Direct Electrochemical Capture and Release of Carbon Dioxide Using an Industrial Organic Pigment: Quinacridone**

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Abstract: Limiting anthropogenic carbon dioxide emissions constitutes a major issue faced by scientists today. Herein we report an efficient way of controlled capture and release of carbon dioxide using nature inspired, cheap, abundant and non-toxic, industrial pigment namely, quinacridone. An electrochemically reduced electrode consisting of a quinacridone thin film (ca. 100 nm thick) on an ITO support forms a quinacridone carbonate salt. The captured CO₂ can be released by electrochemical oxidation. The amount of captured CO₂ was quantified by FT-IR. The uptake value for electrochemical release process was 4.61 mmol g⁻¹. This value is among the highest reported uptake efficiencies for electrochemical CO₂ capture. For comparison, the state-of-the-art aqueous amine industrial capture process has an uptake efficiency of ca. 8 mmol g⁻¹.

The potential problems of climate change caused by anthropogenic carbon dioxide emissions constitute major issues faced by scientists today.[1] Technologies aim at capturing CO₂ followed by sequestration or utilization, for example by reduction to useful hydrocarbons, such as formic acid,[2] carbon monoxide,[3,4] methanol,[5,6] or methane.[7] A key step for both sequestration and utilization of CO₂ is controlled capture, storage, and release. The most efficient and widely used method in industry is post-combustion capture using various amines as the capturing agents. After chemical release process was 4.61 mmol g⁻¹. This value is among the highest reported uptake efficiencies for electrochemical CO₂ capture. For comparison, the state-of-the-art aqueous amine industrial capture process has an uptake efficiency of ca. 8 mmol g⁻¹.

The method demonstrated herein relies on quinacridone (QNC), a common mass-produced industrial organic pigment, which we found can function to electrochemically capture and release CO₂ with remarkable efficiency. Quinacridones (QNCs) belong to the extensive family of carbonyl quinone structures to support the mechanism proposed by Wrighton and Mizen studied similar quinone structures showing that CO₂ undergoes reductive addition to chemically reduced 9,10-phenanthrenequinone, forming a biscarbonate dianion.[22] Later Stern et al. conducted theoretical calculations on 1,4-benzoquinone structures to support the mechanism proposed by Wrighton and Mizen.[23] Herein we conduct an analogous electrochemical reaction using a solid organic-pigment thin film, combining the advantages of electrochemistry with those of an organic solid active material. With this method, we were able to achieve CO₂ uptake values on par with amine-mediated capture and exceeding most reported carbon-based methods. To our knowledge, this is the only process reported working with such an efficiency level while operating entirely at room temperature.
pigments are reduced to form water-soluble anionic dyes which readily penetrate into fabrics. QNC and similar materials are known to be stable organic semiconductors as well.[26]

QNC films (100 nm thickness) deposited on indium tin oxide (ITO) coated glass slides are electrochemically reduced in an acetonitrile electrolyte solution. We found that the introduction of CO2 gas into the solution results in a reaction with the reduced QNC pigment, forming a QNC-carbonate anion with tetrabutylammonium (TBA) acting as the counterion, according to Figure 1a. Based on the experiments discussed herein, we propose the mechanism shown in Figure 1b.

CO2-loaded QNC films are stable over several hours in ambient conditions. The trapped CO2 can be released either by electrochemically oxidizing or heating the film. In all cases, Fourier transform infrared (FT-IR) measurements were used to quantify the amounts of captured and released CO2. We found that 20 wt % capture (20 g CO2/100 g QNC) is possible using this reduce-and-capture method, corresponding to CO2 uptake values of 2.28 mmol g\(^{-1}\) and 4.61 mmol g\(^{-1}\) in thermal and electrochemical cases, respectively. This figure of merit considers the weight of the active CO2-capturing quinacridone film alone, excluding weight of the glass substrate and electrodes. Especially in the electrochemical release case, the obtained value is higher than most of the literature values[8,11–13] and very close to the uptake efficiencies achieved by activation at higher temperatures and high pressures.[16,14,27] For comparison, the established aqueous amine-based capture processes are the most efficient available, and have an approximately 8 mmol g\(^{-1}\) CO2 uptake.[28] Although the monoethanolamine system is applied industrially, it is not energy efficient owing to the high heat capacity of the sorbent solution in combination with the required temperature swing to regenerate the sorbent. The method demonstrated herein has about half the uptake efficiency, but the energy input is mild in comparison: CO2 can be released by heating, beginning at roughly 40 °C (Figure 2a). CO2 can also be released by oxidation, using an overpotential of approximately 10 mV vs. Fe/Fe\(^{+}\) (Fe = [(η-C5H5)2Fe]; Figure 3). The processes are reversible and the same QNC films can be used over roughly five cycles efficiently, with the limiting factor being dissolution of quinacridone in the electrolyte over time.

For the capture of CO2 an electrochemical cell consisting of three electrodes: (ITO/QNC as working, Pt foil as counter, etc.)

Figure 1. a) Electrochemical formation of the QNC-dicarbonate salt. b) Proposed mechanism for electrochemical capture and release of CO2 using the QNC pigment. Hydrogen-bond stabilized carbonate salts are formed in the film.

