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Further study of CO₂ electrochemical reduction on palladium modified BDD electrode: influence of electrolyte

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Abstract: The study of CO2 electrochemical reduction to useful compounds using bare or modified BDD electrode attracts numerous attentions. Meanwhile, the efficiency of products obtained from CO2 electrochemical reduction is known to be determined by the electrode material and the electrolyte. Formic acid as main product and CO as a minor product, have also been known on the CO2 reduction using BDD electrode. Recently, we reported the successful improvement of CO production from the reduction of CO₂ by decorating the surface of BDD electrode with palladium particles. Following this, herein, we present further investigation on electrolyte dependence, including cation and anion dependence and also concentration effect in order to understand deeply the CO2 reduction on surface of palladium modified BDD electrode. The results suggest the use of NaCl and KCl as a catholyte for optimum performance, in addition to the improvement of CO₂ reduction product in higher electrolyte concentration.

Introduction

In the recent years, the electrochemical reduction of CO₂ into useful chemicals necessities is noteworthy, by considering the rising emissions of CO₂ gas in the atmosphere, which leads to the experimental evidence of adverse environmental impact ^[1]. Many simultaneous approaches have been proposed, whether reducing the emission in atmosphere through CO₂ scrubbing or converting CO₂ gas to useful and valuable chemicals ^[2-5]. Among many methods to convert CO₂ gas into valuable compound, electrochemical reduction has widely been employed by many researchers around the world due to its easy controllable operation.

Meanwhile, a suitable electrode is noted to be an important part for a maximum system performance. Many experiments have been carried out and reported, by modifying and finding suitable electrode for CO₂ electrochemical reduction system ^[6-8]. Recently, boron-doped diamond (BDD) electrode, which has been known to have low background current and wide potential window, is studied for CO₂ electrochemical reduction, either on bare ^[9,10], or modified surface ^[11-13]. In addition, it was suggested that the high overpotential of BDD electrode could be decreased by decorating its surface with metal particles. Our previous report used palladium (Pd) particles modified on surface of BDD (PdBDD) electrode, in which, it could improve the production of CO, in comparison with bare BDD electrode at the same applied potential ^[14]. Therefore, a further study on CO₂ reduction to CO on PdBDD electrode was carried out, specifically on electrolyte dependence study, that is believed to promote more active catalytic reaction. As a significance, CO is an important feedstock and intermediate for the production of methanol ^[15], acetic acid ^[16], and ethanol ^[17,18].

There have been many reports on enhancing the efficiency of CO2 reduction by changing the electrolyte. However, to the best of our knowledge, study of electrolyte dependence on PdBDD electrode is the first time. Our group has been successfully enhanced the production of HCOOH up to 95% efficiency using bare BDD by changing the electrolyte to RbCl aqueous solution, and also by changing the selectivity using different anions ^[19,20]. Y. Huang et al ^[21] studied the effect of anion for CO₂ reduction to ethylene and ethanol on Cu (111) and Cu (100) electrode, and found that the production of ethylene was improved as the anion changed from CIO⁻ to I⁻. Therefore, we believe that studying the electrolyte dependence is in a high interest to deeply understand the behavior of CO₂ reduction on PdBDD electrode specifically, also in intension to possibly improve the production of CO. In this report, we report a detail study of electrolyte dependence, including various cations and anions, different concentrations, and potential dependence study.

Results and Discussion

Firstly, the study of cation dependence on PdBDD electrode was evaluated by performing linear sweep voltammetry in 0.1 M MCI solutions in the presence of CO_2 gas. As we can see in Fig. 1, the current density of hydrogen evolution was decreased as the cation size increases. It is suggested that the hydrogen evolution could be restrained in the solution containing larger cation size, and thus, promoting more electrons in the solution for CO_2 electrochemical reduction.

