RSC Advances

PAPER

View Article Online
View Journal | View Issue

Cite this: *RSC Adv.*, 2017, 7, 22510

Effect of alkali-metal cations on the electrochemical reduction of carbon dioxide to formic acid using boron-doped diamond electrodes

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Received 22nd March 2017
Accepted 16th April 2017

DOI: 10.1039/c7ra03370b

rsc.li/rsc-advances

The electrochemical reduction of carbon dioxide in aqueous solutions using boron-doped diamond (BDD) electrodes was investigated at ambient pressure and temperature. We discuss the effects of the alkali-metal (AM) cations, K^+, Na^+, Rb^+ and Cs^+, on the faradaic efficiency (FE) for the formation of formic acid. An FE of 71% was achieved in the case of a 0.075 M Rb^+ solution neutralized to pH 6.2 by the addition of HCl. In the case of a Cs^+ solution neutralized to pH 6.2, the highest FE was obtained with the more dilute concentration of 0.02 M. Of the four different solutions examined, the lowest FE was observed for the Na^+ solution. Moreover, we found that the productivity for the production of formic acid is higher at higher current densities.

Introduction

The large amount of CO_2 emissions has become a serious problem from the point of view of global warming. For example, thermal power plants that generate electric power have been discharging large amounts of CO_2 into the atmosphere. So, for the past several decades, much attention has been paid to the recycling of CO_2 to produce valuable chemicals such as CO, CH_4, formic acid, formaldehyde, methanol and products derived from these.[1]

The CO_2 molecule is sufficiently thermodynamically stable that CO_2 cannot be converted into any other useful substance without activating it. However, it is easy to activate CO_2 molecules at ambient pressure and temperature using electrochemical methods. There have been many reports presented on the electrochemical reduction of CO_2 using various kinds of metal and semiconductor electrodes.[2,3] Some noble metal electrodes such as Pt, Au and Cu convert CO_2 to CO or CH_4 molecules without the formation of formic acid owing to the different catalytic pathways on these electrode surfaces.[4] Although Sn electrodes enable us to produce formic acid from CO_2 with a very high faradaic efficiency (FE) of 65–90%, this electrode material is unstable and unable to maintain a stable FE for the production of formic acid.[5,6] Using a methanol-based electrolyte, Mizuno *et al.* have reported that formic acid could be formed with a high yield of around 70% using Pb electrodes at ambient pressure.[7] Considering the practical use of an energy conversion system, water-based solutions are more convenient than organic solvents. Compared with such metal electrodes, BDD electrodes have greater chemical and mechanical stability. As previously reported, formaldehyde can be produced with high yield from CO_2 using BDD electrodes and water-based solvents.[8]

Recently, the effect of the size of the AM cation on the production of CO, C_2H_4 and C_2H_5OH using Ag and Cu electrodes has been discussed.[9]

In this paper, we report on a systematic study of the effect of AM cations on the FE for the production of formic acid using BDD electrodes. We found that the optimum conditions, obtained using 0.075 M Rb^+ solution neutralized to pH 6.2 with HCl, gave an FE of 71%.

Experimental

BDD thin films were grown using microwave plasma assisted chemical vapor deposition (MPCVD). The boron source, $B(OCH_3)_3$, was dissolved in acetone (the carbon source) with a B/C atomic ratio of 1.0 w/w. BDD was deposited on Si(100) wafers in an MPCVD chamber at 5 kW using high-purity hydrogen as a carrier gas.

To confirm the film quality of the BDD, Raman spectroscopy was performed with Ar laser illumination (Acton-SP2500). The Raman spectra show a narrow peak at 1324 cm^{-1}, which is attributed to the zone center phonon of diamond in the BDD together with larger bands observed around 477 cm^{-1} and 1204 cm^{-1}. The electric resistivity was about 2 mΩ cm, as we reported before.[10]

The electrochemical experiments were performed in a two-compartment H-type cell (100 mL), using a platinum counter

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electrode and Ag/AgCl reference electrode. Water was obtained from a Millipore Milli-Q Plus system. All the chemicals used here, except RbOH, were purchased from Wako pure chemicals. $RbOH\cdot H_2O$ was purchased from Yoneyama Chemicals.