Figure 2. a) Amount of released CO2 by increasing temperature that is, decarboxylation b) CV of a QNC film under N2 (blue), under CO2 (red) during formation of the carbonate salt, and again under N2 (green) after thermal release of CO2.
and Ag/AgCl (pseudo-reference which is calibrated against
the Fc/Fc⁺ couple) was used. The cell was purged with N₂ first
and the QNC-coated ITO electrode was submerged into the
solution. Cyclic voltammograms (Figure 2b) were recorded in
N₂-purged and CO₂-purged solutions. Upon purging with CO₂
the characteristic reduction peak of QNC at ≈1820 mV
diminished and the amount of cathodic current decreased
(Figure 2b). This phenomenon was related to the formation
of a QNC-carbonate salt (Figure 1b). To confirm that CO₂
diminished was observed to largely recover and electro-
chemical activity of QNC returned to the previous state
(green curve, Figure 2b). A control experiment of the same
system and time without heat treatment did not yield any
significant release of CO₂, thus the quinacridone-CO₂ adduct
is relatively stable. Likewise, heating quinacridone films that
had been stored under CO₂ did not yield any CO₂ capture/
release—thus electrochemical reduction is necessary for
reaction of CO₂.

After reduction and capture, CO₂ could also be released
by electrochemically oxidizing the film. This was observed by
mounting the electrochemical setup in a gas-tight vial. First,
a full scan ranging between −1900 mV and 1010 mV vs. Fc/
Fc⁺ was performed (Figure 3, blue curve), showing the
characteristic reduction and oxidation peaks for QNC. Then
the sealed vial was purged with CO₂ for 20 min and QNC was
reduced to capture the CO₂ (Figure 3, red curve following
capture). The vial was then purged extensively with N₂ to
avoid any remaining CO₂ from the previous experiment.
Scanning from 0 V towards positive potentials furnished a
new peak with onset around 10 mV, followed by the
characteristic oxidation peak of QNC at more positive
voltages (Figure 3, green curve). Using a gas-tight syringe,
a sample was taken from the headspace of the vial used
throughout the experiment and injected to the gas-cell
compartment of the FT-IR. The measurement confirmed
that captured CO₂ was released by electrochemical oxidation,
starting at around 10 mV. Cyclic voltammograms recorded
before, during, and after CO₂ capture are shown in Figure 3.
The amount of CO₂ released upon oxidation was found to be
2 ppm.

The molar ratio between QNC and released CO₂ was
calculated for both thermal and electrochemical release cases.
The amount of QNC in the film was calculated using the
dimensions of a film (width, length, height: 0.9 cm, 3 cm, 1 ×
10⁻³ cm) as 1.35 × 10⁻⁷ mol. For the thermal release case, the
amount of CO₂ was determined as 9.60 × 10⁻⁸ mol. Corre-
spondingly, the released amount in the electrochemical case
was found to be 1.94 × 10⁻⁷ mol. Molar ratios acting in CO₂
release were determined to be 0.70 and 1.43 for the thermal
and electrochemical CO₂ capture, respectively. In this respect
it can be concluded that the electrochemical release is more
effective than the thermal release. Next, based on these
results we cannot definitively determine the stoichiometry of
the reaction, that is, whether one or two carbonates attach to
each QNC molecule, as the reaction is likely more complete
at the surface of the film than in depth. Nevertheless it is
likely that there are two carbonate groups per QNC molecule
based on the 1.43:1 ratio found in the electrochemical release
case, and also based on the assumed formation of a dienolate
structure[25] in the QNC molecules. The carbonyl family of
dyes and pigments are known to undergo electrochemical
reduction owing to the electron-accepting properties of
conjugated segments with carbonyl groups. Like the better-
known indigoid and anthraquinone vat dyes,[24] QNC forms
a dienolate structure upon two-electron reduction.[25] We
propose that each enolate attacks a CO₂ molecule, forming
a dicarbonate structure that is stabilized by the extensive
hydrogen bonding in the QNC solid state. The ultimate
dicarbonate QNC carries a net −2 charge, with two tetrabu-
tylammonium counterions. The formation of such a salt
explains the disappearance of the cathodic behavior of QNC

Figure 3. Cyclic voltammograms of QNC upon electrochemical capture
and release of CO₂.

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upon exposure to CO2 during electrochemical reduction. This mechanism was proposed for CO2 reaction with the quinone in the work of Wrighton and Mizen.[22]

A disadvantage of using vat dyes is that they are soluble in their reduced forms. Thus, with successive cycles of capture and release, the quinacridone film will dissolve. The capture–release process was subjected to a cyclic stability test over 15 cycles and the system showed a decrease in the amount of released CO2 with each subsequent cycle. The highest amount of captured carbon dioxide is released at first cycle. By the 15th cycle the process is no longer measurable. To see the effects of water, we conducted experiments in aqueous electrolytes. However, the required potentials to reduce quinacridone are out of the electrochemical window of aqueous solvents hence the process is superseded by H2 evolution in water.

This direct electrochemical capture of CO2 is a low-energy, low-temperature process and the combination of the mild capture/release conditions with a nontoxic and cheap industrial pigment make this route potentially advantageous for carbon capture and utilization processes. To overcome the issue of solubility of the reduced species in the electrolyte, we are currently working on polymeric carbonyl vat dyes, with the ultimate goal of stable electrochemistry in aqueous media. The ‘old’ chemistry of organic dyes and pigments may indeed contain interesting and unexplored potential solutions to modern problems.

Received: March 23, 2014
Published online: May 21, 2014

Keywords: carbon dioxide capture · electrochemistry · organic pigments · vat dyes