The electrolyte concentration dependence was then evaluated by performing the CO₂ electrochemical reduction in NaCl aqueous solution as catholyte, with various electrolyte concentrations, ranging from 0.1 M, 0.3 M, 0.5 M, and 1 M (Fig. 2A). FE of the products and its partial current density (*j_p*) were increased as the electrolyte concentration increased. A CO partial current density (*j_{co}*) value of 0.45 mA/cm² was achieved in catholyte concentration of 0.5 M NaCl. Whereas, a 46.9% FE of CO was achieved at catholyte concentration of 1 M NaCl. As it can be seen in Fig. 2, the efficiency of all products does not show a significant different value, after reaching concentration of 0.5 M,

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explaining that it has attained a maximum value. The rise of the FE as well as the current density at higher electrolyte concentration is suggested, due to the higher ionic conductivity in accordance to the more positive value of the potential at outer Helmholtz plane, leading to the improvement of driving force for the reaction ^[23].



Figure 1. Linear sweep voltammograms of PdBDD electrode in 0.1 M MCI solution with scan rate of 100 mV/s.

Furthermore, concentration dependence was studied in electrolyte with other cations (K⁺, Rb⁺, and Cs⁺) (Fig.2B-2D). The FE of CO in NaCl, KCl, and CsCl shows similar trend, in which, the increasing of electrolyte concentration could improve the production of CO. Therefore, it is assumed that there is no direct correlation between cation type and electrolyte concentration. However, overall results show that by increasing the concentration of the electrolyte, the CO2 reduction products efficiency could be improved and H₂ evolution could be suppressed. A special phenomenon was observed while applying RbCl as an electrolyte, in which, formic acid dominates the products rather than the CO, in spite of the similar total current density achieved (data not shown). As only small part of BDD surface covered by Pd particles, it is obvious that the behavior of BDD electrode contributes to overall performance, in which, our previous report of CO2 reduction on bare BDD electrode reported that the maximum production of formic acid achieved while using Rb⁺ cation as a catholyte ^[19,24]. It is said that Rb⁺ hydrated with water easily and cover the surface of electrode, enable the decomposition of water or hydrogen evolution production.



Figure 2. FE and j_p of CO₂ electrochemical reduction products in correlation with various concentrations of (A) NaCl, (B) KCl, (C) RbCl, and (D) CsCl aqueous solution as catholyte. The electrochemical reduction was performed at potential -1.6 V for 1 h. Linear sweep voltammograms of PdBDD electrode in 0.1 M MCl solution with scan rate of 100 mV/s.

To study in detailed about cation effect, Fig. 3 shows a plot between different cation (Na⁺, K⁺, Rb⁺, Cs⁺) in correlation with FE and jp of products. In a concentration of 0.1 M, production of CO, explained by the FE and the j_{CO} , is increased as the cation size is bigger. Study by Ringe S. et al [25] has proved that the larger the cation, the smaller hydrated cation is. Thus, resulted in a high concentration of cation near surface of electrode, leading to larger surface charge density and stronger interfacial electric field, in which, the adsorption of CO₂ on the surface of electrode could be improved. Besides, H₂ evolution relatively could be suppressed as cation size is bigger, in agreement to the result reported by Thorson M. R. et al [26]. Nevertheless, as describes above, an exception using PdBDD electrode was found only in RbCl solution, in which, formation of formic acid was dominant, therefore selectively suppressing the formation of CO. This is in contrast with the result on Cu (111) and Cu (100) electrode reported by Resasco J. et al [27], in which, rate of CO production is less affected by cation size.

Following the different behavior in RbCl solution, it was considered that to produce a maximum efficiency of CO, the applied potential could be shifted to more positive potential. Thereafter, we performed a potential dependence varied from - 1.4 V to -1.8 V (Fig. 4). The result shows that at more negative potential, faradaic efficiency of formic acid was increased in contrast with the suppression of H₂ evolution. Meanwhile, CO production was maintained in similar efficiency. In point of fact, faradaic efficiency of CO was decreased at potential -1.4 V, and H₂ evolution dominated. Therefore, it is concluded that on bare or Pd modified BDD electrode, cation Rb⁺ is specifically a formic acid catalyst, and is not a suitable support for CO production.

