Investigation on electrochemical capture of CO$_2$ in p-Benzquinone solutions by in situ FT-IR spectroelectrochemistry

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Abstract
The electrochemical capture of carbon dioxide in p-Benzquinone (BQ) - acetonitrile and BQ - aqueous solutions have been investigated by cyclic voltammetry (CV). Two well-defined couples of anodic and cathodic peaks in CV curve of BQ in acetonitrile solvent are substituted by one redox couple peaks with $E_{1/2} = -0.30$ V once CO$_2$ is added. The absorption peak at 2348 cm$^{-1}$ of in situ FT-IR spectroelectrochemistry indicates that CO$_2$ is involved in the electrochemical reactions. Cyclic voltabsorptometry (CVA) and derivative cyclic voltabsorptometry (DCVA) of BQ - acetonitrile with different concentration of CO$_2$ are investigated to demonstrate the reaction stoichiometry. The absorbance value of BQ at 2348 cm$^{-1}$ is a constant during reduction process when CO$_2$ concentration is lower than 50%. However, there is a decrease at $-1.3$ V potential due to the CO$_2$ reduction when it is higher than 50%. This indicates the stoichiometry of BQ$^+$ to CO$_2$ is 1:1 during electrochemical capture of CO$_2$ in CH$_3$CN solution. Similar reaction between CO$_2$ and BQ is observed in aqueous solution. However, the stoichiometric number of BQ$^+$ to CO$_2$ is 1:2, forming [BQ-2CO$_2$]$^+$, which is finally reduced to [BQ-2CO$_2$]$_2^-$. The mechanism proposed is consistent with theoretical calculation since the activation energy of [BQ-CO$_2$]$^+$ formation is much lower than that of BQ$^+$ reduction. The stable structures of CO$_2$ adduct of the reactions in aprotic and aqueous solvents are also proposed according to density functional theoretical (DFT) calculations.

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1. Introduction

With the development of industrialization and increase of fossil fuel consumption, carbon dioxide, the largest greenhouse gas source, is becoming a serious environmental problem [1,2]. Therefore, strategies to decrease the CO$_2$ emission, such as CO$_2$ capture, storage, and reduction, have attracted worldwide attention. CO$_2$ capture is a process to capture and collect CO$_2$ from fuel gas. Generally, it can be classified into four techniques: pre-combustion, post-combustion, oxy-fuel combustion, and electrochemical capture [3]. In pre-combustion approach, fossil fuel is gasified and reacted to form H$_2$ and CO$_2$, which is further captured to avoid greenhouse gas emission. However, CO$_2$ concentration is usually high in pre-combustion capture, which is a barrier for its practical use [3]. Post-combustion capture is usually retrofitted to the existing power plants to capture CO$_2$ after fossil fuel combustion. CO$_2$ needs to be separated and compressed before post-combustion capture due to the lower partial pressure of CO$_2$. Therefore, it is an energy-intensive process due to solvent loss and regeneration, and CO$_2$ separation and compression [4]. Oxy-fuel combustion of fossil fuel is conducted in oxygen-rich gas. It requires large cryogenic air separation units for oxygen production, leading to the high cost of this technology [5]. Currently, CO$_2$ capture approaches relying on various types of chemical reactions, such as CO$_2$ with amines to form carbamates, CO$_2$ with aqueous ammonia to produce ammonium carbonate, dual alkali absorption, have been studied in detail [6–8]. However, there are lots of disadvantages presented in these traditional CO$_2$ capture methods limited its large scale use: (1) low CO$_2$ loading capacity [9]; (2) low CO$_2$ absorption rate [10]; (3) solvent loss and regeneration increase the cost [3]; (4) special equipment requirement and corrosion cause the high maintenance cost [8].

