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CO2 Summit II: Technologies and Opportunities

Electrochemical Membrane Technology for Carbon Dioxide Capture from Flue Gas

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Abstract

To address concerns about climate change resulting from emission of CO₂ by fossil-fuel power plants, FuelCell Energy, Inc. (FCE) has developed Combined Electric Power and Carbon-dioxide Separation (CEPACS) system concept. The CEPACS system utilizes Electrochemical Membrane (ECM) technology derived from the Company's Direct FuelCell[®] products. The system separates the CO₂ from the flue gas of other plants and produces electric power using a supplementary fuel. FCE is currently evaluating the use of ECM to cost effectively separate CO₂ from the flue gas of Pulverized Coal (PC) power plants under a U.S. Department of Energy contract. The overarching objective of the project is to verify that the ECM can achieve at least 90% CO₂ capture from the flue gas with no more than 35% increase in the cost of electricity. The project activities have included: 1) techno-economic analysis for an ECM-based CO₂ capture system applied to a 550 MW existing PC plant, 2) laboratory scale operational and performance tests of a membrane assembly, 3) performance tests of the membrane to evaluate the effects of impurities present in the coal plant flue gas, and 4) bench scale testing of an ECM-based CO₂ separation and purification system.

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1. Introduction

FuelCell Energy, Inc. (FCE), in collaboration with AECOM Corporation and Pacific Northwest National Laboratory (PNNL), is developing a novel Combined Electric Power and Carbon-dioxide Separation (CEPACS)

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system [1]. The CEPACS system is based on electrochemical membrane (ECM) technology derived from FCE's carbonate fuel cell products featuring internal (methane steam) reforming and carrying the trade name of Direct FuelCell® (DFC®). The CEPACS system separates the CO₂ from the exhaust of other plants such as an existing coal-fired plant. The development effort is being carried out under a cooperative agreement with the U.S. Department of Energy (DOE). The overall objective of this project is to successfully demonstrate the ability of FCE's ECM-based CEPACS system technology to separate $\geq 90\%$ of the CO₂ from a simulated Pulverized Coal (PC) power plant flue gas stream and to compress the captured CO₂ to a state that can be easily transported for sequestration or beneficial use. In addition, a key objective is to show, through Technical and Economic Feasibility Study and bench scale testing, that the ECM-based CEPACS system is an economical alternative for CO₂ capture in PC power plants, and that it meets DOE's objective related to the incremental cost of electricity (COE) for post-combustion CO₂ capture (no more than 35% increase in COE). The operational principle of ECM cell and the process concept for CEPACS system are briefly described here.

1.1. Electrochemical Membrane Technology - Operational Principle, Attributes and Status

The operating principle of the ECM cell, including the mechanism for transport of CO₂ (by migration of carbonate ions through electrolyte) from the cathode to the anode of the cell, is shown in Fig. 1, along with the electrochemical reactions.

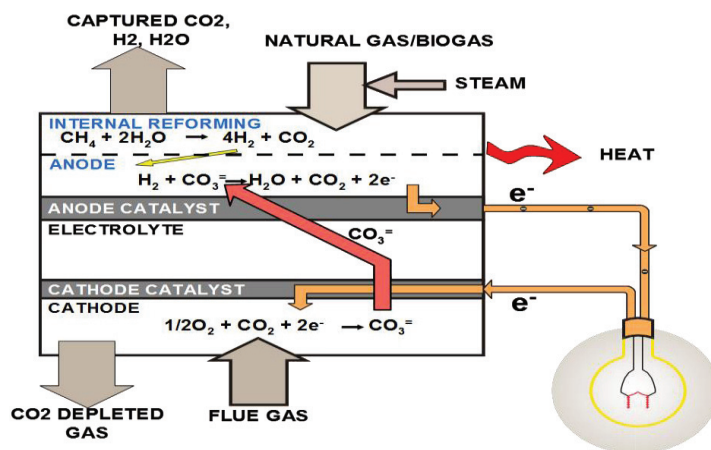


Fig. 1. Transport of CO₂ in the Electrochemical Membrane Cell: CO₂ is used at cathode as an oxidant and transferred to anode via carbonate ions