The BDD electrodes were sonicated in ultrapure water prior to use. The experimental procedure was as follows: first, N_2 gas was bubbled into the electrolytes for 30 min at a rate of 200 sccm to remove oxygen. Then, CO_2 gas was bubbled into the electrolytes for 5 min at a rate of 500 sccm. After that, the bottle containing the electrolytes was shaken for 5 min to obtain a saturated solution of CO_2. The pH of the saturated solution was neutralized to 6.2 with the addition of HCl. 50 mL of the saturated solution, to be used as the catholyte, was poured into the cathode part of the electrochemical cell. As for the anolyte, a solution with the same concentration as the catholyte, but without the pH adjusted, was used. All the electrolysis experiments were performed at a constant current of −10 mA for 1 h. The faradaic efficiency was calculated from the mass of the product compared with the amount of charge (36 C) used in the experiments. The CO and hydrogen were analyzed by gas chromatography with a flame ionization detector (FID) and a thermal conductivity detector (TCD) (GC-2014, Shimadzu Corp.). The formic acid was analysed by high performance liquid chromatography (HPLC) with an electroconductivity detector (Prominence, Shimadzu Corp.). The electrodes were characterized by scanning electron microscopy (JCM-6000, JEOL).

Results and discussion

Effect of pH on the faradaic efficiency for the production of formic acid

Since alkaline solutions strongly absorb CO_2, we chose NaOH, KOH, RbOH and CsOH as the supporting electrolytes. For 0.5 M KOH, the pH stayed at around 9.5 after saturation of the CO_2. At pH 9.5, we confirmed that no formic acid was produced after electrolysis at 10 mA for 1 h. Upon dissolving CO_2, CO_3^{2-}, HCO_3^- or H_2CO_3 is formed in the solution.[11] At high pH, CO_3^{2-} is the dominant species formed. By adjusting the pH to lower values, the presence of HCO_3^- becomes evident, which is deemed to be the species responsible for the formation of formic acid. Using a 0.05 M Rb^+ solution, we determined the optimum pH required to produce formic acid from CO_2. After shaking for 5 min, the pH stays at around 7, with the CO_2 concentration above 2020 mg L^{-1}.

The FE was calculated by the following equation.

$$\mathrm{FE}\ (\%) = (n \times C \times F)/Q \times 100$$

here, n is the number of electrons for the formation of products, C is the amount of the products (mol), F is the faradaic constant (C mol^{-1}), Q is the charges consumed for the formation of the products (C). The error of the liquid products was evaluated to 5% by measuring the same samples repeatedly. Also, the error of gaseous products was estimated to 10%.

Fig. 1 shows the relationship between the pH of the CO_2 saturated 0.05 M Rb^+ solution neutralized with HCl and the FE for the formation of formic acid. The optimum pH was found to be around 6.2. In the case of the 0.05 M Rb^+ electrolyte, the maximum FE was 66%. These results show that HCO_3^-, produced from the bubbled CO_2, plays an important role in forming formic acid on the surface of the BDD electrode. The potential during electrolysis was highly negative, about −2.2 to −3 V, which is sufficient to form co-adsorption structures comprising alkali-cations and HCO_3^- on the BDD electrode.

The reaction mechanisms for the formation of formic acid and CO have been reported elsewhere.[5,6,9] Two electrons are involved in each of these reactions.

The overall reactions for the formation of formic acid and CO are as follows,

$$CO_2 + 2H^+ + 2e^- = HCOOH \quad (1)$$

$$CO_2 + 2H^+ + 2e^- = CO + H_2O \quad (2)$$

Both reactions (1) and (2) are related to $^{\bullet}CO_2$ radicals adsorbed on the electrode surface. As noted in a previous review,[12] the weakly adsorbed $^{\bullet}CO_2$ radicals form the formic acid. On the other hand, the stably adsorbed $^{\bullet}CO_2$ radicals produce gaseous CO.

