# Electrochemically induced CO<sub>2</sub> capture enabled by aqueous quinone flow chemistry

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#### Abstract

Climate change caused by the accumulation of anthropogenic  $CO_2$  emissions motivates the development and deployment of cost-effective, scalable, and energetically efficient techniques to capture CO<sub>2</sub> from point or diffuse sources. Electrochemically-driven CO<sub>2</sub> capture processes utilizing redox-active organics in aqueous flow chemistry show promise for nonflammability, continuous-flow engineering, and the possibility of being driven at high current density by inexpensive, clean electricity. We show that the deprotonated hydroquinone-CO<sub>2</sub> adducts, whose insolubility limits the utility of the quinone-hydroquinone redox couple, become soluble when alkylammonium cations are introduced. Consequently, we introduce alkylammonium groups to anthraquinone via covalent bonds, making the resulting bis[3-(trimethylammonio)propyl]-anthraquinones (BTMAPAQs) soluble. We report the first aqueous quinone flow chemistry-enabled electrochemical CO<sub>2</sub> capture/release process, which occurs at ambient temperature and pressure, and show that it proceeds via both a pH-swing and a nucleophilicity-swing mechanism. 1,5-BTMAPAO reaches the theoretical capture capacity of two CO<sub>2</sub> molecules per quinone from 1-bar CO<sub>2</sub>-N<sub>2</sub> mixtures for which the CO<sub>2</sub> partial pressure is as low as 0.05 bar, or the applied current density is as high as 100 mA/cm<sup>2</sup>, or the organic concentration is as high as 0.4 M. The energetic cost ranges from 48 to 140 kJ/molCO<sub>2</sub>. In a crude simulated flue gas composed of 3% O<sub>2</sub>, 10% CO<sub>2</sub>, and 87% N<sub>2</sub>, 1,5-BTMAPAQ electrolyte reversibly captured and released 50% of the theoretical capacity during an exposure of over 4 hr. It outperforms its isomeric counterparts 1,4-, and 1,8-BTMAPAQ in capture capacity and O<sub>2</sub> tolerance, demonstrating a substituent position effect on the reactivity of isomers with  $CO_2$  and  $O_2$ . The results provide fundamental insight into electrochemical  $CO_2$  capture with aqueous quinone flow chemistry and suggest that oxygen tolerance of reduced quinones may be significantly advanced through molecular engineering.

# Introduction

Accumulating atmospheric CO<sub>2</sub> concentrations from anthropogenic emissions compose the major source of global climate change. While progress is being made in switching from fossil fuel combustion to virtually emissions-free electricity sources, hard-to-abate sectors such as aviation and shipping will remain large sources of emissions for decades even in the most optimistic scenarios. Consequently, CO<sub>2</sub> removal – whether by capture from combustion exhaust or directly from the air or the ocean – is the subject of greatly increased attention, as it has become urgent to develop techniques that can be scaled up in a timely manner and globally deployed in the real world at reasonably low material and energetic cost.<sup>1</sup> Even after the attainment of a net zero emissions economy, it is likely that CO<sub>2</sub> removal will be desired in order to cut atmospheric concentrations toward pre-industrial levels. In an increasingly-electrified society, electrochemically-driven CO<sub>2</sub> capture at ambient conditions becomes an increasingly attractive option.<sup>2-5</sup>

Quinones are ubiquitous electron-transfer carriers found in a range of living organisms.<sup>6,7</sup> Featuring structural diversity, richness, and tunability as well as the earth-abundance of the compositional elements (C, H, O, N, S), quinones have been used as industrial dyes and for large-scale industrial production of hydrogen peroxide.<sup>8,9</sup> Aqueous quinone flow batteries are approaching commercialization as a new generation of large-scale energy storage

technique.<sup>10</sup> Apart from energy storage, it has been reported that quinone cores can also be utilized for electrochemically induced carbon capture via two different mechanisms, depending on the use of solvents (Figure 1a). First, CO<sub>2</sub> can be directly chemisorbed by reduced quinones (Q<sup>2-</sup>), forming adducts [Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>] in aprotic solvents.<sup>11,12</sup> Second, quinones can undergo proton-coupled electron transfer (PCET) to be reduced to the hydroquinone form (H<sub>2</sub>Q) in protic solvents,<sup>13-15</sup> accompanied by the accumulation of hydroxide ions, indirectly leading to chemisorption of CO<sub>2</sub>.<sup>16,17</sup> For both mechanisms, the captured CO<sub>2</sub> can be reversibly released upon electrochemical oxidation. For simplicity, we name the first (direct) capture mechanism the nucleophilicity-swing mechanism and the second (indirect) capture mechanism the pH-swing mechanism. In both cases, a CO<sub>2</sub> capture–release cycle involves quinone reduction (an electron transfer process, abbreviated as *E*: Q + 2e<sup>-</sup>  $\rightarrow$  Q<sup>2-</sup>; Q + 2e<sup>-</sup> + H<sub>2</sub>O  $\rightarrow$  HQ<sup>-</sup> + OH<sup>-</sup>; Q + 2e<sup>-</sup> + 2H<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>Q + 2OH<sup>-</sup>), CO<sub>2</sub> absorption (a chemical reaction, abbreviated as *C*: Q<sup>2-</sup> + CO<sub>2</sub>  $\rightarrow$  Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>; HQ<sup>-</sup> + CO<sub>2</sub>  $\rightarrow$  HQ(CO<sub>2</sub>)<sup>-</sup>; OH<sup>-</sup> + CO<sub>2</sub>  $\rightarrow$  HCO<sub>3</sub><sup>-</sup>), and concerted electrochemical oxidation and CO<sub>2</sub> release (*E*: Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>  $\rightarrow$  Q + 2CO<sub>2</sub> + 2e<sup>-</sup>; H<sub>2</sub>(CO<sub>2</sub>)<sup>-</sup> + HCO<sub>3</sub><sup>-</sup>  $\rightarrow$  Q + H<sub>2</sub>O + 2CO<sub>2</sub> + 2e<sup>-</sup>; H<sub>2</sub>Q + 2H<sub>2</sub>O + 2e<sup>-</sup>). Therefore, both mechanisms undergo *ECE* processes in principle.