The flue gas from an existing power plant, containing CO₂, is fed to the cathode side of the cell. A supplemental fuel is supplied to the anode side of the cell. The ECM technology is compatible with numerous methane-containing fuels such as: coal and biomass derived syngas, natural gas (NG), and biogas (e.g. anaerobic digester gas). Natural gas has been assumed as the supplemental fuel source for this study. Due to the internal reforming capability of the ECM cell, methane in the fuel is converted (steam reformed) into hydrogen according to the following reaction:



Hydrogen is used as a reactant at the anode. Carbon dioxide and oxygen present in the flue gas are used as reactants at the cathode. The electrochemical reaction at the ECM cell cathode (Fig. 1) involves the formation of carbonate ions (CO₃²⁻) by combination of O₂, CO₂ and two electrons. Carbonate ions produced at the cathode migrate to the anode side via the electrolyte in the cell. At the anode, the reaction of carbonate ion with H₂ produces H₂O, CO₂ and two electrons. The internal transport of carbonate ions in the ECM cell and the flow of electrons in the external circuit results in power generation as a consequence of the CO₂ separation process. DC power produced is converted to AC power using an inverter. The operating mechanism of the ECM cell results in the separation (from flue gas) and transfer of CO₂ into the anode exhaust stream which has a much reduced volumetric flow

compared to the flue gas stream. The CO₂-rich anode exhaust gas is further processed in the ECM-based CEPACS system to purify the CO₂ for sequestration, as described in the CEPACS system process concept that follows.

The ECM cell operates at 550-650°C and atmospheric pressure. Unlike the conventional membranes, the driving force for CO₂ separation in an ECM cell is electrochemical potential, not pressure differential across the membrane. Therefore, pressurization of flue gas is not required. ECM offers complete selectivity for CO₂ compared to N₂ present in the flue gas. Fast electrode kinetics at the operating temperature make ECM suitable for flue gases containing from 3 to over 20 vol% CO₂, typical of coal or natural gas-fired plants. Because of planar geometry and large gas flow channels, ECM can process large flow rates of flue gas without significant back pressures (pressure drop in the range of 5-8 cm of water column). The ECM membrane is fabricated from inexpensive organic materials and is a modular technology. Planar ECM cell assemblies can be stacked and incorporated into MW-scale modules. The technology offers ease of scale-up and transport. It is suitable for incremental phased applications to almost any type of CO₂-emitting plant. ECM module commercialization is expected to be heavily leveraged by FCE's DFC commercialization experience. FCE's global DFC manufacturing capacity is 200 MW per year.

1.2. CEPACS System – Process Concept

FCE has developed the CEPACS system concept (US Patent 7,396,603 B2) as a novel solution for greenhouse gas emission reduction. A simplified diagram of the CEPACS system concept is shown in Fig. 2.

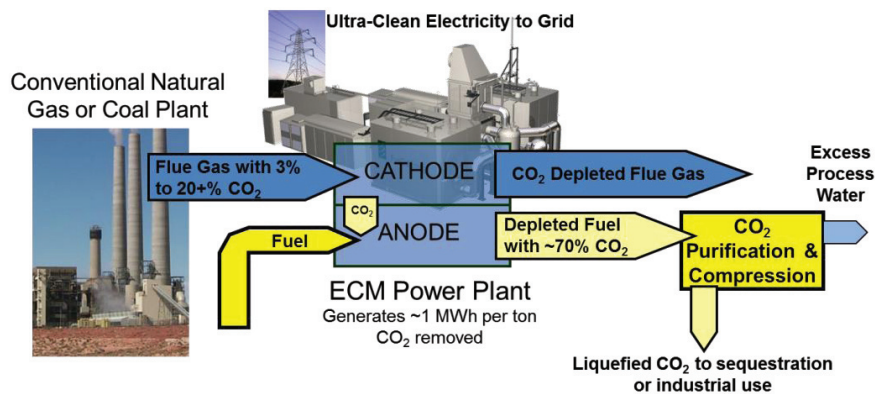


Fig. 2. CEPACS CO₂ Separation and Power System Concept: The system can be used with a variety of CO₂-containing greenhouse gases