We have often experienced that the FE value of 55% with a newly-grown BDD electrode settled down to 20% after *ca.* 30 batch tests in 0.1 M K^+ solutions with pH 6.2. Each batch test consists of an hour electrochemical reduction experiment of CO_2. The immersion of BDD electrodes into aqua regia solution overnight often gives good restoration effect. However, the FE for formic acid production eventually degraded down to 20%. Once the FE degraded 20%, the FE never recovered in the case of 0.1 M K^+ solutions with pH 6.2 even if we applied the electrochemical oxidation of BDD electrodes. On the contrary, in Rb^+ solution, the FEs easily recovered by the electrochemical methods. The question is why the FEs obtained in 0.1 M K^+ solution never recover again. There are a couple of possible explanations for this question. First, the oxygen species formed by electrochemical pretreatment consist of several kinds of adsorbates. Namely, atomic oxygen, hydroxyl group or other chemical species are thought to be mixed on BDD surfaces. Among them, some species might hamper the adsorption of alkali-metal cations. So, in 0.1 M K^+ solution, K cations would be adsorbed on the oxygen, not on the hydroxyl groups formed on oxidized BDD electrodes. It can be speculated that the population of each oxygen species

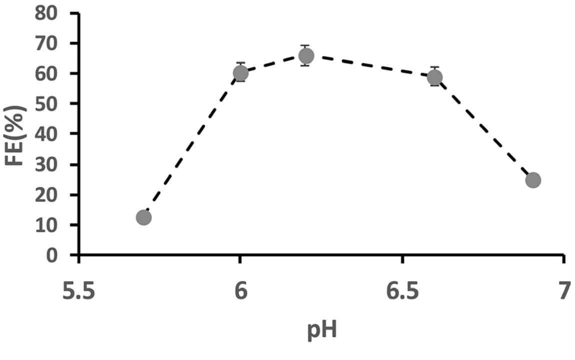

Fig. 1 Effect of pH on the FE for the formation of formic acid in a Rb^+ solution.

changes irreversibly in the course of the successive electrochemical reduction process and electrochemical oxidation cycles. That causes the hysteresis of the effect of conversion of CO_2 to formic acid using 0.1 M K^+ solution. Compared with K^+, the larger Rb cations would easily stick to oxidized BDD electrode surfaces, which provide the reversible results. Another possible explanation of the irreversible effect of conversion of CO_2 in K^+ solution would be the adsorbates-induced surface restructuring on BDD electrode surfaces. In the case of Au(110) electrode surface, Weaver and Gao have reported that the reconstructed structures of this surface are different depending on the cation species between K and Cs in aqueous solutions.[13] Although there have been no papers reported on single crystal BDD surfaces in solutions, there might be the irreversible structural changes occurred in K^+ solution.

Effect of AM cations on the faradaic efficiency for the production of formic acid

We fixed the pH to 6.2 for all the electrolytes and chose NaOH, KOH, RbOH and CsOH to examine the effect of AM cations on the formation of formic acid. For all the electrolytes, the FE changes depending on the concentration of the electrolyte, as shown in Fig. 2(a). The FE reaches 71% for a 0.075 M Rb^+ solution. For the Rb^+ solution, the FE stays above 50% over a wide concentration range from 0.02 M to 0.2 M. Also, for the Rb^+ solution, the FE for the formation of CO is very low, being less than 0.1%, as shown in Fig. 2(b).