Quinones explored for  $CO_2$  capture have been, almost without exception, immobilized on electrodes<sup>18-21</sup> or dissolved in organic electrolytes.<sup>18,22,23</sup> Solution-based capture inherits many of the advantages of flow batteries, including simple maintenance/top-off of active species, decoupled electrolyte activation and  $CO_2$  capture, and continuous-flow engineering.<sup>23-27</sup> In particular, aqueous electrolytes possess the advantage<sup>16,17,28-31</sup> that water is non-flammable with virtually no cost; furthermore, high ionic conductivity of aqueous electrolytes allows high current density, enabling high areal throughput at ambient temperature and pressure. Combined, these advantages illustrate the opportunity for a capture system based on electrochemically-driven aqueous-soluble quinone flow chemistry. The sole aqueous-soluble quinone studied to date for  $CO_2$  capture, disodium 4,5-dihydroxy-1,3-benzenedisulfonate (tiron), was studied only in static H-cells.<sup>15,32</sup> One  $CO_2$  per quinone was released via pH-swing caused by the electrochemical oxidization of tiron. Unfortunately, more than 60% of the initial capacity was lost after the first cycle due to the instability of the oxidized tiron molecule, which undergoes Michael addition and subsequent polymerization. To our knowledge, aqueous quinone flow chemistry-enabled electrochemical  $CO_2$  capture and release has not previously been demonstrated.

Theoretically, to utilize a quinone for PCET-mediated electrochemical CO<sub>2</sub> capture cycle in aqueous electrolyte, the initial pH of the quinone electrolytes should be somewhat below pKa<sub>1</sub> of H<sub>2</sub>CO<sub>3</sub> (~6), so that bicarbonate and carbonate concentrations are negligible compared to that of CO<sub>2</sub>(aq). Upon electrochemical reduction, the quinone undergoes a PCET process, increasing the electrolyte pH until it reaches pKa<sub>2</sub> of the corresponding H<sub>2</sub>Q; upon further reduction of the electrolyte, the quinone undergoes zero-proton, two-electron transfer, generating Q<sup>2-</sup> dianions without further altering the electrolyte pH.<sup>13,33</sup> Because H<sub>2</sub>Qs are weak acids and their pKa values are usually less than 13,<sup>13,33,34</sup> concentrated quinone electrolytes, when reduced, are expected to be predominantly in dianionic form rather than H<sub>2</sub>Q form, favoring nucleophilicity-swing carbon capture. The two OH<sup>-</sup> ions generated from the formation of hydroquinones would capture 1 or 2 CO<sub>2</sub> molecules via carbonate (2OH<sup>-</sup> + CO<sub>2</sub>  $\rightarrow$  H<sub>2</sub>O + CO<sub>3</sub><sup>2-</sup>) or bicarbonate (OH<sup>-</sup> + CO<sub>2</sub>  $\rightarrow$  HCO<sub>3</sub><sup>-</sup>) formation. The two oxygen sites on the dianionic form of the reduced quinone can each bind one CO<sub>2</sub> molecule, yielding QCO<sub>2</sub><sup>2-</sup> or Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>. Therefore, the CO<sub>2</sub> capture capacity of aqueous quinones is expected to range up to 2 CO<sub>2</sub> per quinone.

In general, aqueous quinones should meet several major criteria if used for electrochemical CO<sub>2</sub> capture. First, quinones should have high aqueous solubility in all states within their operational pH range. Second, the CO<sub>2</sub>-reactive reduced species, including H<sub>2</sub>Q, HQ<sup>-</sup>, Q<sup>2-</sup>, and HQ(CO<sub>2</sub>)<sup>-</sup>, Q(CO<sub>2</sub>)2<sup>2-</sup>, should resist reaction with O<sub>2</sub> long enough for most of the CO<sub>2</sub> capture capacity to be realized. Additionally, for the adduct formation mechanism, rate constants should be reasonably high and the binding constants should be high enough for most of the maximum capture capacity of 2 CO<sub>2</sub> per quinone to be attained, but not so high as to lead to unnecessarily large adduct oxidation potentials.



**Figure 1** | (a) In previous works, electrochemical CO<sub>2</sub> capture in non-aqueous media is driven by electrochemically activated Lewis bases (nucleophiles) which undergo nucleophilic additions with CO<sub>2</sub>;<sup>18,20,21,27</sup> electrochemical CO<sub>2</sub> capture in aqueous media is driven by electrochemically activated Brønsted bases which undergo proton-coupled electron transfer induced acid–base reactions<sup>16,17,24,28,29</sup>. In this work, electrochemical CO<sub>2</sub> capture with aqueous anthraquinone solutions is driven by AQ<sup>2–</sup> which is both a Lewis base and a Brønsted base. The electrochemical CO<sub>2</sub> capture & release cycle involves both nucleophilicity- and pH-swing. (b) Six anthraquinone candidates that are soluble at neutral pH. Screened molecules: AQDS, 2,6-D2PEAQ, and AQ-1,8-3E-OH. Re-designed molecules: 1,4-, 1,5-, and 1,8-BTMAPAQ.