Compared with these traditional CO$_2$ chemical capture techniques, a precursor, supplying nucleophile to attack the electrophilic carbon atom of CO$_2$ to form adducts, can be easily regenerated during the CO$_2$ electrochemical capture process. Quinones and their derivatives have been studied widely because of their contribution in chemical and biology system [11–13]. Also, they are redox-active molecules with high binding affinity of CO$_2$ in...
their reduction state [14]. Quinone reduction in non-aqueous media is reported to undergo a “two-step one-electron” process [15,16]. BQ is reduced to the anion radical, BQ^-. And then, BQ^+ reacts with CO2 immediately, leading to O–C bond or C–C bond formation. The O–C bond has better thermodynamic stability according to Gibbs free energy calculation. The electrochemical reduction of BQ in aprotic solvent has been widely studied previously. G. March et al. and B. Jin et al. proposed the two-step one-electron (EE) transfer of BQ electrochemical behavior in buffer solution, aqueous solution, and acetonitrile solvent, respectively [15,16]. BQ is reduced in normal EE mechanism, forming BQ^+ in the first step and the dianion BQ^{2-} in the second step. Actually, the research on the electrochemical capture of CO2 by quinones has become research focus. Wrighton and Mizen proposed that after the process of electrochemical capture, two molecules of CO2 add to reduced 9,10-phenanthrenequinone (PAQ) in CH3CN/[n-Bu4N]BF4 to give the bis(carbonate) [17]. M. Namazian et al. studied the electrochemical reduction process of BQ in CO2 DMF solvent [18]. M.C. Stern described the configurations of an electrochemically-modulated process capturing and regenerating CO2 with high efficiency using benzoquinone [19]. However, only electrochemical result is not enough to confirm the proposed mechanism of the capture of CO2 by the electrochemical reduction product of quinone. The specific structure of the intermediate and final product produced by CO2 capture during electrochemical reduction of benzoquinone is also uncertain. Hence, more extensive techniques should be used to investigate the mechanism of CO2 electrochemical capture in benzoquinone. In addition, current researches are concentrated on non-aqueous systems. Compared with organic solvents, water is green, non-toxic, and cheap. Therefore, electrochemical capture of carbon dioxide in aqueous solutions should be focused on in future study.

In this paper, infrared spectroscopy combined with cyclic voltammetry is employed to investigate the electrochemical capture of CO2 in BQ – based acetonitrile and aqueous solutions. Cyclic voltabsorptometry (CVA) is used to quantify the concentration variation of [BQ-Co2]^2- and CO2. The stoichiometry of electrochemical capture of CO2 is proposed with different concentrations of CO2 both in acetonitrile and aqueous solutions by CV and CVA. The results show that the mechanisms of BQ in acetonitrile in the presence of CO2 are different from that in aqueous solution. The possible structures of anion radical and dianion (CO2 adducts) are explored by density functional theoretical calculation.

2. Experimental section

2.1. Chemicals and reagents

BQ (97%), acetonitrile (HPLC), D2O (HPLC), tetrabutylammonium perchlorate (TBAP) and KCl are all used as received from Sigma-Aldrich. 0.2 mmol/L TBAP and 0.5 mol/L KCl are used as supporting electrolyte in acetonitrile and H2O, respectively. High purity carbon dioxide (Nanjing special gas Co. Ltd, CO2 (99.99%), and high purity Ar (Nanjing special gas Co. Ltd, 99.99%) are used for Solution A (with saturated CO2) and Solution B (BQ degassed with Ar), respectively. Solution A and solution B are mixed with different volume fractions, and then BQ solutions with different CO2 concentrations are prepared.

2.2. Electrochemistry

Electrochemical experiments are performed with an electrochemical analyzer CHI630 potentiostat (Shanghai Chenhua Instruments). The homemade thin-layer is used as a spectroelectrochemical cell [20]. A 4 mm diameter platinum disk electrode is used as a working electrode [21]. It is polished with alumina slurry on a polishing cloth initially, and then rinsed in deionized water and ethanol before use. Ag/AgCl and a platinum wire electrode are employed as reference electrode and counter electrode, respectively [14,22].

2.3. In situ FT-IR spectroelectrochemistry

In situ FT-IR spectroelectrochemistry experiments and electrochemical measurements are carried out simultaneously. Nicolet iS50 (Thermo Nicolet Corporation) spectrometer equipped with a specular reflectance accessory (SMART iTR) and a HgCdTe/A (MCT/A) detector cooled with liquid nitrogen are employed in spectroscopic measurement. A total of 20–60 interferometric scans are accumulated for an averaged spectrum in subtractively normalized interfacial fourier transform infrared (SNIFTIR) experiment with a resolution of 16 cm^-1, and the sampling interval is 0.7–1.8 s. Experimental results are depicted with Grams/3D software.