CO₂-containing flue gas from a fossil fuel power plant, such as the exhaust from a PC power plant or other industrial source, is utilized as the oxidant for the ECM cathode. A supplementary fuel such as natural gas is internally reformed in the cell to provide the hydrogen needed to complete the electrochemical power generation cycle. The CO₂-rich anode exhaust gas is processed (post-processing) in the ECM-based CEPACS system to further concentrate and compress the CO₂ for sequestration. The H₂O (product of ECM anode-side electrochemical reaction) is removed by simple condensation during downstream processing. There is also some unused fuel (mainly H₂) in the CO₂-rich anode exhaust stream. This remaining H₂ is separated by liquefaction of the CO₂. After the water has been condensed out and the H₂ removed, the resulting CO₂-capture stream is ready for compression (pumping of supercritical fluid) and sequestration. The CO₂-lean cathode exhaust (flue gas after CO₂ removal) is vented to atmosphere after recovering the heat for process use (e.g. preheating of feed streams, steam generation). Water condensed during post-processing of the CO₂-rich anode exhaust stream is used to provide water (steam) needed for internal reforming of CH₄ in supplementary fuel, eliminating the need for external process water. H₂ separated during post-processing of CO₂-rich anode exhaust stream is recycled to provide additional preheat in the system and as part of the supplementary fuel (thereby reducing NG fuel needed).

The key difference between the ECM-based CEPACS system technology, and existing membrane and amine scrubbing technologies (competing technologies) is that electric power is produced during the CO₂ separation process in the ECM-based system. This synergistic coupling of the separation of CO₂ from flue gas of an existing plant and the production of clean electric power is unlike any other carbon capture technology.

2. Case Study: CEPACS System for 90% CO₂ Capture from 550 MW Reference PC Plant

In this study, a reference 550 MW (net AC) Pulverized Coal Rankine Cycle power plant was retrofitted with an ECM-based CEPACS plant to capture and compress >90% of the CO₂ (for sequestration or beneficial use) from the PC plant's flue gas. The study was conducted in accordance with the U.S. DOE – NETL (National Energy Technology Laboratory) report entitled 'Cost and Performance Baseline for Fossil Energy Plants, Volume 1: Bituminous Coal and Natural Gas to Electricity, Revision 2' [2], and was specifically focused on developing technical and economic comparisons to Cases 9 and 10 of the referenced report. Fig. 3 shows a block flow diagram of the CEPACS process applied to the reference PC plant. Flue gas from the PC plant bulk Flue Gas Desulfurization (FGD) unit is first passed through a secondary polishing FGD unit to reduce total sulfur to less than 1 ppmv. The cleaned flue gas is then preheated before it enters the ECM modules. Within the ECM modules, CO₂ is transferred from the cathode side to the anode side of the membrane. The CO₂-depleted flue gas (cathode exhaust) is then exhausted to the atmosphere. NG is supplied as a supplemental fuel (along with steam) to drive the CO₂ separation in ECM modules, producing additional electric power in the process. The ECM-separated CO₂-rich stream (anode exhaust) is cooled (to condense out water vapor), compressed and chilled to liquefy CO₂ and to separate H₂ from the stream. The water recovered is used for steam (required for NG reforming) generation. In this study, the separated H₂ is recycled internally within the system. However, the CEPACS system could be easily configured for co-production of H₂ as a value-added product. The liquid CO₂ stream is then easily pressurized (via pumping) for sequestration or beneficial use.

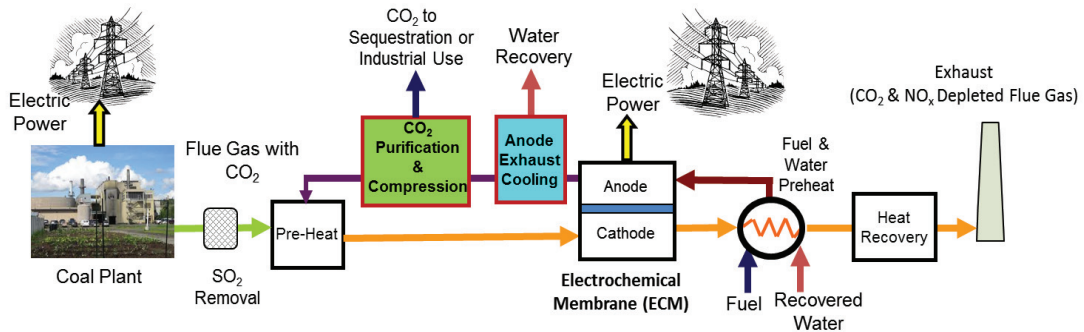


Fig. 3. Block Flow Diagram of CEPACS System Applied to a 550 MW Pulverized Coal Plant.

