Review of the Carbon Dioxide Splitting Patent Literature

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Increasing concentrations of carbon dioxide (CO_2) in the atmosphere have stimulated significant global research and development efforts regarding the reduction in CO_2 emissions from all point and non-point sources. In addition to technologies that do not use carbon feedstocks or which capture and "permanently" store CO_2 (*i.e.*, sequestration), there is considerable worldwide interest among the academic, industrial, and government communities regarding methods for dissociating waste stream carbon dioxide molecules into their constituent carbon and oxygen ("CO_2 splitting") atoms as a final "end-of-pipe" treatment option. This document presents a review of on-point issued and applied for patents in the field of carbon dioxide splitting.

Bockris applied for a US Patent with a priority date of March 22, 2005 entitled “Method and Device for Dissociating Carbon Dioxide Molecules.”[1] The intent of this invention is to thermal catalytically and/or electrochemically split carbon dioxide, and to use electrochemical methods to transport oxygen ions across a membrane and create a solid carbon residue inside the reactor. While the primary means of splitting CO_2 in this application appears to be electrochemical, the patent speaks to using elevated temperatures at the membrane interface where CO_2 is to be adsorbed and subsequently split, and thus also likely appears to contemplate potential thermal catalytic processes.

The abstract of this patent reads as follows:

"An apparatus is provided for dissociating carbon and oxygen from carbon dioxide molecules. The apparatus includes a thin plate made of a solid permeable ion-conducting membrane having a partial coating of platinum on a first side and ruthenium oxide on a second. An electric potential is applied between two surfaces of the membrane and the membrane heated by a heating element. Carbon dioxide gas is brought into contact only with the negatively charged first side of the membrane. The oxygen atoms are put under an electric field, separate from the carbon atoms and enter the membrane, and become oxygen ions. The ions are transported across the membrane to the positively charged side, where they lose their negative charge and exit the membrane as pure oxygen. The carbon does not pass through the membrane and is left behind. The carbon is detached from the membrane and collected as powder for use or disposal."

As noted in the patent's Detailed Description (emphasis added), "[t]he present invention … overcomes problems with the prior art by efficiently dissociating carbon dioxide molecules (CO_2) into the environmentally friendly elements of oxygen (O_2) and carbon (C). It is well known that CO_2 is a stable molecule and therefore difficult to dissociate. A thermodynamic analysis … of the standard free energy of formation of CO_2 from C and O_2 shows that the formation of CO_2 is highly favored and the reverse reaction <u>cannot occur unless forced to do so by means of an electrical potential</u> … The present invention utilizes a solid electrolyte, raised to a temperature of more than 1000°C, with an applied electric potential."

Thus, this patent does not address the direct uncatalyzed thermal gas-phase splitting of carbon dioxide, but rather considers the coupled thermal and electrochemical splitting of carbon dioxide at a solid-gas interface.

The three broadest claims are claims 1, 11, and 19 (emphases added).

Claim 1 states as follows:

"1. An apparatus for dissociating carbon dioxide molecules, the apparatus comprising:

an ion-conducting oxygen-permeable membrane having a first surface and a second surface opposite the first surface;

a power source for applying a first voltage to the first surface and a second voltage, which is greater than the first voltage, to the second surface; and

a chamber, mechanically coupled to the first surface, for containing CO_2 gas, such that the CO_2 gas within the chamber contacts the first surface of the membrane such that O atoms from the CO_2 gas contacting the first surface exit the second surface of the membrane."

Claim 11 states as follows:

"11. An apparatus for dissociating carbon dioxide molecules, the apparatus comprising:

membrane means for dissociating CO_2 gas into C and O atoms, the membrane means including a first surface for contacting the CO_2 gas and a second surface through which the O atoms exit; and

a power source for applying a first voltage to the first surface and a second voltage, which is greater than the first voltage, to the second surface so as to cause the membrane means to transport the O atoms from the first surface to the second surface."