2.4. Theoretical computation

All theoretical calculations are implemented in Gaussian 09 package. Structural optimizations and frequency calculations (corresponding characteristic infrared spectrum wave numbers) are carried out using the hybrid B3LYP method with the basis set of 6-311 + G** level of theory with the solution effect [23,24].

3. Results and discussions

3.1. Electrochemical capture of CO2 in BQ - acetonitrile solution

Fig. 1A shows the cyclic voltammograms curve of acetonitrile containing single CO2 (curve a), BQ without (curve b) and with CO2 (curve c). As shown in Fig. 1A (a), there is no Faraday current observed in CV curve in scan range of +0.2 V to −1.2 V. In Fig. 1A (b), a typical CV curve of BQ in aprotic media is observed with two well-defined couples of anodic and cathodic peaks, with potential values of \( E_{1/2} = -0.39 \) V and \( E_{2/1} = -0.73 \) V (defined \( E_{1/2} = (E_{pa} + E_{pc})/2 \)). This is in accordance with previous reports [16]. However, there is only one redox couple with \( E_{1/2} = -0.30 \) V observed when CO2 is added (voltammogram c). Moreover, the cathodic peak current is almost double as that of voltammogram (b). Obviously, the CV of BQ with CO2 is similar to that of BQ in acetonitrile solvent with added proton donors [25]. Therefore, the second couple of redox peak shifts positively and merges with the first one, which might be related to chemical reaction of CO2.

The rapid-scan IR spectra is simultaneously conducted and recorded from 1000 cm^-1 to 3000 cm^-1 during the electrochemical process (Fig. 1B). The 3D rapid-scan IR spectra are gathered during the CV scan between 0.2 V and −1.2 V with reference spectrum recorded at 0.2 V. There are two types of IR bands observed in the 3D spectra. One type is downward band at 2348 cm^-1 (assigned to \( \nu_{e} = 0 \) of CO2), and the other type is the upward bands at 1249 cm^-1, 1356 cm^-1, 1518 cm^-1 (assigned to \( \nu_{e} = \nu_{c} \) of the final product dianion (BQ-Co2)^2-) and 1641 cm^-1 (assigned to \( \nu_{c} = 0 \) of reduction product of (BQ-Co2)^2-). The characteristic absorption peak at 2348 cm^-1 suggests that CO2 is involved in the electrochemical reaction. This implies the chemical reaction between CO2 and BQ^+ because CO2 cannot be electrochemical reduced in this potential range [26].

To illustrate CO2 absorption behavior, the rapid-scan IR spectra is conducted to CVA to track the concentration variation of (BQ-Co2)^2- and CO2 (Fig. 2A). According to Fig. 2A, there is a significant increase of absorbance at 1356 cm^-1, while a dramatical decrease of absorbance is observed at 2348 cm^-1. The absorbance variation at
1641 cm\(^{-1}\) (BQ-CO\(_2\))\(^{2-}\) is similar to that at 1356 cm\(^{-1}\). As the potential (time) scanning, the original electrochemical reduction intermediates, BQ\(^{\ast}\) [25], combines with CO\(_2\) immediately after its appearance, corresponding to the reduction process maybe from BQ to (BQ-CO\(_2\))\(^{\ast}\), and then, (BQ-CO\(_2\))\(^{\ast}\) is further reduced to (BQ-CO\(_2\))\(^{2-}\) quickly.

It has been demonstrated that \(\frac{dA}{dt}\) vs E shape is morphologically consistent with the cyclic voltammogram [16]. According to Fig. 2B, the wave form of DCVA at 2348 cm\(^{-1}\) represents of CO\(_2\), and 1356 cm\(^{-1}\) represents of (BQ-CO\(_2\))\(^{2-}\), which are similar to that of the CV shown in Fig. 1. A.

Different from the normal two-step one-electron transfer [16], the results of CV and IR spectroelectrochemistry with a couple of single peaks show that BQ in the presence of CO\(_2\) undergoes a ECE transfer mechanism.