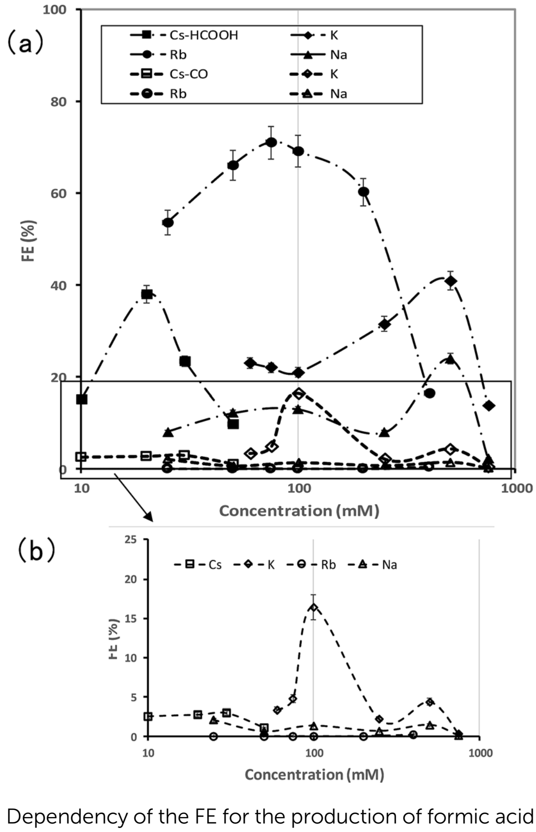

Fig. 2 Dependency of the FE for the production of formic acid (a) and CO (b) on the concentration of the solutions. The dotted lines in the figures are guides for the eye.

For the Cs^+ solution, the peak of the FE curve for the production of formic acid appears at 0.02 M. The maximum FE is at 38% at. Despite Cs^+ being the largest size among the AM cations described here, the peak FE is much lower than that obtained with Rb^+. The reason for this is still unclear, unfortunately.

In contrast to these two solutions, the FE peaks for the K^+ and Na^+ solutions stay at around 0.5 M. For the K^+ solution, the maximum FE is 41%. The FE of 24% in case of the Na^+ solution is the lowest value.

We measured the electrical conductivities of Cs^+ and Rb^+ solutions, and found they were twice those of K^+ and Na^+ solutions. One of the reasons why the positions of the peaks move toward lower values for CsOH and RbOH is the difference in electrical conductivities.

Fig. 3 shows cyclic voltammograms recorded for a BDD electrode in CO_2 saturated Na^+, K^+, Rb^+ and Cs^+ solutions with pH 6.2. The hydrogen evolution behaviors in the Cs^+ and K^+ solutions were quite similar. Of the four electrolytes, hydrogen evolves most easily in Na^+ solution. In Rb^+ solution, however, we can confirm that the hydrogen evolution was suppressed. These phenomena partly explain why the maximum FE for the production of formic acid was observed in the Rb^+ solution.

The interactions between Na^+, K^+, Rb^+ and Cs^+ and water molecules have been calculated using *ab initio* molecular orbital calculations.[14] The interaction energies between these four AM cations and water molecules are *ca.* −32, −22, −20, and −16 kcal mol^{-1}, respectively. So, the stronger the interaction between the AM cation and water is, the lower the FE for the production of formic acid. In the potential range where the electro-reduction of CO_2 proceeds, the AM cations are thought to be adsorbed on the BDD surface. In the case of the Na^+ solution, we consider that the strong interaction between Na^+ and the water molecules hampers the adsorption of Na^+ cations on the BDD surface. As for the K^+ solution, interestingly, 50% of the product formed with a 0.1 M solution was CO. On increasing the concentration of the K^+ solution, more formic acid was produced and was the main product with a 0.5 M solution. When CO_2 anion radicals are stably adsorbed on the surface of

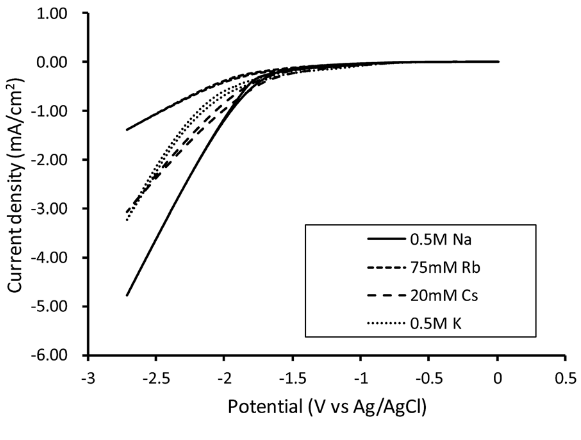

Fig. 3 Cyclic voltammograms for BDD electrodes in Na^+, K^+, Rb^+ and Cs^+ solutions with pH 6.2. The scan rate was 100 mV s^{-1}.

