mV dec<sup>-1</sup> in 2.0 M KOH. This suggests the same mechanism for CO<sub>2</sub> reduction to CO despite different [OH<sup>-</sup>] in the catholyte.

Comparing eCO<sub>2</sub>RR in GDE cell with KHCO<sub>3</sub> catholyte (Fig. 2b) and KOH catholyte (Fig. 3a), the selectivity of the carbonaceous products is greater with KOH solution than with KHCO<sub>3</sub> solutions shown by higher FE in KOH at the same potentials. Also in both KOH and KHCO<sub>3</sub> electrolytes, the carbonaceous FE was enhanced with increasing electrolyte concentrations. 1.0 and 2.0 M KOH at -0.17 V had similar FE of carbonaceous products to KHCO<sub>3</sub> at -1.17 V. This 1 V shift suggests lower energy required in catholyte with higher alkalinity.

C<sub>2</sub> products (ethylene and ethanol) were notably produced in KOH catholyte with the concentration higher than 0.5 M. At -1.17 V, the C<sub>2</sub>

FE reached almost 40% in 2.0 M KOH. Within the potential range in this study, C<sub>2</sub> selectivity was increased with more negative potentials and higher KOH concentration. Although the highest FE for C<sub>2</sub> was obtained in 2.0 M KOH, the differences between 1.0 and 2.0 M were insignificant indicating the applied potential related to the energy level of the reaction interface at higher pH more critical.

The current density (*j*) increased with increasing the overpotential and catholyte concentration. Under the same potential, the current density of KOH was much higher than KHCO<sub>3</sub> with the same concentration. EIS measurement with the CO<sub>2</sub> atmosphere was used to survey the effect of KOH concentration on resistances. The results displayed in Figure S7 and Table S4 indicate that KOH with higher concentration has smaller resistances of solution and charge transfer. The charge transfer resistance decreased with [OH<sup>-</sup>], corresponding to the increasing exchange current density *j*<sub>0</sub> shown in Table 2. -234 mA cm<sup>-2</sup> current density was achieved at -1.17 V in 2.0 M KOH, with 40% FE of C<sub>2</sub>. The production rate of ethylene and ethanol was respectively 0.105 mg min<sup>-1</sup> and 0.035 mg min<sup>-1</sup> on 2 cm<sup>2</sup> electrode with CO<sub>2</sub> flow rate 15 ml min<sup>-1</sup>, implying the industrialisation potential for C<sub>2</sub> production.

The high alkalinity catholyte showing improved eCO<sub>2</sub>RR kinetics and C<sub>2</sub> selectivity could be due to the adsorbed OH on catalyst surface. Zhang et al. [34] compared eCO<sub>2</sub>RRs on three different local oxygen-induced surfaces: 1. fully oxidized Cu<sub>2</sub>O surface, 2. partially oxidized Cu(110)-(2 × 1)O surface, 3. presence of OH spectators. The existence of OH groups as spectators on Cu<sup>o</sup> surface could flip the selectivity between CH<sub>4</sub> and CH<sub>3</sub>OH, playing the similar role with the oxidized Cu surface. It has been widely accepted that oxide-derived electrocatalysts applied in eCO<sub>2</sub>RR can reduce the energy barrier of CO<sub>2</sub> activation through enhancing the adsorption strength<sup>35</sup> and stability of the active species CO\* on reaction sites [3,36,37]. The CO\* dimerization is the rate determining step of C<sub>2</sub> products formation [38–42], which occurs at high local pH (≥12) [43], and easier to take place on an oxygen-induced Cu surface than bare metallic Cu [44,45].