#### **Aqueous soluble quinones**

Informed by a decade of endeavors in developing aqueous anthraquinone flow batteries,<sup>35-41</sup> we selected three anthraquinone derivatives that are aqueous-soluble at neutral pH: 2,7-disulfonated anthraquinone (AODS), 1,8-bis(2-(2-(2-hydroxyethoxy)ethoxy)ethoxy)anthracene-9,10-dione (AQ-1,8-3E-OH),<sup>33</sup> and 2,2'-((9,10-dioxo-9,10dihydroanthracene-2,6-diyl)bis(oxy))-dipropionic acid (2,6-D2PEAQ)<sup>42</sup> (Figure 1b). Although those quinones show decent aqueous solubility in both oxidized and reduced states, bright yellow precipitates formed when CO<sub>2</sub> was introduced to the reduced electrolytes. The yellow precipitates did not form, and clear solutions were afforded when tetra-alkyl ammonium chlorides were used as the supporting salts (Figure 2, Table S1). Specifically, substituting 1 M NaCl with 1 M tetramethylammonium chloride (TMACl) as the supporting salt in 0.1 M AODS electrolyte (Figure S1), replacing 1 M KCl with 1 M tetrabutylammonium chloride (TBACl) as the supporting salt in 0.1 M 2,6-D2PEAQ (Figure 2) or in 0.1 M AQ-1,8-3E-OH electrolytes produce transparent bright yellow solutions. One plausible explanation is that the bulky, amphiphilic tetra-alkyl ammonium cations and  $Q(CO_2)2^{2-}$  can form loose ion pairs rather than the tight ion pairs between alkali metal cations and  $Q(CO_2)_2^{2-.43}$  There are more water molecules separating positively and negatively charged ions in loose ion pairs than in tight ion pairs, weakening the Coulomb attraction and enhancing solubility. However, the bulkiness of tetra-alkyl ammonium cations causes extremely high cell resistance (Figure S2a) in the flow cell systems because, in such cells, cation-exchange membranes must be used, resulting in prohibitively high energetic cost.



Figure 2 | Affect of supporting salt cations on solubility of  $Q(CO_2)_2^2$ . (a) 0.1 M 2,6-D2PEAQ in 1 M TBACI; (b) 0.1 M reduced 2,6-D2PEAQ in 1 M TBACI; (c) 0.1 M reduced 2,6-D2PEAQ with saturated CO<sub>2</sub> in 1 M TBACI. (d) 0.1 M reduced 2,6-D2PEAQ with saturated CO<sub>2</sub> in 1 M KCl. (e) AQ possessing alkyl ammonium ending groups connected via covalent bonds, enhancing aqueous solubility and affording compatibility with anion-exchange membranes.

Inspired by the observation of dramatic change in aqueous solubility of reduced AQs in the presence of  $CO_2$  caused by tetra-alkyl ammonium salts (Figure 2, Table S1), we hypothesized that anthraquinone derivatives tethered with bulky alkyl ammonium cations via covalent bonds might not only have high aqueous solubility in all states, but also be compatible with anion exchange membranes: the oxidized forms are positively charged and the reduced forms are charge-neutral but large in size, with correspondingly low expected cross-over rates. We designed and synthesized 1,4-, 1,5-, 1,8-,<sup>44</sup> and 2,6-bis[3-(trimethylammonio)propyl]-anthraquinone (BTMAPAQs) in which the numbers represent the positions of water-solubilizing chains (TMAP) bonded to anthraquinone (AQ) core. Of the four isomers, 2,6-BTMAPAQ exhibits very limited solubility (< 0.1 M) even in its oxidized state (Table S1); 1,8-BTMAPAQ( $CO_2$ )<sub>2</sub><sup>2-</sup> becomes soluble when TBA<sup>+</sup> is used as the supporting salt cation (Figure S3); 1,4-, and 1,5-BTMAPAQs are soluble in all states even if KCl is used as the supporting salt. Therefore, 1,4-, 1,5-, and 1,8-BTMAPAQs (Figure 1b) were investigated for electrochemical CO<sub>2</sub> capture.

### CO<sub>2</sub> capture mechanism verification



Figure 3 | Electrochemical and physiochemical characterization of BTMAPAQ in N<sub>2</sub> and CO<sub>2</sub>. (a) Cyclic voltammogram (CV) of 10 mL, 5 mM 1,4-, (1,5-)BTMAPAQs in 1 M KCl, 5 mM 1,8-BTMAPAQ in 1 M KCl under streams of pure N<sub>2</sub> (dashed) or CO<sub>2</sub> (solid) at a scan rate of 100 mV s<sup>-1</sup>. (b) Pourbaix diagram of 1,5-BTMAPAQ (AQ  $+ 2e^- + 2H_2O \rightarrow H_2AQ + 2OH^-$ ; AQ  $+ 2e^- + H_2O \rightarrow HAQ^- + OH^-$ ; AQ  $+ 2e^- \rightarrow AQ^{2-}$ ) and 2-electron oxygen reduction reaction ( $\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow H_2O_2$ ;  $\frac{1}{2}O_2 + 2e^- + H_2O \rightarrow HO_2^- + H^+$ ). (c) Voltage profiles of 1,5-BTMAPAQ | FcNCl in 100% N<sub>2</sub> (black) and 10% CO<sub>2</sub> + 90% N<sub>2</sub> for (red). (d) Structure of 1,5-BTMAPAQ, 1,5-BTMAPAQ<sup>2-</sup>, and 1,5-BTMAPAQ(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>. (e) NMR specimens, from left to right in the same order as the molecular structures in (d), and their <sup>1</sup>H NMR (f) and <sup>13</sup>C NMR (g) spectra. Note that <sup>1</sup>H NMR peak broadening was initially observed from the electrochemically reduced aqueous quinone due to the occurrence of residual radicals, but addition of a tiny amount of HCl afforded well-defined peak splitting in the aromatic region (Figure 3f, orange). The chemical shift at 124.6 ppm in 1,5-BTMAPAQ(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup> (Figure 3g, purple, identified with asterisk) is from the dissolved CO<sub>2</sub>.<sup>45</sup>

Cyclic voltammetry (CV) was employed to investigate BTMAPAQs in buffered and unbuffered solutions. As shown in Figure 3a, at pH 7 in N<sub>2</sub>, 1,5-BTMAPAQ exhibits a redox potential of -0.465 V vs. SHE with a peak separation of 90 mV. When the solution was constantly purged with CO<sub>2</sub>, the major cathodic peak appears at -0.51 V along with a minor cathodic peak at -0.28 V (Figure 3a), which might be caused by a CO<sub>2</sub> buffering effect, enabling 1,5-BTMAPAQ to partially undergo a PCET process.<sup>13</sup> The anodic peak of 1,5-BTMAPAQ largely shifts to +0.28 V, suggesting that extra energy is required to trigger the electrochemical oxidation: 1,5-BTMAPAQ(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>  $\rightarrow$  1,5-BTMAPAQ + 2CO<sub>2</sub> + 2e<sup>-</sup>. Similar electrochemical behaviors were also shown by 1,4- and 1,8-BTMAPAQs.