### 3.2. Stoichiometry study of electrochemical capture of CO\(_2\) in BQ-acetonitrile solution

To investigate the correlation between CO\(_2\) and BQ in the electrochemical process, CVs of 20 mmol/L BQ with different CO\(_2\) concentration and single saturated CO\(_2\) (marked as blank) in acetonitrile are conducted and presented in Fig. 3A. As shown in blank, there is no redox peaks appeared in the scan region of 0.2 to −1.2 V. However, a miniature irreversible reduction peak exists at about −1.6 V corresponding to 100% CO\(_2\), indicating the electrochemical reaction of CO\(_2\) itself [28]. There are two couples of redox peaks presented in CV curve when CO\(_2\) concentration is 25%, and there redox potential \(^{\text{1}}E_{1/2} = −0.42\) V and \(^{\text{2}}E_{1/2} = −0.97\) V corresponds to the reduction of BQ [25]. The result indicates that CO\(_2\) is consumed completely, while excessive BQ still follows EE mechanism. It is found that the reduction peak currents increase with the increase of CO\(_2\) concentration at \(−0.42\) V, while it decreases with the increase of CO\(_2\) concentration at \(−0.97\) V. In saturated CO\(_2\) (100%) solutions, the reduction peak at 1.6 V is clearly observed, which attributes to electrochemical reduction of CO\(_2\) itself. The corresponding 3D spectra of BQ in acetonitrile with different percentage of CO\(_2\) concentration is provided in the supporting information.

Fig. 2B shows the corresponding CVA of BQ with different percentages of CO\(_2\) at 2348 cm\(^{-1}\). As can be seen from Fig. 3B, the absorbance value of BQ solution with low concentration of CO\(_2\) (20%−50%) at 2348 cm\(^{-1}\) decreases at about 42s (−0.21 V), and a minimum value is obtained at about 80s (−0.60 V). And the absorbance value is a constant during reduction process, which illustrates that all CO\(_2\) is reacted with BQ. The variation of absorbance value of BQ solution with high concentration of CO\(_2\) (75%, 100%) at 2348 cm\(^{-1}\) is the same with that of BQ solution with low concentration of CO\(_2\) (20%−50%) initially. However, there is a further decreases at −1.3 V potential due to the reduction of CO\(_2\), which suggested that CO\(_2\) are
over capacity in high concentration of CO₂ (75%, 100%) solution. IR absorbance at 2348 cm⁻¹ does not return to its initial value when the potential scan back to the original value (0.2 V), implying that the reduction product of excessive CO₂ is not completely oxidized under this potential range.

According to Lambert-Beer’s law, the absorbance value at 2348 cm⁻¹ reflects the change of CO₂ concentration in electrochemical process. Therefore, the absorbance value at −1.8 V is linearly related to the percentage of saturated CO₂ concentration with coefficient of determination \( R = 0.9958 \) (Fig. 3D). The fitting results further prove that CO₂ is consumed completely at −1.8 V. A similar linear relationship between CO₂ concentration and absorbance value at −1.0 V is also observed in Fig. 3C. It can be found that the absorbance gradually decreases with the increase of CO₂ concentration (<50%). However, the absorbance value remains unchanged when the CO₂ concentration increases further (>50%). Further analysis of the obtained linear regression equations shows that the slope of the regression curve under the low concentration CO₂ in Fig. C is consistent with that of Fig. D. The results strongly suggest that all CO₂ in the solution reacts completely with benzoquinone at −1.0 V if CO₂ concentration is less than 50%. When the CO₂ concentration is greater than 50%, excessive CO₂ can be reduced at a more negative potential (−1.3 V). The saturated CO₂ in acetonitrile media is 40 mmol/L [33]. Hence, 50% CO₂ saturated concentration is 20 mmol/L, which is equivalent to the concentration of BQ in solution. Therefore, the electrochemical process can be described as following:

3.3. Electrochemical capture of CO₂ in aqueous solution

The CV of BQ in aqueous solution with different CO₂ concentrations is studied and presented in Fig. 4. Since proton electrolyzed at the large negative potential, the scan range is limited to a small range from 0.5 V to −0.3 V to avoid its reaction potential. As shown
in Fig. 4, a couple of redox peaks are observed with potential values of $E_{1/2} = -0.17$ V (defined as $E_{1/2} = (E_{pa} + E_{pc})/2$) in the absence of CO$_2$. The reduction peak of BQ moves positively with the gradual increase of CO$_2$ concentration, and the reduction peak area is almost a constant.

However, the oxidation peak shifts positively with peak current gradually decreased from $-36.49$ µA to $-0.49$ µA when CO$_2$ concentration increases from 0% to 80%. Meanwhile, a new oxidation peak appears at about $+0.43$ V with the increase of CO$_2$ concentration, and the maximum peak current of $-29.18$ µA is obtained at 80% of CO$_2$.