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Figure 3. FE of products in electrolyte with different cation, in various concentrations of 0.1 M (A), 0.3 M (B), 0.5 M (C), and 1.0 M (D). *j_p* of products in electrolyte with different cation, in various concentration of 0.1 M (a), 0.3 M (b), 0.5 M (c), and 1.0 M (d). All measurements were performed at potential -1.6 V for 1 h.

Moreover, to study the effect of anion, CO₂ electrochemical reduction in electrolytes of NaCl, Na₂SO₄, Na₂CO₃, and NaClO₄ were performed. The study using CV from potential of -0.5 V to 1.2 V was performed after N₂ and CO₂ gas purging, in which, the peak shift could be observed (Fig. 5). As an example, in 0.1 M NaCl, a cathodic peak of Pd (known as a deposition step of Pd) at around -0.1 V was shifted to 0.2 V after CO₂ gas bubbled into the solution. It could be explained that as the pH of the solution decreased, the potential window is narrower, and therefore the peak shift to more positive potential could be observed ^[28,29], in agreement with our previous work ^[14]. Similar peaks could also be observed in NaCl, Na₂SO₄, and NaClO₄ catholyte. On the other hand, Na₂CO₃ shows a different behavior. The peak shift was relatively in more negative potential, in which, it could be explained by the buffering effect described later.



Figure 4. Various potentials vs. faradaic efficiency of products on the CO_2 electrochemical reduction in 0.5 M RbCl.

In Fig. 6, shows that Cl⁻ and ClO₄⁻ anions could improve the production of CO, and CO₃²⁻ shows a highest hydrogen evolution. It is known that several anions, such as SO₄²⁻ and halides (i.e. Cl⁻) could specifically adsorbed on electrode and restrained CO₂ strongly on surface of electrode, promoting products, and suppressing H₂ evolution ^[30].



Figure 5. CV of PdBDD electrode in 0.1 M NaCl (A), Na₂SO₄ (B), NaClO₄ (C), and Na₂CO₃ (D) solution after N₂ (dash line) and CO₂ (solid line) gas purging with scan rate of 100 mV/s from potential -0.5 V to 1.2 V vs. Ag/AgCl.

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The result present here is also linear to the recent report, mentioning that the presence of Cl^- favoring CO production ^[31]. Meanwhile, a high H₂ evolution in an electrolyte of Na₂CO₃ is suggested due to buffering effect, as described by the following reactions (Eq (1-2)):

$$CO_{2(aq)} + H_2O_{(l)} \subseteq H^+_{(aq)} + HCO_{3^-(aq)} \qquad pK_1 = 6.35$$
 (1)

 $H^{+}_{(aq)} + HCO_{3^{-}(aq)} \leftrightarrows 2H^{+}_{(aq)} + CO_{3^{2^{-}}(aq)} \qquad pK_{2} = 10.33 \quad (2)$

After CO₂ purging into the Na₂CO₃ solution, the pH was around neutral, and the concentration of HCO_3^- is higher. The high amount of HCO_3^- could drive the increasing of hydrogen evolution, as following reaction (Eq. (3-4)):

$$H_2O + e^- \rightarrow {}^*H + OH^-$$
(3)

$$HCO_3^- + e^- \rightarrow {}^*H + CO_3^{2-}$$
(4)

In addition, the partial current density of each products is following the trend of products faradaic efficiency as shown in Fig. 6. Among all electrolytes, Na_2CO_3 shows highest total current density, which can be interpreted to have a higher electron transfer, and thus promoting hydrogen evolution.



Figure 6. Anion effect on the CO_2 electrochemical reduction products efficiency performed at potential -1.6 V during 1 h.