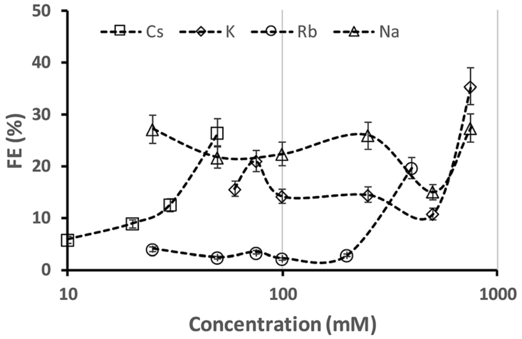

Fig. 4 Dependency of FE for the generation of H_2 on the concentration of the solutions. The dotted lines in the figure are guides for the eye.

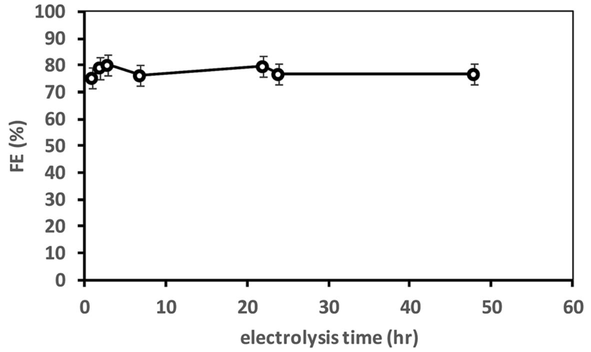

Fig. 5 Variation in the FE with time for continuous electrochemical reduction at 2 mA cm^{-2} with a 0.1% BDD electrode.

BDD, the production of CO becomes more dominant as previously reported.[9] From this result, we can speculate that the composition of the adsorbates, which includes K^+, HCO_3^- and water molecules, changes depending on the concentration of K^+. Other than with K^+ solution, such changes in the products with the concentration of AM cations were not observed, and the FE for CO is independent of the concentration of cations. Fig. 4 shows the FE curve for H_2 as a byproduct of the reduction of CO_2. Although in our experiments the sum of all the products and byproducts, inexplicably, does not reach 100%, we are able, nevertheless, to discuss the behavior of the formation of H_2 on BDD surfaces. The dependency on concentration seems to be similar for all the electrolytes. The FE of H_2 increases with the increasing concentration of the AM solution. Note that the FE for the production of H_2 in Rb^+ solution remains at a very low value of less than *ca.* 5% over a wide concentration range from 0.02 M to 0.2 M. Rb^+ cations hydrated with water molecules are thought to be strongly adsorbed and to completely cover the BDD surface. As a result, atomic hydrogen arises from the decomposition of water molecules that are unable to occupy any surface sites. Our results encourage us to carry out further studies of the atomic-level structure of electrochemical double-layers formed on BDD electrodes.

Singh *et al.*[9] studied the effect of the size of the AM cation on the FE for the production of CO with Ag and Cu electrodes. As the size of the cation is increased, the evolution of hydrogen decreases and the FE for the production of CO increases. They considered that the pH buffering effect near the electrode enhances the FE for the production of CO. However, our results for the FE for the production of formic acid simply don't concur with this premise. Rb^+ ions hydrated with water molecules are the best cations for enhancing the production of formic acid.

Under ultra-high vacuum conditions, the adsorption behaviors of K and Cs on both hydrogen and oxygen terminated C(100) surfaces have been reported.[15,16] However, no data were obtained for the adsorption of Rb on C(100). DFT calculations were done with AMs on both hydrogen and oxygen terminated C(100) surfaces in which no extraordinary changes in work function or band structure were observed for Rb adsorbed surfaces.[17–19] X-ray standing wave spectroscopy studies have shown that a cation like Rb^+ is able to form inner sphere complexes at the surface of $TiO_2(110)$ when the surface is strongly negatively charged.[20,21] In such a case, the cation is partially dehydrated and directly coordinated to the surface groups.

Therefore, the reasons for the extraordinary effect of Rb on the production of formic acid can't be clarified but it might be related to the structure of the electric double layer formed on the BDD electrode.

