

Review of Novel Methods for Carbon Dioxide Separation from Flue and Fuel Gases

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Introduction

The President recently announced the U.S. Global Climate Change Initiative (GCCCI) to reduce greenhouse gas (GHG) intensity by 18% by 2012.¹ The GCCCI proposal would slow the growth in U.S. emissions of carbon dioxide. Alkaline sorbents and scrubbing solutions are often employed to separate carbon dioxide from various gas matrices. Cryogenic separation of carbon dioxide is also commonly used. A comprehensive review of carbon dioxide capture methods is given by White.²⁻⁴ Novel methods could have the potential to reduce the cost of carbon dioxide sequestration. These methods include electrochemical, membrane, enzymatic, photosynthesis, and catalytic routes for CO₂ separation or conversion.²⁻⁵

This paper reviews some of the more novel methods for carbon dioxide separation from flue and fuel gas streams. These methods include electrochemical pumps, photosynthesis, membranes, and biomimetic-enzyme approaches to CO₂ separation. Electrochemical pumps discussed include carbonate and proton conductors. The various bioreactors employed for photosynthesis are surveyed. Selective membranes for hydrogen separation are discussed as a method for carbon dioxide concentration in fuel gas streams. The selective membranes include mixed ionic-electronic (solid electrolyte-metal) films as well as palladium-based materials. Biomimetic methods utilizing the enzyme carbonic anhydrase are reviewed. The fundamental mechanisms behind these techniques will be explained, and recent advances in these methods are emphasized. Future research directions are suggested and an extensive list of references is provided.

Electrochemical Pumps for Separation of CO₂ from Flue Gas

Carbonate Ion Pumps

The molten carbonate and aqueous alkaline fuel cells have been studied for use in separating carbon dioxide from both air and flue gases.⁶⁻¹³ Operation of the molten carbonate fuel cell in a closed circuit mode (with application of an external emf) will result in the transport of carbonate ions across the membrane.⁶⁻¹³ The molten carbonate electrochemical separator requires oxidizing conditions for the formation of carbonate from carbon dioxide, and is less applicable for direct separation of CO₂ from fuel gases. This pioneering work was first performed by Winnick.⁶⁻⁸ Winnick proposed the use of molten carbonate fuel cell membranes for separation of carbon dioxide from air for space flight (Sky Lab).⁶⁻⁸ Winnick first examined molten carbonate membranes for separation of CO₂ from power plant flue gas.⁶⁻⁸ More recently the Osaka Research Institute in Japan, British Petroleum in the UK, and Ansaldo Fuel Cells in Italy have also experimented with molten carbonate electrochemical systems for CO₂ capture from flue gas.⁹⁻¹³

There are several advantages of molten carbonate electrochemical cells for CO₂ separation. A large knowledge base exists for the use and application of molten carbonate from its use in fuel cells. Molten carbonate is nearly 100% selective for the transport of carbonate anions at elevated temperatures. It exhibits high conductivity of around 1 S/cm at 1100EF, or equivalently a diffusivity of 10⁻⁵ cm²/sec for the carbonate anion.⁶⁻⁸ The parasitic power requirements for the separation of carbon dioxide from power plant flue gases are low and estimated to be less than 5%.⁸ The cost

for CO₂ capture from flue gas was estimated at \$20/ton in 1990 by Winnick.⁸

Unfortunately there are major disadvantages in the application of molten carbonate electrochemical cells for separation of carbon dioxide from power plant flue gas. Molten carbonate is a corrosive paste. The high temperatures, along with the extremely corrosive nature of the molten carbonate, make fabrication and handling extremely difficult. The small applied voltages allowable in order to avoid decomposition of the molten carbonate result in low currents. The current represents the flux of carbonate anions across the membrane. This necessitates the use of huge stacks to obtain a significant flux of carbonate ions across the device.⁸⁻¹³ Sulfur dioxide present in flue gas poisons the cell, resulting in sulfate formation.⁸⁻¹³ There are also severe problems with electrolyte segregation and electrode degradation in the severe high temperature flue gas environment.⁸⁻¹³

A solid electrolyte membrane for the separation of carbon dioxide from flue gas could solve many of the problems associated with molten carbonate.¹⁴⁻¹⁶ Solid electrolytes are solid ionic conductors, and are used in sensors, catalyst studies, and fuel cells.¹⁷ Millions are used in automobiles as the oxide air-fuel ratio sensors. Most solid electrolytes are ceramics. Solid electrolytes often operate at lower temperatures than molten carbonate cells. A solid electrolyte would be easier to handle, have far reduced corrosion problems, and would possess a longer operating life than its molten carbonate counterpart. The development of a highly conductive carbonate ion solid electrolyte is an area of active research.¹⁴⁻¹⁶ The possibility of using alkali carbonate or alkaline earth carbonate solid electrolytes for the separation of carbon dioxide from flue gas is discussed by Granite.¹⁴⁻¹⁶ Granite and Pennline propose doping alkaline earth carbonates in order to increase the ionic conductivity by orders of magnitude.¹⁴⁻¹⁶ Recent evidence suggests that it will be difficult to obtain mobile carbonate anions within a solid electrolyte matrix.

Electrochemical Pumps for Concentrating CO₂ from Fuel Gas

Proton Pumps

Hydrogen gas can be produced by IGCC plants, steam gasification reactions, the pyrolysis of coal, the electrolysis of water, and biochemically. Each of these processes generate hydrogen with associated impurities, such as carbon monoxide, carbon dioxide, methane, nitrogen, water, and oxygen. Oxygen must be removed from hydrogen streams in order to avoid explosion hazards.