The rapid-scan IR spectroelectrochemistry analysis of quinone aqueous solution with different CO$_2$ concentration is conducted to explore the mechanism of CO$_2$ captured during the reduction of quinone in aqueous solution. D$_2$O is used to replace H$_2$O to avoid the interference (H$_2$O generates serious infrared noise). As presented in Fig. 5, infrared absorption peaks of intermediates in aqueous solution without CO$_2$ (1497 cm$^{-1}$, assigned to $\nu$C=O of BQ) periodically appear and disappear in both reduction and oxidation process, which are similar to that of benzoquinone in acetonitrile solution. Although only one pair of redox peaks appears in the CV diagram (Figs. 4 and 0%), the intermediate absorption peaks in the infrared spectra indicates that benzoquinone exhibits a “two-step one-electron transfer” in aqueous solution [16].

IR peaks at 1664 cm$^{-1}$, 1356 cm$^{-1}$ and 1641 cm$^{-1}$ are selected to track the electrochemical process of 8 mmol/L BQ in D$_2$O solution with CO$_2$ (Fig. 5B–F). The CO$_2$ absorbance peaks at 1497 cm$^{-1}$ (assigned to $\nu$C=O from BQ$^*$) and 1342 cm$^{-1}$ (assigned to $\nu$C=C from BQ$^*$) reduce dramatically, and finally disappear when CO$_2$ concentration is 40% (Fig. 5C). The absorbance peak at 1418 cm$^{-1}$ (assigned to $\nu$C=C from BQ$^{2-}$) gradually decreases with the increase of CO$_2$ concentration, and cannot be observed in 60% CO$_2$ (Fig. 5D). There are no peaks in the 3D IR spectrum observed at 1497 cm$^{-1}$, 1342 cm$^{-1}$, 1418 cm$^{-1}$ when CO$_2$ concentration is higher than 60%. Meanwhile, there are new absorption peaks observed at 1518 cm$^{-1}$, 1641 cm$^{-1}$ and 1356 cm$^{-1}$, assigned to $\nu$C-C, $\nu$C=O and $\nu$C=C from (BQ-CO$_2$)$_2^-$. The results indicate that the intermediate BQ$^*$ rapidly reacts with CO$_2$ to form (BQ-CO$_2$)$^*$, and then it accepts the second electron quickly to form dianion (BQ-CO$_2$)$^{2-}$ in the presence of CO$_2$. Eventually, four peaks of IR peaks are observed under the condition of high concentration of CO$_2$ (>60%), the
Scheme 1. Reaction process of BQ in the presence of CO₂ in aprotic solvent (reduction 1, 3, and 4). $E^0$: activation energy of the reaction.

Fig. 7. The monomer and low-energy isomers for anion radical and dianion in acetonitrile solvent at B3LYP/6-311++G** level and corresponding possible structures of anion radical and dianion. X indicates instability.
The absorbance of 1356 cm\textsuperscript{-1} increases simultaneously with the decrease of 1664 cm\textsuperscript{-1} in the reduction process, and recovers to the original value while (BQ-CO\textsubscript{2})\textsuperscript{2-} is oxidized at the end of potential scans. These changes of absorption peaks clearly illustrate the dominant reaction mechanism in the system changes from EE mechanism to E\textsubscript{Cr}E mechanism in the presence of CO\textsubscript{2}.

The corresponding CVA of BQ at 1664 cm\textsuperscript{-1} in different concentrations of CO\textsubscript{2} is depicted in Fig. 6A. As it shows, the peak value starts to decrease at 28s (-0.04 V), and a minimum value is observed at 72s (-0.26 V). Similarly, it increases from 93s (-0.24 V) to 124s (-0.08 V) and restores to the original value in the oxidation process, which indicates that BQ is reduced to BQ\textsuperscript{2-} completely at -0.26 V, and then all reduction product is oxidized back to BQ. This result is consistent with the CV results (Fig. 4), which might be due to the easier reduction of BQ caused by the combination of CO\textsubscript{2} with reduction states of BQ. Interestingly, during the oxidation process, the infrared absorption peaks at 1664 cm\textsuperscript{-1} show a tendency to change in relation to CO\textsubscript{2} concentration. The absorbance value gradually change in solution with 20%–60% CO\textsubscript{2} concentration until became stable in 80% and 100% solution.