Claim 19 states as follows:

19. A <u>method</u> for dissociating carbon dioxide molecules, the method comprising the steps of:

"heating an ion-conducting membrane having a first surface and a second surface opposite the first surface;

applying a first voltage to the first surface of the ion-conducting membrane;

applying a second voltage, which is greater than the first voltage, to the second surface of the ion-conducting membrane; and

contacting carbon dioxide gas with the first surface of the ion-conducting membrane."

This patent application appears to have received an unfavorable review by the International

Searching Authority (ISA) acting on behalf of the World Intellectual Property Organization (WIPO), which held that while the content was novel and had industrial applicability, all claims lack an inventive step as being obvious over previous US patents.

Claims 1, 11, and 19 by Bockris were held obvious as Joshi [2] teaches the following: (a) an ion-conducting oxygen-permeable membrane having a first surface and a second surface opposite the first surface; (b) a power source for applying a first voltage to the first surface and a second voltage, which is greater than the first voltage, to the second surface; and, (c) a chamber, mechanically coupled to the first surface, for containing O_2 gas, such that the O_2 gas within the chamber contacts the first surface of the membrane such that O atoms from the O_2 gas contacting the first surface exit the second surface of the membrane. Joshi's patent refers to "[a] leak detector employing … an oxygen ion-conducting membrane", demonstrating the breadth of prior patent art considered in the obviousness test for Bockris' application.

While Joshi does not teach an apparatus for dissociating CO_2, or that the chamber contains CO_2, the search authority held that Gomberg [3] does teach dissociating CO_2 gas in a chamber (albeit using radiolytic methods), and that it would have been obvious to one of ordinary skill in the art to combine the teachings of Joshi with those of Gomberg to provide Bokris' apparatus for dissociating CO_2 molecules. The remaining more specific dependent claims of Bokris were rejected as obvious using similar reasoning.

Claim 23 of Bokris utilized a method of removing solid carbon deposits from the membrane, and the search authority held that while neither Gomberg nor Joshi teach on this subject, that

Rankin [4] teaches a method of removing carbon deposits from a surface (a coke oven ascension pipe), and that it would have been obvious to combine the teachings of Gomberg, Joshi, and Rankin to develop a method for dissociating CO_2 molecules, separating the oxygen from the reactor using an oxygen selective membrane, and collecting and removing the solid carbon product from the reactor interior.

The ISA decision on Bokris appears to have set a high obviousness standard for CO_2 splitting patent applications. While Bokris' method proposed thermal catalytic and/or electrochemical methods to split carbon dioxide, the authority appears to have held that Gomberg's use of radiolytic CO_2 dissociation made alternate means of splitting CO_2, as in Bokris, obvious. This implies that all non-catalytic and catalytic means (*e.g.*, thermal, electrochemical, radiolytic, etc.) of splitting CO_2 are obvious by way of Gomberg. Gomberg also appears to only contemplate the partial dissociation of CO_2 to CO and O_2 (*e.g.*, $CO_2 \rightarrow CO + ½O_2$), and thus the search authority extended their obviousness argument in Bokris to the complete splitting of CO_2 to C and O_2.

Similarly, the authority held that prior use of oxygen-selective membranes (such as zirconia) for leak detectors made the use of these membranes obvious for selectively removing oxygen from a CO_2 splitting reactor. Finally, the authority also held that prior use of carbon cleaning systems in coke oven ascension pipes made obvious the use of carbon collection systems in a CO_2 splitting reactor.

It is also of note that the search authority did not need to refer to the prior art in the peer-reviewed literature for their obviousness decision in Bokris. As is discussed in the companion paper to this review, the peer-reviewed literature sets compelling obviousness issues for CO_2 splitting patent applications due to the extensive work conducted in this field over the past several decades.