Conclusion

In this work, the effect of electrolyte, including cation and anion effects on the CO₂ electrochemical reduction on the surface of PdBDD electrode were studied. Finally, to improve the production of CO specifically on CO₂ reduction using PdBDD or BDD based material as an electrode, the used of cation Na⁺ or K⁺ is suggested, in addition to the used of Cl⁻ anion. Moreover, higher concentration of the electrolyte could also improve the efficiency

and current density of the CO_2 reduction products, whereas lower concentration of the electrolyte will favor the hydrogen evolution.

Conflict of Interest

The authors declare no conflict of interest.

Experimental Section

Chemicals

All chemicals were purchased from Wako Pure Chemical Industries except PdCl₂ (99%) was purchased from Sigma Aldrich. All reagents were used without any further purification. Ultra-pure water was obtained from a Simply-Lab water system (Direct-Q UV3, Millipore) to prepare aqueous solutions.

Preparation of BDD and PdBDD electrode

Boron-doped diamond (BDD) electrode was prepared by depositing it on the surface of Si (111) wafers for 6 hours using micro-wave plasmaassisted chemical vapor deposition system (Model AX-5400, CORNES Technology Corp.). A mixture of trimethoxyborane and acetone was used as carbon and boron sources to achieve a B/C ratio of 1%. A detailed procedure was explained in previous report ^[22]. To prepare palladium modified on surface of BDD (PdBDD) electrode, 10 mL of 1 mM PdCl₂/0.1 M HCI was prepared and electrodeposition with chronoamperometric technique was performed during 300 s at potential of -0.15 V. All modified electrodes were treated as described in previous report [14], and characterization using field emission scanning electron microscopy-energy dispersive X-ray (SEM-EDX INSPECT F50, FEI) was performed to convinced the well-prepared modified electrode for analysis (Fig. S1). The Pd particles were dispersed homogeneously all over the surface of BDD electrode with the percent weight of 4.73 % and average particle size of around 50 nm. In addition, the detailed study on PdBDD characterization was explained in our previous report [14].

CO2 electrochemical reduction and products analysis

Two cells separated by Nafion membrane was used to conduct the electrochemical reduction of CO₂. The anolyte side was 0.1 M Na₂SO₄. Various MCI (M= Na, K, Rb, and Cs) electrolytes with different concentrations of (0.1, 0.3, 0.5, and 1.0 M) were used as catholyte. Pt mesh and PtBDD were used as counter and working electrode respectively. All potentials were measured against Ag/AgCl (3 M NaCl). N₂ and CO₂ gas purging for 15 min were performed prior to each reduction process. CO₂ electrochemical reduction was carried out for 1 h under mild CO₂ gas flow rate (<50 sccm) to maintain the saturation of CO₂ gas in the electrolyte. N₂ gas was then purged into the catholyte side at about 50 sccm to collect the gas product in the solution. All the electrochemical measurements were recorded using potentiostat (Autolab PGSTAT204, Metrohm Autolab B.V.).

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Figure S1. SEM-EDX of PdBDD electrode.

One liter of collected gas was then analyzed using gas chromatography with a flame ionization detector and a thermal conductivity detector (GC-2014, Shimadzu Corp.). Whereas the liquid sample from catholyte side was analyzed using high performance liquid chromatography (HPLC) with an electroconductivity detector (Prominence, Shimadzu Corp.). The analysis detail was explained in our previous report ^[19]. Faradaic efficiencies (FE) were calculated by this equation (Eq. (1)):

$$FE = (n F M)/(I t) x 100\%$$

where n is electron involved in reduction, F is faraday constant (96.485 C mol-1), M is concentration of sample, I is current and t is reduction time. Meanwhile, current density of each product was measured by multiplying the FE and the total current density for CO₂ reduction process.

Keywords: CO₂ reduction • palladium • boron-doped diamond • electrolyte

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The CO_2 electrochemical reduction to CO and HCOOH on PdBDD electrode was studied, showing the dependence of different catholyte and anolyte. The result suggests the use of electrolyte NaCl or KCl with higher electrolyte concentration to improve the production of CO on PdBDD electrode.