The use of oxide-derived Cu as the catalyst for CO<sub>2</sub> reduction has been recognized for the purpose of C<sub>2</sub> production in some studies [22,37,44,46,47]. However, J. Albo et al. [48–50] used Cu<sub>2</sub>O with 0.5 M KHCO<sub>3</sub> catholyte in a two-chamber cell and found methanol to be the major product, which was not detected in this work. Analyzing the methanol absence in this study compared to their work is hard as different type of Cu oxide catalyst applied. Also, the results above indicate, even with the same Cu<sub>x</sub>O catalyst, the distribution of carbonaceous products varied by CO<sub>2</sub> supply method, catholyte, and applied potential. XRD and XPS were applied to investigate the status of Cu<sub>x</sub>O catalyst and reaction interfaces, as shown in Fig. 4.

Cu<sub>x</sub>O applied as the catalyst in this study is a mixture of Cu<sub>2</sub>O (main), CuO and Cu as observed in its XRD pattern (Fig. 4a). The reduction of Cu<sub>x</sub>O to Cu<sup>o</sup> has much less negative potential than eCO<sub>2</sub>RR as found in the CV results in Figure S3. Thus, under the reaction potential of eCO<sub>2</sub>RR, the Cu<sub>x</sub>O catalyst should be reduced to Cu<sup>o</sup> rapidly. The XRD patterns of the two “after reaction” samples indicate the main component in the bulk catalyst after reaction either in 1.0 M KHCO<sub>3</sub> or 1.0 M KOH was metallic Cu. However, even though the bulk Cu<sub>x</sub>O catalyst reduced to Cu<sup>o</sup>, the catalytic activity maintained over 4 h with stable C<sub>2</sub> FE between 30–40%, as shown in Figure S6, suggesting the catalytic activity of Cu based catalyst may still be from Cu and OH or oxygen groups from oxide-derived catalyst could further reduce the activation energy and be favourable to carbonaceous products formation. XPS which was used to characterise the catalyst surface further proved this. Fig. 4b displays the XPS spectra on Cu<sub>x</sub>O-GDE before eCO<sub>2</sub>RR and after 3 h eCO<sub>2</sub>RR in GDE cell with 1.0 M KOH and 1.0 M KHCO<sub>3</sub>. The reduction of the catalyst after reaction is also observed since the satellite peaks of Cu 2p<sub>3/2</sub> and Cu 2p<sub>1/2</sub> on the fresh catalyst are both largely attenuated after reaction [51]. These peaks are stronger mitigated in the “after reaction (KHCO<sub>3</sub>)” catalyst than those of “after reaction (KOH)”, indicating the catalyst surface after reaction remains