To extract the relationship between redox potentials of 1,5-BTMAPAQ and electrolyte pH, we ran CVs in a series of buffered electrolytes to plot its Pourbaix diagram (Figure 3b). The pKa<sub>1</sub> and pKa<sub>2</sub> of 1,5-BTMAPH<sub>2</sub>AQ are estimated at 10.9 and 12.8, consistent with other aqueous soluble anthrahydroquinones (H<sub>2</sub>AQ).<sup>33,34,42</sup> Because of the dominance of the nucleophilicity-swing mechanism in concentrated solutions, hereafter the oxidized, reduced, and CO<sub>2</sub> bonded states of quinones are abbreviated as Q,  $Q^{2-}$ , and Q(CO<sub>2</sub>) $z^{2-}$ .

We assembled BTMAPAQs | (ferrocenylmethyl)trimethylammonium Chloride (FcNCl)<sup>46</sup> flow cells separated by anion-exchange membranes. Thanks to the compatibility between membrane and electrolytes, the alternating

current area-specific resistance of the cells, measured via high-frequency electrochemical impedance spectroscopy, is as low as ~1.5  $\Omega$  cm<sup>2</sup> (Figure S4). While operating in 0.1 bar CO<sub>2</sub> and 0.9 bar N<sub>2</sub>, we noticed a distinct discharge voltage decrease (Figure 3c, Figure S5), consistent with the anodic peak shifts in CVs (Figure 3a), confirming that  $Q(CO_2)_2^{2^-}$  is the major product when the reduced form is exposed to CO<sub>2</sub>. Interestingly, the color of BTMAPAQ solution changed dramatically in different states. For instance, 1,5-BTMAPAQ solution turned from bright yellow to light orange to pale yellow, corresponding to 1,5-BTMAPAQ, 1,5-BTMAPAQ<sup>2-</sup>, and 1,5-BTMAPAQ(CO<sub>2</sub>)\_2<sup>2-</sup> (Figure 3e); the structure change was reflected by the distinct chemical shifts in both <sup>1</sup>H and <sup>13</sup>C NMR spectra (Figure 3f, 3g). Dramatic color changes as well as distinct chemical shifts were also exhibited by AQDS and 1,8-BTMAPAQ in their corresponding three states (Figure S1, S3).

# **Electrochemical CO<sub>2</sub> capture and release**

To examine the CO<sub>2</sub> capture capability of BTMAPAQs, we first conducted chemically induced CO<sub>2</sub> capture from pure, flowing CO<sub>2</sub>, release into N<sub>2</sub>, and sequestration as BaCO<sub>3</sub>(s), from which we validated the CO<sub>2</sub> capture capacity of two CO<sub>2</sub> per quinone (Figure S6). Subsequently, we investigated the electrochemically induced CO<sub>2</sub> capture performance of 1,5-BTMAPAQ at 0.5 bar CO<sub>2</sub> and 0.5 bar N<sub>2</sub>. (Figure 4a). The electrochemical reduction and oxidation were accompanied by CO<sub>2</sub> capture and release, which were reflected by the periodic oscillation of downstream CO<sub>2</sub> partial pressure and downstream gas flow rate, as well as the pH swing of 1,5-BTMAPAQ electrolyte. A 45-min. interval between reduction and oxidation was chosen as the minimum rest time to complete the gas-liquid reaction, which is the rate-limiting step (Figure S7). Integrating the downstream gas flow rate change during the CO<sub>2</sub> release indicates that the measured volume of released CO<sub>2</sub> is almost the same as the theoretical value (Figure S8), suggesting that each 1,5-BTMAPAQ can capture and release two CO<sub>2</sub> molecules. Through analyzing the round-trip voltage efficiency and coulombic efficiency over five cycles of the electrochemical reduction and oxidation, we found the energetic cost ranges from 65 to 80 kJ/molCO<sub>2</sub> at 20 mA/cm<sup>2</sup> at a fixed inlet CO<sub>2</sub> partial pressure of 0.5 bar. The close correspondence between the coulombic efficiency and the CO<sub>2</sub> release/capture efficiency in Figure S8e, defined as the ratio of the amount of CO<sub>2</sub> released to the amount captured in the immediately preceding half-cycle, indicates that CO<sub>2</sub> capture/release is triggered by the electrochemical reactions and mirrored by coulombic efficiencies.

In real applications, the partial pressure of CO<sub>2</sub> in feed gas varies over a broad range; hence we performed a series of tests in feed gas with varied partial pressure of CO<sub>2</sub> at 0.05, 0.1, 0.2, and 0.5 bars. To increase the CO<sub>2</sub> capture capacity, we adjusted the corresponding rest time intervals as 210, 105, 52, and 45 min., respectively (Figure 4a, Figure S9). During the electrochemical reduction of 1,5-BTMAPAQ, the pH range went from wide to narrow while the CO<sub>2</sub> partial pressure was adjusted from 0.05 to 0.5 bar. For instance, the pH swung from near neutral to ~12 at 0.05 bar CO<sub>2</sub>, but to only ~9 at 0.5 bar CO<sub>2</sub>. According to Henry's law, a higher partial pressure of CO<sub>2</sub> can lead to a higher CO<sub>2</sub> solubility in solution, thus enabling the prompt buffering of pH increase induced by electrochemical reduction. Despite of the variation in CO<sub>2</sub> partial pressure, two CO<sub>2</sub> molecules were captured by one 1,5-BTMAPAQ with energetic cost of 48 to 50 kJ/molCO<sub>2</sub> at 20 mA/cm<sup>2</sup>.