With the decision in Bokris seeming to hold obvious all means of splitting CO_2, the recent patent application by the Global Research division of General Electric (Ku *et al.* [5]) appears to be the test of whether catalytic means of splitting CO_2 will be held obvious based on the decision in Bokris. In their patent, Ku *et al.* disclose "a multifunctional catalyst systems comprising a substrate; and a catalyst pair disposed upon the substrate; wherein the catalyst pair comprises a first catalyst and a second catalyst; and wherein the first catalyst initiates or facilitates the reduction of carbon dioxide to carbon monoxide while the second catalyst initiates or facilitates the conversion of carbon monoxide to an organic compound." Claim 1 is the broadest in this application, and is equivalent to the disclosure quoted above.

Ku *et al.* likely contemplates the splitting of CO_2 to CO and O_2, but the restriction of the second catalyst facilitating the conversion of carbon monoxide to an organic compound suggests that the splitting of CO to C and O_2 may not be contemplated. Organic compounds are generally defined as those containing carbon and hydrogen, and may not include solid carbon phases such as graphite and amorphous carbon. Reverse water gas shift and Fischer-Tropsch reactions are contemplated in the application, further suggesting that the second catalyst is likely not for the splitting of CO to C.

While this may appear to be a "loophole" in the Ku *et al.* application, several mitigating factors warrant caution in this regard. Obviousness issues, technical difficulties, and previous peer-reviewed literature may have played a role in restricting the scope of the claims. The obviousness issues in Bokris may have been felt by General Electric to apply to all attempts to split CO_2 to carbon and oxygen, whether they be thermal, radiolytic, electrochemical, or catalyzed, or any combination of these. As well, General Electric may have not been able to achieve the complete splitting of CO_2 to C and O_2 using any studied catalyst systems. However, as noted above and based on the broad prior art used, the decision in Bokris also appears to contemplate as obvious any attempt to split CO_2 to C and O_2. The decision in Ku *et al.* will be interesting, as it will determine whether the decision in Bokris did indeed contemplate all forms of splitting CO_2 as obvious by way of Gomberg.

The pending decision on Ku *et al.* may also depend not only on the prior art in peer-reviewed literature and the decision in Bokris, but also on a Canadian patent by Iwanami *et al.*[6] This patent teaches, in its broadest claim, "a catalyst for the reduction of carbon dioxide comprising a transition metal on zinc oxide alone or on a composite containing zinc oxide and at least one metal oxide of a metal selected from the metals in Group IIIb and Group IVa in the Periodic Table." Although the chemical makeup of the catalyst in Iwanami *et al.* appears specific, in concert with the prior art from the peer-reviewed literature, the pending application by Ku *et al.*, and the decision in Bokris, catalytic splitting of CO_2 appears to be a difficult area with regard to obviousness issues.

Given the usual test standards for obviousness, it could reasonably be construed that patents in this area are subject to a higher standard because of the global importance of the carbon dioxide issue. Authorities may be hesitant, on policy grounds, to issue broad-ranging patents for CO_2 splitting in order to prevent a worldwide reluctance towards adopting feasible treatment methods because of the high patent licensing costs that may accrue.

References

[1] Bockris, B. "Method and Device for Dissociating Carbon Dioxide Molecules." *United States Patent Application 2006/0213782 A1*. Filed March 22, 2005.

[2] Joshi, A.V. "Leak Detector." *United States Patent 4674321*. Filed December 6, 1985.

[3] Gomberg, H.J., Lewis, J.G., Powers, J.E. "Radiolytic Dissociative Gas Power Conversion Cycles." *United States Patent Re. 31697*. Reissued October 9, 1984.

[4] Rankin, R.C. " Apparatus for cleaning coke oven ascension pipe." *United States Patent 4039393*. Filed July 21, 1976.

[5] Ku, A.Y.C., Ruud, J.A., Manoharan, M., Kool, L.B., Martins-Loureiro, S.P., Blohm, M.L., Norman, B.G. "Reactor for Carbon Dioxide Capture and Conversion." *United States Patent Application 2007/0149392 A1*. Filed December 22, 2005.

[6] Iwanami, H., Yoshizawa, T., Suzuki, T. "Catalyst for Reduction of Carbon Dioxide." *Canadian Patent 2126502*. Filed June 25, 1993.