The system configuration, simulations and analyses were performed using CHEMCAD process simulation software to guide the conceptual design of the CEPACS plant. Process simulations were developed based on ECM performance realized in lab-scale testing. Technical information provided by leading balance-of-plant equipment manufacturers was utilized for system analyses. The performance assessment included estimation of the parasitic power consumption for >90% CO₂ capture and compression, and the efficiency impact on the PC plant. The ECM-based CEPACS system applied to the 550 MW PC plant simultaneously generates 421 MW of additional (net AC) power (after compensating for the auxiliary power requirements of CO₂ capture and compression) while capturing >90% of CO₂ from the flue gas. The CO₂ emissions from the plant are 107 lb/MWh, a 94% reduction from the reference plant. The net electrical efficiency of the PC plant equipped with a CEPACS system (for CO₂ capture) was estimated to be 39.0% (based on higher heating values of coal and NG fuels used by PC plant and CEPACS plant, respectively). This represents a 6.0% increase in the net electrical efficiency compared to that of the baseline PC plant without CO₂ capture.

The economic feasibility study included estimation of CEPACS plant capital cost, cost of electricity analyses and estimation of cost per tonne of CO₂ captured and avoided. AECOM Corporation developed the cost estimates through a combination of vendor quotations and historical equipment costs from their in-house database. The rigorous economic analysis was performed in accordance with published DOE-NETL guidelines [3]. Fig. 4(a) shows the COE with component breakdown and Incremental COE (Case 1 basis) calculated for each case in year 2007 US dollars (USD). The CEPACS-equipped PC plant configuration (Case 3) offers the lowest COE of all cases with carbon capture, at 80.4 mills/kWh. The incremental COE for Case 3 is 35.4%. Fig. 4(b) shows the estimated costs of

CO₂ captured and avoided, presented in year 2011 USD for comparison against DOE targets. The CEPACS system cost of CO₂ captured (\$38.46/tonne) meets the DOE target of less than \$40/tonne (2011 USD). The cost of CO₂ captured for the CEPACS-based process is 27.2% lower than that for the Econamine-based process (Case 2).

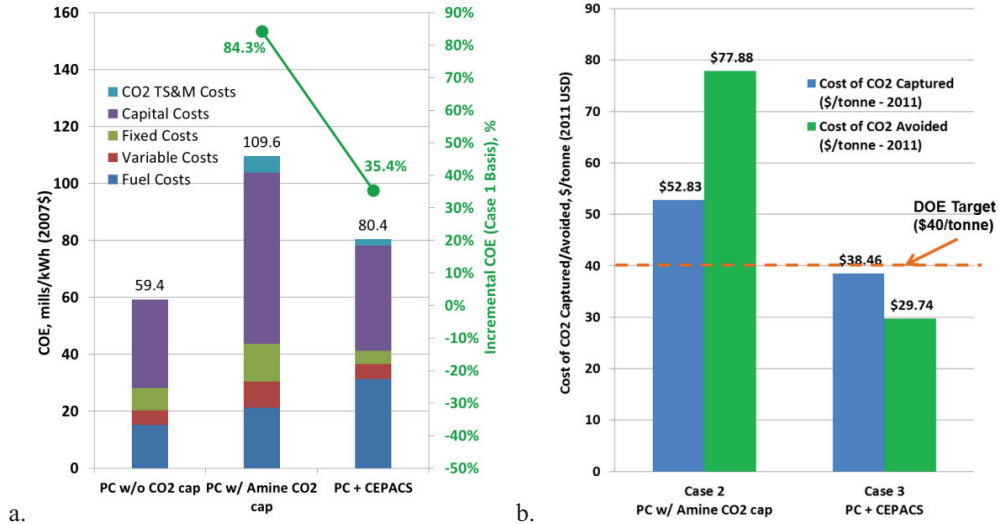


Fig. 4. (a) Cost of Electricity and Incremental COE Comparison. (b) Comparison of CO₂ Captured and Avoided Costs.

3. Lab-Scale ECM Technology Demonstration

Performance of FCE’s molten carbonate fuel cell (MCFC), at ECM conditions, was demonstrated through single cell testing. The performance evaluation utilized a 250 cm² active area cell in FCE’s Single Cell Test Laboratory. After completing preliminary qualification testing, system parametric testing was conducted to validate and optimize system operating conditions based on the fuel cell performance. The testing included variations in cell operating temperature, fuel and CO₂ utilization, current density, and cathode and anode inlet gas compositions. The cathode inlet compositions used for testing simulated the pulverized coal and natural gas combined cycle power plant flue gases (13.5% and 4% CO₂, respectively). The characteristic cell performance curves for NG-derived and coal-derived flue gases are shown in Fig. 5. Throughout the demonstration; cell performance, CO₂ flux, and the percentage of CO₂ transferred from the cathode side to the anode side were characterized. The parametric testing successfully demonstrated the ability to transfer more than 90% of the CO₂ from the cathode to the anode at a wide range of flue gas compositions and operating temperatures.