One advantage of aqueous flow chemistry is the capability to operate electrochemical reactions at high current densities. Although extremely diluted CO<sub>2</sub> essentially limits the CO<sub>2</sub> capture heterogeneous chemical reaction rate regardless of technology, CO<sub>2</sub> release in our system is coupled with electrochemical oxidation; thus the CO<sub>2</sub> release rate can be readily accelerated by applying high current densities. We electrochemically reduced and oxidized 1,5-BTMAPAQ at 20, 40, 60, 80, and 100 mA/cm<sup>2</sup> in the presence of 0.1 bar CO<sub>2</sub> (Figure 4b, Figure S10). The depression of downstream CO<sub>2</sub> partial pressure and gas flow rate caused by CO<sub>2</sub> capture was almost the same at different current densities, indicating that CO<sub>2</sub> capture reaction rate is limited by mass transport of 0.1 bar CO<sub>2</sub> rather than by the electrochemical reduction rate, i.e., the applied current density. However, the peaks of downstream CO<sub>2</sub> partial pressure and gas flow rate caused by CO<sub>2</sub> release during that the CO<sub>2</sub> release rate can be accelerated with increased current density, thus shortening the CO<sub>2</sub> release time. It is worth noting that the calculated volumes of the released CO<sub>2</sub> reach the theoretical values at different current densities (Figure S10). The mid-point voltage difference between charge and discharge curves increases with current density, which is caused by internal cell resistance, resulting in a broad energetic cost range of 65 to 140 kJ/molCO<sub>2</sub>.



Figure 4 | 1,5-BTMAPAQ electrochemical CO<sub>2</sub> capture capability in CO<sub>2</sub>–N<sub>2</sub> mixtures. (a) CO<sub>2</sub> capture and release cycling at 20 mA/cm<sup>2</sup>. The partial pressure of CO<sub>2</sub> is set to  $\approx$  0.05, 0.1, 0.2, and 0.5 bar for the experiments,

separately. The plots in Fig. 4a share the same Y-axis titles and units on the far left. Flow cells comprising 10–12 mL of 0.115 M 1,5-BTMAPAQ in 1 M KCl and 40 mL of 0.2 M FcNCl in 1 M KCl were used for the experiments at 0.05, 0.1 and 0.2 bar. A flow cell comprising 10 mL of 0.115 M 1,5-BTMAPAQ in 1 M KCl and 40 mL of 0.2 M BTMAPFc (bis((3-trimethylammonio)propyl)ferrocene dichloride)<sup>47</sup> in 1 M KCl was used for the experiment at 0.5 bar. (b) Plot presents the downstream CO<sub>2</sub> partial pressure and the downstream total gas flow rates when the electrochemical redox reactions were triggered at 20, 40, 60, 80, and 100 mA/cm<sup>2</sup>. A flow cell comprises 10 mL of 0.057 M 1,5-BTMAPAQ in 1 M KCl and 40 mL of 0.1 M FcNCl in 1 M KCl. (c) CO<sub>2</sub> capture and release cycling where the capture occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.1 bar and the release occurred in an inlet CO<sub>2</sub> partial pressure of 0.4 M 1,5-BTMAPAQ in 1 M KCl and 40 mL of 0.2 M FcNCl in 1 M KCl and 40 mL of 0.4 M 1,5-BTMAPAQ DI water and 30 mL of 0.9 M FcNCl in DI water at 20 mA/cm<sup>2</sup>. Plots present current density, voltage, pH, downstream CO<sub>2</sub> partial pressure, and the downstream total gas flow rate of 1,5-BTMAPAQ electrolyte. The initial gas flow rate is set to 11.76 mL/min.

It is important to evaluate the  $CO_2$  capture capacity and energetic cost when a system is used to capture  $CO_2$ from a diluted source and release pure  $CO_2$ . Hence, we performed our experiment using 1,5-BTMAPAQ with 0.1 bar inlet  $CO_2$  and 1.0 bar pure  $CO_2$  exit stream (Figure 4c). The volume of released  $CO_2$  approaches the theoretical value over five cycles (Figure S11). The energetic cost and coulombic efficiency are either comparable to or slightly higher than those measured under previous conditions (Figure S9, S10).

A concentrated quinone flow system comprising 0.4 M 1,5-BTMAPAQ was set up to demonstrate high volumetric CO<sub>2</sub> capture capacity (Figure 4d). Because of the low pKa values (<13) of 1,5-BTMAPH<sub>2</sub>AQ (Figure 3b), the pH swing for 0.4 M 1,5-BTMAPAQ is the same as that for 0.1 M 1,5-BTMAPAQ, further supporting our interpretation of the results as the formation of  $Q(CO_2)2^{2-}$ . Although the increased concentration of 1,5-BTMAPAQ took a longer time to complete the capture, it still reaches the theoretical capacity at the energetic cost of 90 kJ/molCO<sub>2</sub>.



## O<sub>2</sub> sensitivity evaluation

**Figure 5** | **CO**<sub>2</sub> **capture and release of 1,4-, 1,5-, 1,8-BTMAPAQs with and without O**<sub>2</sub>. Calculated volumes of captured and released CO<sub>2</sub> by (a) 1,4-, (b) 1,5-, (c) 1,8-BTMAPAQs in a feed gas stream of 90% N<sub>2</sub> and 10% CO<sub>2</sub> at 1.0 bar. Calculated volumes of captured and released CO<sub>2</sub> by (d) 1,4-, (e) 1,5-, (f) 1,8-BTMAPAQs in a feed gas stream of 87% N<sub>2</sub>, 10% CO<sub>2</sub>, and 3% O<sub>2</sub> (simulated flue gas) at 1.0 bar. 5 mL 0.1 M 1,4-, 1,5-BTMAPAQs, 1 M KCl solutions were paired with 40 mL 0.1 M FcNCl, 1 M KCl solution. 5 mL 0.1 M 1,8-BTMAPAQ 1 M TBACl solution was paired with 40 mL 0.1 M FcNCl, 1 M TBACl solution. The BTMAPAQs were electrochemically reduced and oxidized at 40 mA/cm<sup>2</sup> and followed by potential holds to complete the reactions. The theoretical CO<sub>2</sub> capture & release capacity for the BTMAPAQ electrolytes is 22.4 mL. Electrochemical reduction/oxidation were followed by

rest time that was adjusted to approach the maximum  $CO_2$  capture/release capacity while minimizing the  $O_2$  induced side reactions. The durations of  $CO_2$  capture/release for 1,4-BTMPAQ are 175/125 min. without  $O_2$  and 170/100 min. in the simulated gas, respectively. The durations of  $CO_2$  capture/release for 1,5-BTMPAQ are 145/80 min. without  $O_2$  and 226/160 min. in the simulated gas, respectively. The durations of  $CO_2$  capture/release for 1,6-BTMPAQ are 145/80 min. without  $O_2$  and 226/160 min. in the simulated gas, respectively. The durations of  $CO_2$  capture/release for 1,8-BTMPAQ are 120/90 min. without  $O_2$  and 100/70 min. in the simulated gas, respectively. The addition of 1 M TBACl to 0.1 M 1,8-BTMAPAQ increased the viscosity of solution, slowing the dissolution of  $CO_2$  and  $O_2$  from gas phase to liquid phase.