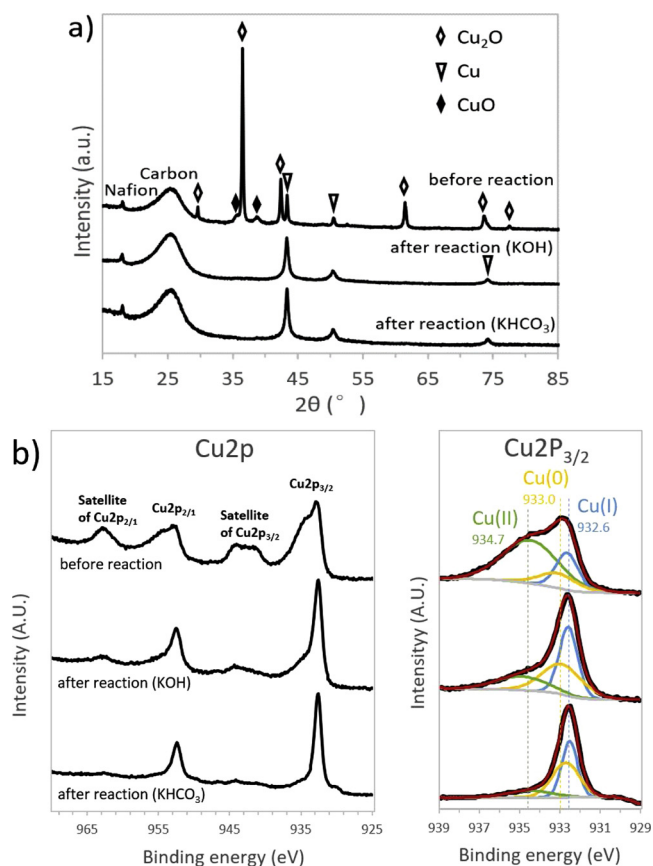


Fig. 4. a) XRD patterns and b) XPS spectra of Cu<sub>2</sub>P and the peak-differentiating of Cu<sub>2</sub>P<sub>3/2</sub> for the Cu<sub>x</sub>O-GDE before eCO<sub>2</sub>RR and after 3 h eCO<sub>2</sub>RR in 1.0 M KOH and 1.0 M KHCO<sub>3</sub>.

higher oxidation degree in KOH than in KHCO<sub>3</sub>. The Cu<sub>2</sub>P<sub>3/2</sub> photoelectric peak was fitted to quantitatively analysis Cu species [52,53]. The fresh catalyst surface contains 14.65% Cu(0), 21.99% Cu(I), and 63.36% Cu(II). After eCO<sub>2</sub>RR, the catalyst surface of “after reaction (KOH)” contains 37.82% Cu(0), 39.92% Cu(I) and 22.26% Cu(II), showing higher oxidation degree than that of “after reaction (KHCO<sub>3</sub>)” containing 44.31% Cu(0), 41.15% Cu(I) and 14.54% Cu(II). Although the bulk Cu<sub>x</sub>O catalyst was substantially reduced to metallic Cu after eCO<sub>2</sub>RR, oxidized Cu partially remained on the catalyst surface.

In summary, the OH groups adsorbed on the catalyst surface may partially prevent the oxidised Cu surface from being reduced to metal and reduce the energy barrier of CO<sub>2</sub> activation through enhancing the adsorption strength [35] and stability of the active species CO\* on reaction sites [3,36,37]. Also, the high concentration of OH<sup>-</sup> on Cu catalyst surface showed reduced CO–CO coupling energy barrier [47], resulting in enhanced selectivity of C<sub>2</sub> products.

#### 4. Conclusions

In this study, the effects of CO<sub>2</sub> supply method and alkalinity on the selectivity of carbonaceous products, and C<sub>2</sub> products were investigated in aqueous electrolyte using Cu<sub>x</sub>O catalyst. The results suggested that GDE cell with CO<sub>2</sub> supplied through gas diffusion has higher selectivity for carbonaceous products and suppression of HER compared to two-chamber cell with CO<sub>2</sub> purging into electrolyte. Faradaic Efficiency of carbonaceous products increased from < 10% in 2C cell to 55% in GDE cell at -1.17 V in 1.0 M KHCO<sub>3</sub>. This was primarily due to different reactants for CO<sub>2</sub> electrochemical reduction in GDE and in reaction solution, being CO<sub>2</sub>\* and hydrated H<sub>2</sub>CO<sub>3</sub>\*, respectively. The alkalinity of catholyte also had a significant influence on the selectivity of

carbonaceous products leading to higher FE from KOH than KHCO<sub>3</sub>. Higher FE of C<sub>2</sub> products, ethanol and ethylene, were observed from KOH with higher concentration ( $\geq 0.5$  M) and at higher overpotentials ( $-0.97$  and  $-1.17$  V), suggesting C–C coupling process occurring with high concentration of OH at catalyst interface with high energy input. XRD and XPS proved the effect of OH groups on the catalysts surface could be favourable to carbonaceous products formation. At  $-1.17$  V with 2 M KOH, C<sub>2</sub> FE achieved at 40% with current density  $-234$  mA cm<sup>-2</sup>, producing 0.105 mg min<sup>-1</sup> ethylene and 0.035 mg min<sup>-1</sup> ethanol on 2 cm<sup>2</sup> electrode with CO<sub>2</sub> flow rate 15 ml min<sup>-1</sup>. This is promising for further development and scale-up.

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### Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.jcou.2019.02.007>.

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