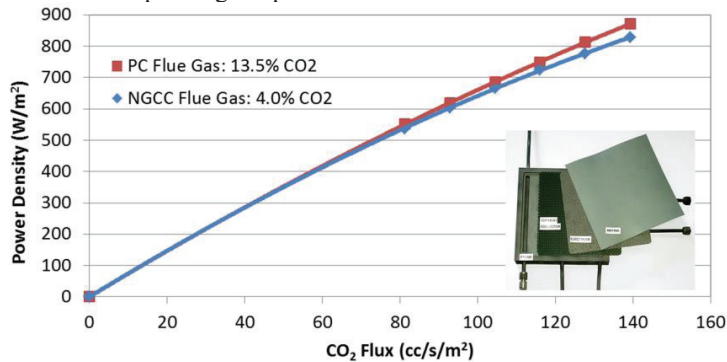


Fig. 5. MCFC (ECM Cell) power density and CO₂ flux performance for NGCC and PC-based flue gases

In addition to having the ability to selectively transfer CO_2 from one side to the other side of the cell while also producing clean and useable energy, FCE's MCFC technology has the tertiary ability to destroy NO_x components in the flue gas. The expected NO_x destruction mechanism is that the NO_x reacts with the carbonate ion and oxygen in the cathode to form nitrates and nitrites that pass through the cell electrolyte by means of the electrochemical reaction during normal operation. These nitrates and nitrites then react with H_2 and CO_2 at the anode, converting into inert N_2 . The NO_x destruction ability was demonstrated in 250 cm^2 active area cell testing by increasing concentrations of NO and NO_2 into the cathode inlet stream while the anode and cathode outlet streams were evaluated using a Thermo chemiluminescent NO_x analyser. The demonstration determined that more than 70% of NO_x was destroyed at high inlet NO_x concentrations of over 200 ppm. These results are shown in Fig. 6.

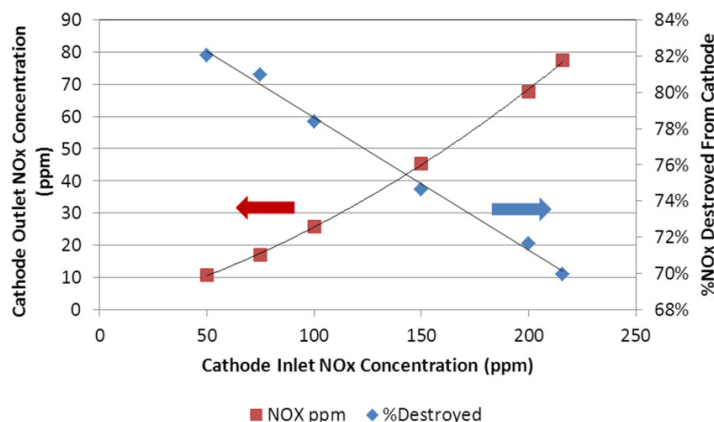


Fig. 6. NO_x destruction in MCFC (ECM cell) at 110 mA/cm^2 while transferring 92.5% CO_2 from cathode side to anode side