In real applications, CO<sub>2</sub> always coexists with O<sub>2</sub> at varying partial pressures depending on CO<sub>2</sub> sources. It has been reported that reduced quinones are susceptible to  $O_2$ ,<sup>23,48,49</sup> which can reversibly chemically oxidize the reduced quinones to their oxidized states. These reduced quinones are the species of interest for binding CO<sub>2</sub>. Hence, we investigated the oxygen sensitivity of the reduced quinones including H<sub>2</sub>Q, HQ<sup>-</sup>, Q<sup>2-</sup>, HQ(CO<sub>2</sub>)<sup>-</sup>, and Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup>, as capture will become practical only if the reduced quinones become oxidized by O<sub>2</sub> sufficiently slowly in an atmosphere with a relatively high O<sub>2</sub> partial pressure.

The reduced quinones are oxygen-sensitive because their oxidation potentials are much lower than the  $O_2$ reduction potential. In contrast, the oxidation potentials of  $Q(CO_2)_2^{2-}$  can positively shift by at least 500 mV compared to those of the reduced quinones (Figure 3a), approaching the reduction potential of O<sub>2</sub> (Figure 3b) and possibly making make Q(CO<sub>2</sub>)<sub>2</sub><sup>2-</sup> more O<sub>2</sub>-tolerant. Through tracking <sup>1</sup>H NMR of the reduced quinones with and without captured  $CO_2$  during air exposure (Figure S13–S18), we observed the reduced quinones gradually converted to the oxidized forms over days with different conversion rates. After operating BTMAPAO flow cells in atmospheres with fixed CO<sub>2</sub> partial pressure but varied O<sub>2</sub> partial pressure (Table S2), we analyzed their coulombic efficiency to compare the oxygen sensitivity of BTMAPAQ isomers. We also performed chemically induced CO<sub>2</sub> capture, release, and sequestration with air exposure (Figure S19) and found that 1.7 equivalents of CO<sub>2</sub> were released when the solution with captured  $CO_2$  was vigorously stirred in air for 15 min. The detailed information is reported in the Oxygen sensitivity section of Supplementary Information. Those measurements inspired us to further evaluate BTMAPAQsbased electrochemical CO<sub>2</sub> capture from simulated flue gases with an upgraded system setup (Figure S20–S22). By integrating the peak area of  $CO_2$  flow rate deviation over  $CO_2$  capture and release cycles (Figure 5), we evaluated the CO<sub>2</sub> capture and release volumes from 1,4-, 1,5-, and 1,8-BTMAPAQs in the absence and presence of O<sub>2</sub>. When 1,4and 1,5-BTMAPAQ were exposed to 1.0 bar feed gas composed of 10% CO2 and 90% N2, the CO2 release/capture volume ratio is close to 1 (Figure 5a, 5b), suggesting the reversibility of CO<sub>2</sub> capture and release. When exposed to 1.0 bar simulated flue gas composed of 3% O<sub>2</sub>, 10% CO<sub>2</sub>, and 87% N<sub>2</sub>, the volumes of released CO<sub>2</sub> greatly decrease, which we attribute to the oxygen-induced side reactions shown in Eqns. 10 and 11 in Table 1. Compared to the CO<sub>2</sub> capture volumes from 1.4- and 1.5-BTMAPAOs in the absence of O<sub>2</sub>, their CO<sub>2</sub> capture volumes in the presence of O<sub>2</sub> become significantly larger, which we attribute to additional CO<sub>2</sub> irreversibly trapped by the hydroxide ions converted from oxygen (Eqns. 7, 8, 10, and 11 in Table 1). The CO<sub>2</sub> capture volumes from 1,8-BTMAPAQ are much smaller than those from 1.4- and 1.5-BTMAPAQ, which we tentatively attribute to the increased electrolyte viscosity caused by the addition of 1 M TBA<sup>+</sup>, which slows down the dissolution of  $CO_2$  to the electrolyte, lowering the capture capacity.

Among the three BTMAPAQ isomers, 1,5-BTMAPAQ shows the highest CO<sub>2</sub> capture capacity of 21.4 mL in the absence of O<sub>2</sub>, which is close to the theoretical value of 22.4 mL assuming one 1,5-BTMAPAQ captures two CO<sub>2</sub> molecules. Under 3% O<sub>2</sub> exposure for 226 min. during CO<sub>2</sub> capture and 160 min. during the release, 1,5-BTMAPAO still released 11.3 mL CO<sub>2</sub>, which is  $\sim$ 50% of the theoretical capacity. It is worth noting that the CO<sub>2</sub> capture/release capacity can be further improved by optimizing the CO<sub>2</sub> capture time duration, as with decreased exposure time there should be fewer  $O_2$ -induced side reactions, and more captured  $CO_2$  will be released. However, if the  $CO_2$  capture duration is too short, both captured and released CO<sub>2</sub> volumes will become small, lowering the faradaic efficiency, defined in this context as the ratio of the amount of CO<sub>2</sub> reversibly captured and released to the theoretical capacity. Thus, a trade-off is apparent between the CO<sub>2</sub> release/capture volume ratio and faradic efficiency. Nevertheless, the O2 resistance and CO2 capture capability shown by 1,5-BTMAPAQ in Figure 5e demonstrates that reduced quinones are not necessarily too oxygen-sensitive to be useful for CO<sub>2</sub> capture. The BTMAPAQ-based electrochemical CO<sub>2</sub> capture-release behavior in a simulated flue gas atmosphere over multiple cycles (Figure S23-S26) illustrates that there is still room for improvement of long-term O<sub>2</sub>-tolerance of reduced quinones through judicious molecular design. The distinct O<sub>2</sub> reactivity difference among the isomers implies that a substituent position effect plays a major role in governing their oxygen tolerance. The substituent positions in the isomers may affect the interaction strength between the positively charged alkylammonium ending groups and the negatively charged phenolate active sites or the organic adducts, further influencing the nucleophilicity-induced CO<sub>2</sub> capture capacity and O<sub>2</sub>-induced chemical redox reactions.