The infrared absorption peak of BQ aqueous solution containing 40% CO\textsubscript{2} begins to rise at 103s (-0.19 V), and reach a stable value at 148s (0.04 V) when BQ\textsuperscript{2-} is oxidized to BQ. While the potential scanning positive, it will rise again at 180s (0.20 V) and finally comes back to baseline. The second rise of the infrared absorption peaks at 1664 cm\textsuperscript{-1} corresponds to second oxidation peaks in the CV diagram. A reasonable explanation is that BQ is excessive in low concentration CO\textsubscript{2} solution. Therefore, excess BQ\textsuperscript{2-} existing in the reduction process is oxidized at -0.1 V, whereas BQ\textsuperscript{2-} bound to CO\textsubscript{2} is oxidized at 0.2 V.

It can be observed clearly from Fig. 6A that the amplitude of the first increase (100s–140s) of infrared absorption peak at 1664 cm\textsuperscript{-1} decreases with the increase of CO\textsubscript{2} concentration. In the BQ aqueous solution with saturated CO\textsubscript{2} (100%), the step of the first rise of the infrared absorption peak completely disappeared. Similar results were observed in BQ solution with a concentration of 80% CO\textsubscript{2}. From the results of CV (Fig. 4) and CVA (Fig. 6A), it can be found that BQ\textsuperscript{2-} has been completely oxidized to BQ, but (BQ-CO\textsubscript{2})\textsuperscript{2-} still exists stably in the oxidation process when the potential is lower than 0.1 V. Therefore, the infrared absorbance value at 0.1 V can reflect the amount of (BQ-CO\textsubscript{2})\textsuperscript{2-} in solution.

Fig. 6B reveals the relationship between the CO\textsubscript{2} concentration

![Table 1](https://example.com/table1.png)

<table>
<thead>
<tr>
<th>Experimental Peak position(cm\textsuperscript{-1})</th>
<th>Assignation</th>
<th>Calculated Peak position(cm\textsuperscript{-1})</th>
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<td>Bending vibration ν\textsubscript{C-C=O} from [BQ-CO\textsubscript{2}]\textsuperscript{2-}</td>
<td>1258 1242</td>
<td>aprotic solution</td>
</tr>
<tr>
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<td>Stretching vibration ν\textsubscript{C=O} from [BQ-CO\textsubscript{2}]\textsuperscript{2-}</td>
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<td>aprotic solution</td>
</tr>
<tr>
<td>1518</td>
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<td>1540 1581</td>
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<tr>
<td>1641</td>
<td>Stretching vibration ν\textsubscript{C=O} from [BQ-CO\textsubscript{2}]\textsuperscript{2-}</td>
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<td>aprotic solution</td>
</tr>
<tr>
<td>1664</td>
<td>Stretching vibration ν\textsubscript{C=O} from CO\textsubscript{2}</td>
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<td>aprotic solution</td>
</tr>
<tr>
<td>2348</td>
<td>Stretching vibration ν\textsubscript{C=O} from CO\textsubscript{2}</td>
<td>2346</td>
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</table>

Scheme 2. Reaction process of BQ in the presence of CO\textsubscript{2} in H\textsubscript{2}O solvent (reaction 1, 4 and 5).
and IR absorbance value (2348 cm\(^{-1}\)) at 0.1 V. As expected, the concentration of CO\(_2\) in 0\%–80\% is linearly related to the infrared absorption value, implying that 80\% CO\(_2\) can react completely with BQ. However, CO\(_2\) is obviously excessive in saturated CO\(_2\) (100\%) solutions because the IR absorbance value is not lineally related to CO\(_2\) concentration. The concentration of CO\(_2\) saturated aqueous solution is 20 mmol/L [27]. 80\% saturated CO\(_2\) concentration is 16 mmol/L, which is double to the concentration of BQ (8 mmol/L) in solution. Therefore, the electrochemical process can be described as follows:

### 3.4. Theoretical computation

Based on the experimental data analysis above, several possible electrochemical reaction mechanisms of BQ in the presence of CO\(_2\) in aprotic solvent are theorized in the Scheme 1. The activation energies of reactions are computed by theoretical computation.