4. Contaminant Effect Evaluation

To determine the interaction of contaminants found in the flue gas of the host plant with the ECM, a series of tests were performed exposing button-cells to known concentrations of contaminant species. This testing performed by PNNL focused on SO_2 , HCl , Hg and SeO_2 , species typically found in PC plant flue gas. The test set up comprised a MCFC (ECM cell) fixture with reference electrodes, containment furnace, and gas and cell current controls. Cells were operated at 650°C and current densities ranging from 50 to 160 mA/cm^2 , in constant current mode. Cell performance degradation was tracked by changes in the resultant cell voltage over the testing period. Additional *in situ* cell evaluation was performed with electrochemical impedance spectroscopy, to identify contaminant effect on specific electrodes. Experimental work to determine if the impurities affect the button cell performance included assessment as a function of concentration and exposure time. Tests with 0.4 - 1 ppmv SO_2 (in simulated PC plant flue gas used as cathode feed) included a cell operated at a constant CO_2 flux of $176 \text{ scc/m}^2/\text{s}$. A steady state was established after ~400 hours of testing, after which no noticeable changes in performance were observed over the remaining 300 hours of testing, even when the SO_2 concentration was increased from 0.4 to 1.0 ppmv. In another test, the ECM was subjected to 10 ppmv SO_2 concentration (simulating an upset in the flue gas cleanup system) for periodic durations of up to 1000 minutes. While the cell performance declined at the high SO_2 levels, upon returning the SO_2 concentration to a 1 ppmv baseline level, cell performance was shown to be fully recoverable. The test results are shown in Fig. 7. CO_2 flux remained constant throughout the tests.

In a button cell test with 0.2 ppm HCl in flue gas (ECM cathode feed gas), no measurable cell degradation (at 80 and 160 mA/cm^2) was observed during a 915-hour experiment. No performance losses were observed in tests of up to 1100 hours (at 110 mA/cm^2 and 650°C) due to the presence of 250 ppb $\text{Hg}(\text{g})$ in flue gas and up to 750 hours with 250 ppb $\text{Hg}(\text{g})+0.2 \text{ ppm HCl}$. No performance degradation was observed over a 600-hour test (at 160 mA/cm^2) with 10 ppb SeO_2 in flue gas. Based on these results, contaminant tolerance levels for the ECM were identified. The contaminant levels expected from the flue gas clean-up (polishing) subsystem were estimated by AECOM. The

contaminant evaluation and comparison with CEPACS plant flue gas polishing system output showed that the ECM tolerance levels are well above the contaminant levels expected in the ECM cathode feed gas (treated flue gas).

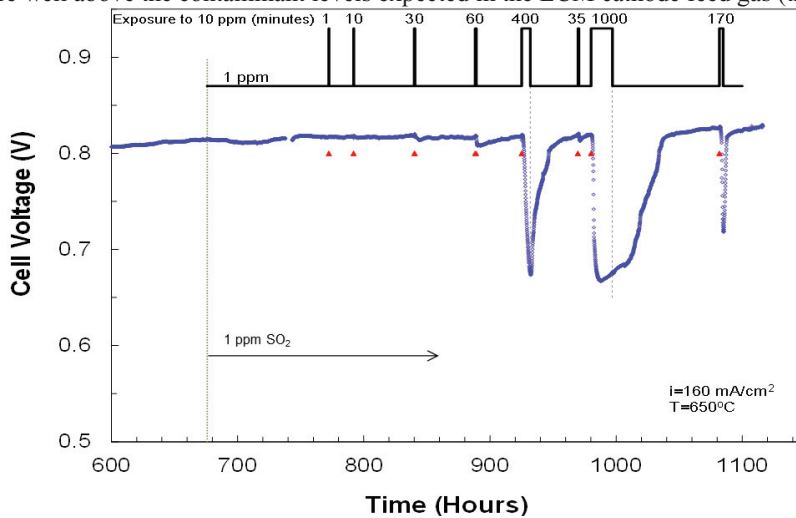


Fig. 7. Continuous exposure to 1 ppmv SO₂ with spikes of 10 ppmv SO₂ showed ECM performance was fully recoverable.

5. Bench-Scale CEPACS System Demonstration

A bench-scale ECM-based CO₂ capture system was designed and fabricated for demonstration testing. The objective of the demonstration was to show the capability of full-size ECM cells to separate >90% of CO₂ from a simulated PC plant flue gas stream through extended duration testing. The system utilized an ECM stack containing cells with a total electrochemical membrane area of 11.7 m². Nominal gross DC output of the stack is ~8 kW. The test stack includes 14 full-area cells, which were obtained from FCE's Torrington, CT commercial fuel cell manufacturing plant. The ECM stack completed nine months of steady state testing and over 15,000 hours including follow-on parametric testing. The test demonstrated stable performance while separating >90% of CO₂ from flue gas at constant CO₂ flux. Three deep thermal cycles, from operating temperature to <80°C and back to operating temperature, with no degradation of CO₂ flux. Peak power and flux testing also demonstrated the ability of ECM technology to operate at CO₂ flux >180 cc/s/m². Fig. 8 shows the test results.