Table 1 | Electrochemical and chemical reactions during CO<sub>2</sub> capture & release when oxygen is involved. The hydroxide ions produced from Eqns. 7 and 8 can irreversibly capture  $CO_2$  via Eqn 6. The captured  $CO_2$  can escape due to the chemical oxidation shown in Eqns. 10 and 11.

Stage 1	Electrochemical reduction	Eqn. 1	$AQ + 2e^- \rightarrow AQ^{2-}$
		Eqn. 2	AQ + 2e <sup>-</sup> + 2H <sub>2</sub> O → H <sub>2</sub> AQ + 2OH <sup>-</sup>
		Eqn. 3	AQ + 2e <sup>-</sup> + H <sub>2</sub> O → HAQ <sup>-</sup> + OH <sup>-</sup>
Stage 2	Electrochemically induced CO <sub>2</sub> capture	Eqn. 4	$AQ^{2-} + CO_2 \rightarrow AQ(CO_2)_2^{2-}$
		Eqn. 5	$HAQ^{-} + CO_2  HAQ(CO_2)^{-}$
		Eqn. 6	$OH^- + CO_2 \rightarrow HCO_3^-$
	$O_2$ -involved chemical reactions lead to irreversible capture and escape of $CO_2$	Eqn. 7	$AQ^{2-}$ + $H_2O$ + 1/2 $O_2$ → $AQ$ + 2 $OH^-$
		Eqn. 8	$HAQ^-$ + 1/2O <sub>2</sub> $\rightarrow$ AQ + OH <sup>-</sup>
		Eqn. 9	$H_2AQ + 1/2O_2 \rightarrow AQ + H_2O$
		Eqn. 10	$HAQ(CO_2)^- + 1/2O_2  AQ + OH^- + CO_2$
		Eqn. 11	$AQ(CO_2)_2^{2^-} + H_2O + 1/2O_2  AQ + 2OH^- + 2CO_2$
Stage 3	Electrochemically induced CO <sub>2</sub> release	Eqn. 12	$AQ(CO_2)_2^{2-} - 2e^- \rightarrow AQ + 2CO_2$
		Eqn. 13	$H_2AQ - 2e^- + 2HCO_3^- \rightarrow AQ + 2H_2O + 2CO_2$
		Eqn. 14	$HAQ(CO_2)^ 2e^- + HCO_3^- \rightarrow AQ + H_2O + 2CO_2$

More broadly, molecular oxygen tolerance can be improved via molecular engineering with the incorporation of steric and electronic effects, intra-molecular interactions, *etc.* induced by quinone cores or covalently bonded functional groups. The both basicity and nucleophilicity-based CO<sub>2</sub> capture mechanisms further enlarge the molecular design space, facilitating the discovery of desired molecules.

- 1. **Steric hindrance** could be introduced to prevent the chemical oxidation between activated molecules and molecular oxygen. Note that the introduction of steric hindrance will make the nucleophilic addition between activated molecules and CO<sub>2</sub> difficult without affecting the basicity of activated molecules, leading to the dominance of pH-swing based CO<sub>2</sub> capture & release.
- 2. Intramolecular hydrogen bonding can potentially stabilize activated molecules, making them difficult to be oxidized by O<sub>2</sub>. Apaydin *et al.*<sup>50</sup> has demonstrated that an activated quinacridone film with captured CO<sub>2</sub> via nucleophilic addition can be stabilized by hydrogen bonds, in which CO<sub>2</sub> can be released only with extra heat, or at an applied oxidation potential of 0.7 V vs. Fc/Fc<sup>+</sup>, which is substantially higher than the oxygen reduction potential (-1.2 V vs. Fc/Fc<sup>+</sup>).<sup>27</sup> It is thus possible that intramolecular hydrogen bonds can also stabilize activated molecules in solutions.
- 3. Elevating the oxidation potentials of activated molecules above the oxygen reduction potential should make them oxygen-tolerant. Meanwhile, increasing potentials might also decrease the basicity and nucleophilicity of activated molecules, thus making them less capable to capture CO<sub>2</sub> via either mechanism, compromising their CO<sub>2</sub> capture capacity.<sup>48</sup>
- 4. Lowering the oxidation potentials of activated molecules may be a counterintuitive approach to increase oxygen-tolerance of activated molecules. When the Gibbs free energy of chemical redox reaction between activated molecules and O<sub>2</sub> is too negative and falling into the Marcus inverted region, the reaction rate will decrease as the driving force increases.<sup>51</sup>
- 5. **Machine learning** is emerging as a powerful approach in materials discovery.<sup>52</sup> It thus has potential to offer valuable guidelines and accelerate the discovery of oxygen-tolerant redox molecules.