As shown in Scheme 1, BQ in aprotic solvent gets an electron to form BQ\(^+\) in reaction (1) firstly. BQ\(^+\) captures CO\(_2\) immediately (the activation energy E\(^0\)\(_2\) is 0.45eV), rather than reduces to BQ\(^2-\) (E\(^0\)\(_6\) is 3.32eV) (E\(^0\)\(_2\) < E\(^0\)\(_6\)\), which is consistent with the only one pair peaks observed in CV diagram. Then, [BQ-CO\(_2\)]\(^-\) is reduced to form dianion 1 (E\(^0\)\(_3\) is 1.87eV). Combining with the results of electrochemical and infrared spectroscopy, we speculate that the reduction of BQ in the presence of CO\(_2\) undergoes the reaction (1), reaction (2), and reaction (3) in sequence. BQ is reduced to BQ\(^+\) in the first step, then [BQ-CO\(_2\)]\(^+\) is generated through the chemical reaction of BQ\(^+\) with CO\(_2\). Furthermore, the anion radical ([BQ-CO\(_2\)]\(^+\)) quickly reduces to dianion ([BQ-CO\(_2\)]\(^2-\)) in the second electrochemical step.

The possible structures and relative energy of the anion radical and dianion are considered and listed in Fig. 7. For anion radical ([BQ-CO\(_2\)]\(^+\)), two kinds of anion radical have been calculated. The results of theoretical computation show carboxylate product (anion radical 1) is more thermodynamic stable than the carbonate one (anion radical 2). The anion radical 2 is not able to be further reduced to form dianion. Based on the density functional theory, dianion 1 is easy to form since dianion 1 is much lower in energy (1.87eV) than that of dianion 2 (2.00eV). The calculation shows that the anion radical and dianion exist in the form of carboxylate product.

The theoretical value of infrared absorption peak position is given in Table 1. The characteristic infrared absorption peak positions of carboxylate structure dianion 1 and carbonate structure dianion 2 are assigned in Table 2.

**Table 2**

<table>
<thead>
<tr>
<th>Experimental Peak position (cm(^{-1}))</th>
<th>Assignment</th>
<th>Calculated Peak position (cm(^{-1}))</th>
<th>Solvent</th>
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<tr>
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<td>Stretching vibration (\nu_{\text{C-O}}) from [BQ](^+)</td>
<td>1489</td>
<td></td>
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<tr>
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<td>Stretching vibration (\nu_{\text{C-O}}) from [BQ-2CO(_2)](^2-)</td>
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<tr>
<td>1641</td>
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<td>Stretching vibration (\nu_{\text{C-O}}) from BQ</td>
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<tr>
<td>2348</td>
<td>Stretching vibration (\nu_{\text{C-O}}) from CO(_2)</td>
<td>2346</td>
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</table>
Three conclusions are obtained according to our study:

1. The results of CV and FT-IR spectroelectrochemical analysis indicated that the presence of CO$_2$ leading to a chemical reaction between BQ$^+$ and CO$_2$. Then [BQ-CO$_2$]$^-$ is further reduced to [BQ-CO$_2$]$^{2-}$.

2. Further CVA and density functional theoretical calculation were conducted for quantitative analysis. The stoichiometric number of BQ$^+$ to CO$_2$ is 1:1 in acetonitrile, while which is 1:2 in aqueous solvent, thus:

\[
\text{in CH$_3$CN solvent}, \quad \text{BQ} \leftrightarrow \text{BQ}^- \\
\text{BQ}^- + \text{CO}_2 \rightarrow [\text{BQ-CO}_2]^-
\]

\[
\text{in aqueous solvent}, \quad \text{BQ} \leftrightarrow \text{BQ}^- \\
\text{BQ}^- + 2\text{CO}_2 \rightarrow [\text{BQ-2CO}_2]^+ \\
[\text{BQ-2CO}_2]^+ \leftrightarrow [\text{BQ-2CO}_2]^2-
\]

3. The possible structures and energy of anion radical and dianion are calculated at B3LYP/6-311+G** level, indicating the carboxylate is the stable product for BQ$^+$ react with CO$_2$. Furthermore, the theoretical calculation value of the infrared characteristic absorption peak is identified the final product corresponding to the experimental infrared peak position, which proves the proposed electrochemical mechanism.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.electacta.2019.134882.

**References**