Continuous electrochemical reduction at a high electrode potential often causes damage to electrode materials such as HOPG (highly oriented pyrolytic graphite) and glassy carbon.[22]

In contrast, BDD is highly durable. We confirmed that continuous operation at 2 mA cm^{-2} for 48 h gave no change in the FE for the production of formic acid, as shown in Fig. 5. In this experiment, 0.1% BDD was used. 0.075 M Rb^+ solution and 0.5 M KOH were chosen as the anolyte and catholyte, respectively.

Higher productivity for formic acid at higher current densities

Not only the FE but also the productivity of the products is important in terms of engineering. Although the FE stays high, the amount of product is sometimes very small.[23] In some cases, only 2–10 mg L^{-1} of formic acid could be obtained despite the high FE. Although the current density in the aforementioned experiments was fixed at 2 mA cm^{-2}, we applied higher current densities up to 20 mA cm^{-2} as the next challenging target, which determines the reaction speed. This allowed us to determine the size and cost of electrochemical reduction plants.

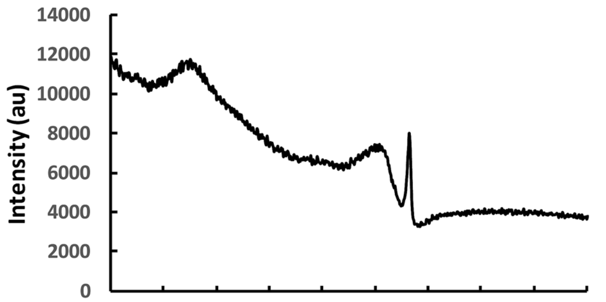

Fig. 6 Raman spectrum of 1% BDD electrode.

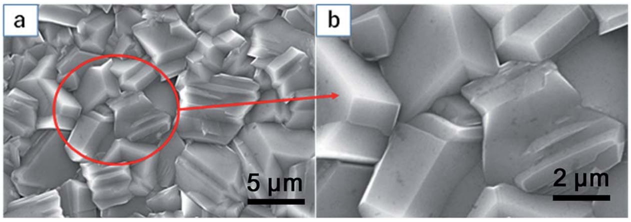

Fig. 7 SEM images of 1% BDD electrode after experiments. Larger-scale image (a) and magnified image (b).

With 0.5–2 M KOH as the anolyte solution, the FE for the production of formic acid in 0.075 M Rb^+ catholyte was extended to 86%. We can confirm that more than 1 g L^{-1} of formic acid can be generated in an hour.

Characterization of BDD electrodes

Fig. 6 shows a Raman spectrum obtained on the 1% BDD electrode before doing experiments. The characteristic sp^3 structure at the band of 1324 cm^{-1} was confirmed. Then, after the CO_2 reduction, the spectrum did not change (data not shown).

Fig. 7 shows the SEM images recorded on the 1% BDD electrode after 30 hour operations. Clearly evident are the facets of the diamond grains and no etching was received on the magnified image (Fig. 7(b)).

Comparison of the present data with the literatures

There were many reports published on the conversion of CO_2 to formic acid by metal electrodes previously. Hori *et al.*[24] reported the formation of formic acid on Pb, Hg, In, Sn, Cd, Tl electrodes. The FE of those electrodes stay high above 78.4–99.5%. Since such metal electrodes have a high environmental load, the usage of them is not recommended. Also, stability of those electrodes seems to be problematic. Recent paper reported the FEs with Sn electrodes.[25] At ambient condition, the FE value of 79.5% was obtained using H-type cell. At high pressure condition the FE reaches 99.2% at maximum. The electrolytes used were 0.05 M–0.5 M $KHCO_3$ solutions. Therefore, it is the first time to report the extraordinary effect of Rb^+ on the formation of formic acid by BDD electrodes.

Conclusions

The electrochemical reduction of CO_2 using BDD electrodes was carried out. We determined the behavior of the FE for the formation of formic acid in alkaline solutions with different AM cations. The formation of formic acid was confirmed with four alkali-metal solutions. The highest FE of 71% was observed for a 0.075 M Rb^+ solution neutralized to pH 6.2 with the addition HCl. The lowest FE was obtained for Na^+ solution, which has the smallest cation. The dependency of FE on the different kinds of alkali-metal cations has been explained by the interaction between the alkali-metal cations and water molecules. We confirmed that more formic acid is produced at higher current densities.

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