# Conclusions

Through molecular screening and modification, we developed three water-soluble and anion-exchange membrane compatible bis[3-(trimethylammonio)propyl]-anthraquinone (BTMAPAQ) isomers that can be used for electrochemical CO<sub>2</sub> capture. With a series of characterizations including cyclic voltammetry, Pourbaix diagram analysis, <sup>1</sup>H and <sup>13</sup>C NMR, electrochemical charge–discharge voltage–capacity profiles, and *in situ* monitoring of pH, pco<sub>2</sub>, and gas flow rate, we showed that aqueous quinone flow chemistry-enabled electrochemical CO<sub>2</sub> capture

proceeds via pH-swing and nucleophilicity-swing mechanisms. The latter is more dominant because of low pKa values of hydroquinones. 1,5-BTMAPAQ electrolyte can capture and release the theoretical limit of two equivalents of  $CO_2$ molecules per quinone from 1-bar  $CO_2$ -N<sub>2</sub> mixtures for which the  $CO_2$  partial pressure is as low as 0.05 bar, or the applied current density is as high as 100 mA/cm<sup>2</sup>, or the organic concentration is as high as 0.4 M, with an energetic cost ranging from 48 to 140 kJ/molCO<sub>2</sub>. When exposed to a simulated flue gas comprising 3% O<sub>2</sub>, 10% CO<sub>2</sub>, and 87% N<sub>2</sub> at 1.0 bar total pressure for over 4 hr., 1,5-BTMAPAQ reversibly captured and released 50% of the theoretical capacity. The distinct position effect on O<sub>2</sub> reactivity exhibited by BTMAPAQ isomers illustrates the opportunity for molecular engineering for further improvement of molecular properties. This may stimulate the progress of oxygentolerant, low-cost, scalable aqueous quinone flow chemistry enabled electrochemical  $CO_2$  capture.

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#### **Author contributions**

M.J.A. and R.G.G. supervised the project. Y.J., K.A., and M.J.A. conceived the idea. Y.J. and K.A. designed the experiment. K.A. performed the half-cell and full-cell electrochemical CO<sub>2</sub> capture experiments in the absence of O<sub>2</sub> and analyzed the data. Y.J. designed and synthesized the molecules, performed the structural characterizations, and ran electrochemical CO<sub>2</sub> capture experiments in the presence of O<sub>2</sub>, and analyzed the data. K.A. prepared NMR samples; Y.J. ran NMR measurements and analyzed the results. D.X. and S.J. built the CO<sub>2</sub> capture setup and compiled the Arduino code for sensor control and data collection. A.A. collected the Pourbaix diagram data. E.F.K. synthesized the 2,6-D2PEAQ molecule. All authors contributed to the discussion. Y.J., K.A. and M.J.A. wrote the manuscript with input from all co-authors.

## **Experiments and methods**

#### Synthesis of BTMAPAQs

To a 1 L of flame dried Schlenk flask, 40 mmol of dihydroxyanthraquinone, 88 mmol of anhydrous K<sub>2</sub>CO<sub>3</sub>, and 9.5 mmol of KI were suspended in 160 mL of anhydrous DMF. After being stirred under nitrogen for 20 min., 88 mmol of 3-bromopropyl trimethylammonium bromide was added to the dark suspension. The dark suspension was sealed to prevent ambient moisture, then was vigorously stirred at 100 °C for 16 hours to afford a brownish slurry.

After being cooling down, the slurry was added with 150 mL of ethyl acetate, stirred at room temperature for 30 min., then filtered to collect the brown cake. The washing procedure was repeated for few times until the filtrate became colorless. The cake was dissolved into methanol, and the solution was filtered to remove insoluble inorganic salts. The filtrate was condensed under vacuo to remove methanol and collect the dark red solid, which was then redissolved in deionized water.

The aqueous quinone solution was then transferred to an anion-exchange resin column prepared in advance to replace bromide with chloride ions. The dark red (bright yellow depending on the concentration) solution was condensed under vacuo to remove water and collect the red solid.

The red solid was re-dissolved in methanol to get the saturated solution, which was then drop-wise added to 200 mL of ethyl acetate and afford precipitates. The precipitates were collected by filtration to get final orange to yellow cakes. The yields range from 85% to 95%.

#### Characterization

<sup>1</sup>H, <sup>13</sup>C NMR spectra were recorded on Varian INOVA 500 spectrometers at 500 MHz. Aliquots were prepared in deuterated water (D<sub>2</sub>O), corresponding NMR spectra were recorded in D<sub>2</sub>O with the residual H<sub>2</sub>O ( $\delta$  4.79 ppm for <sup>1</sup>H NMR). Electrochemical characterizations

#### Cyclic voltammetry measurements

Glassy carbon was used as the working electrode for all three-electrode CV tests with a 5 mm diameter glassy carbon working electrode, an Ag/AgCl reference electrode (BASi, pre-soaked in 3 M NaCl solution), and a graphite counter electrode. All cyclic voltammetry, linear sweep voltammetry, and chronoamperometry measurements were conducted on Gamry Instruments and CHI Instrument electrochemical analysers.

### Flow cell assembly

Flow cell experiments were constructed with cell hardware from Fuel Cell Tech (Albuquerque, NM). The flow cell was assembled into a zero-gap flow cell configuration using pyrosealed POCO graphite flow plates with identical interdigitated flow fields. Each electrode was composed of 1 layer of AvCarb HCBA carbon cloth with a 5 cm<sup>2</sup> geometric surface area. Selemion DSV-N was used as the anion exchange membrane. The flow rate was set at 50–70 mL/min. Biologic SP-150e and Gamry Reference 3000 potentiostat was used as our electrochemical workstation. KNF diaphragm pumps were used to circulate electrolytes through the flow fields and electrodes in the cell stack. For some tests, a Cole-Parmer Digital gear pump was used.

Bis((3-trimethylammonio)propyl)ferrocene dichloride (BTMAPFc) and (ferrocenylmethyl)trimethylammonium Chloride (FcNCl) were purchased from TCI-America chemical company. Tetramethyl ammonium chloride, tetrabutylammonium chloride were purchased from Sigma Aldrich. All those chemicals were directly used without further purification.

#### Electrochemical CO<sub>2</sub> capture and release

Flow cells were charged at constant current, followed by voltage holds until current hits the background current values. Then the flow cells were set in rest mode for certain time to complete carbon capture. The cells were discharged at constant current, followed by a voltage hold. After the voltage hold, the battery was set in rest mode to complete  $CO_2$  release.

A stream of feed gas composed of  $N_2$ ,  $CO_2$ , and  $O_2$  was introduced to the anthraquinone electrolytes and kept flowing constantly with pre-set partial pressure. The total pressure is 1 bar, and the total flow rate is 11.76 mL/min. FS4001 MEMS Mass Flow Sensor, LuminOX  $O_2$  sensor (CM-42990), SprintIR  $CO_2$  sensor (GC-0018) were used in our tests.

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