Previous hydrogen purification processes involved the step-wise removal of the impurities through absorption processes such as MEA (ethanolamine) washing to remove the carbon dioxide, TEG (glycol) dehydration of the gas, as well as the catalytic (Pt) removal of trace oxygen. A far simpler and potentially more cost-effective means of hydrogen separation and carbon dioxide concentration can be accomplished in one step by an electrochemical pump.¹⁷⁻²² These electrochemical pumps are efficient, silent, and non-polluting. The electrochemical pumps can be based upon the readily available β -alumina, nafion, and barium cerium oxide solid electrolytes.¹⁷⁻²² An analysis of the electrochemical hydrogen pump, similar to the analysis of the carbon dioxide pump above, follows

The application of an external EMF (voltage) to a proton-conducting solid electrolyte through a closed circuit will cause hydrogen to be selectively transported (pumped) to/or from a metal electrode. The rate of hydrogen transport is given by the current

(flux of protons) across the membrane as:

$$\text{flux of H}_2 = I/2F \quad (1)$$

where F is Faraday's constant, 96,487 coulombs/mole.

There are several factors which limit the transport of hydrogen (current) across the membrane, and these are the conductivity of the electrolyte, thermodynamic stability of the electrolyte, and the electrode kinetics.

For an ohmic membrane ($V = IR$), current is inversely proportional to the resistance or proportional to the conductivity. The doped barium cerium oxide, $\text{BaCe}_{0.9}\text{Y}_{0.1}\text{O}_{2.95}$, has a conductivity of $10^{-1} \text{ ohm}^{-1}\text{cm}^{-1}$ at 1832EF.¹⁸⁻²⁰ The conductivity of β -alumina is $10^{-6} \text{ ohm}^{-1}\text{cm}^{-1}$ at 212EF.^{17,21-22} Nafion (polymer electrolyte) is typically employed at temperatures of around 212EF. The higher conductivity of the doped barium cerium oxide allows a higher flux of protons to be pumped to a metal electrode.

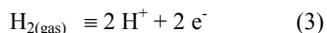
The maximum value for the applied external voltage is determined by the decomposition potential of the solid electrolyte. This is found from the thermodynamic stability, the free energy of formation, ΔG_f , of the material, namely:

$$\Delta G_f = -nFE \quad (2)$$

where E is the maximum applied voltage.

More stable electrolytes can be subjected to higher applied voltages. Typically a one to two volt potential can be applied to a ceramic membrane. Therefore, the rate of transport of protons across the membrane is limited by both the conductivity (resistance) and stability of the electrolyte.

Electrode kinetics also plays a key role in the rate of separation of hydrogen. Consider the example of a closed β -alumina electrochemical cell having palladium electrodes. Hydrogen must be first adsorbed from the impure gas stream on to the palladium electrode. Hydrogen then dissociates to hydrogen atoms. Charge transfer occurs, with protons forming. The protons migrate across the electrolyte under the influence of the externally applied field (voltage). Finally, the protons reverse the earlier steps, and form hydrogen gas at the opposite palladium electrode. At the interface between the gas, metal electrode, and solid electrolyte (the three-phase boundary), the overall reaction can be written as:



Therefore an electrode must efficiently adsorb and dissociate hydrogen so as to not limit the rate of hydrogen transport across the electrolyte. The electrode must be porous to allow gas to diffuse in and out, yet continuous, to avoid short-circuits. Electrodes can be formed by thermal decomposition of organometallic precursor compounds on the electrolyte surface or with metal pastes.

The overall resistance of the pump is the sum of the resistances due to the electrode, electrolyte, and the electrode and electrolyte contact. Overall resistance can be minimized by: 1. use of a thin electrolyte and electrodes, 2. having intimate contact between electrode and electrolyte, and 3. selecting an electrolyte with high conductivity.

The power consumed by the membrane separator is given by:

$$\text{Power} = VI = I^2R$$

For the lab-scale separator, with an applied voltage of around one volt, and a resulting current in the milliamp range, the power requirements will be on the order of milliwatts. Granite and Jorne applied external voltages to β -alumina and barium cerium oxide membranes to obtain the selective transport of deuterium from $\text{D}_2\text{-N}_2$ mixtures.^{17, 21-22} Balachandran recently applied an external voltage to a yttria-doped barium cerium oxide membrane to obtain the selective transport of protons.¹⁸⁻²⁰ The mechanism of proton conduction by $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ is discussed by Balachandran.²⁰

Conclusions

The novel CO_2 capture technologies have advantages and disadvantages when installed in a power-generation system. Initial evaluations by Herzog²³ indicate that certain technologies for CO_2 control from flue gas from conventional PC-fired power plants create a substantial thermal efficiency power loss. A study by Kosugi²⁴ investigated the various technologies by using a graphical evaluation and review technique. The target CO_2 capture technologies were compared for different levels of development. Although some of the technologies presently have larger penalties than others, future research and development will improve the projected energy efficiencies.

Electrochemical membranes have the potential to economically separate carbon dioxide from flue gas. Material science issues such as reducing corrosion (molten carbonate pumps) and increasing conductivity (solid electrolyte pumps) need to be addressed. More research on electrochemical methods for the separation of carbon dioxide from flue and fuel gases is recommended.

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