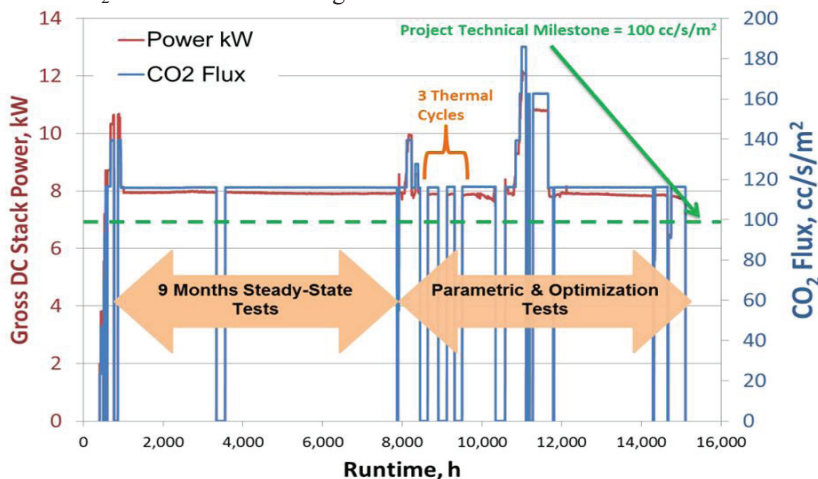


Fig. 8. Bench-scale CEPACS System Demonstration Test Results. The system utilized a 14-cell full-area ECM stack capable of 100 Tons/Year CO₂ Separation

The bench-scale test facility includes a CO₂ compression/ liquefaction skid for post-processing the anode exhaust stream to produce high-purity liquid CO₂ product. Process control checkout testing of the CO₂ compression/liquefaction skid was conducted in parallel with the bench-scale 8 kW ECM stack CO₂ capture tests. The skid has been evaluated under simulated ECM stack exhaust conditions, and demonstrated the ability to produce liquid CO₂ with purity of > 99.6%.

6. Conclusion

A Technical and Economic Feasibility Study evaluated the merits of the ECM technology for Carbon Capture, Use, and Sequestration application against the amine scrubbing technology applied to a Reference 550 MW PC plant. The system studies indicated that the ECM-based CEPACS plant provides substantial additional power to the grid and has the potential for achieving the DOE incremental COE target of 35%. The cost of CO₂ captured for the Reference Plant equipped with CEPACS is \$38.46/tonne (2011 USD), which is lower than the amine-based carbon capture alternative.

Testing was performed using a 250 cm² ECM cell to characterize the ECM's ability to reduce NO_x emissions from the PC plant flue gas. NO_x (as NO) concentration in cathode feed stream (flue gas) was increased from 50 to 216 ppm. At least 70% of the NO_x was removed at 110 mA/cm². This significant finding may eventually result in further reduction in the incremental COE associated with CEPACS system if credits are given to elimination of the SCR (selective catalytic reduction) in the coal power plant. ECM button cell tests were performed to assess potential interactions of flue gas impurities with cell components. The cell performance was evaluated using simulated flue gas with additions of SO₂, HCl, Hg and SeO₂. Contaminant tolerance levels for the ECM were identified. The contaminant (effect) evaluation and comparison with CEPACS plant flue gas polishing system output showed that the ECM tolerance levels are well above the contaminant levels expected in the ECM cathode feed gas (treated flue gas).

Demonstration testing of a bench-scale ECM-based CO₂ capture system was completed. The system utilized an ECM stack containing full-area cells taken directly from FCE's commercial manufacturing line, with a total electrochemical membrane area of 11.7 m². Nominal gross DC output is approximately 8 kW, with high-purity liquid CO₂ production of ~100 tons/year. The ECM stack was operated for more than 15,000 hours, demonstrating stable performance while separating >90% of CO₂ from flue gas at constant CO₂ flux.

ECM, utilizing commercially proven Direct FuelCell technology, is a compelling alternative for CO₂ capture that is efficient and cost effective for central generation and industrial applications. Commercial-scale demonstration of ECM-based CO₂ capture from flue gas of coal and/or natural gas-fueled plants will further confirm viability of this application. As the next step in commercialization of the CEPACS system, FCE, under a cooperative agreement with the DOE, is currently developing a 3MW ECM-based pilot-scale CO₂ capture system for demonstration at a Pulverized Coal power plant. Installation and operation of the plant is planned to commence in 2017/18.

Acknowledgements

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