

State of Wyoming Clean Coal Technologies Research Program

**Advanced Solvent for CO₂ Capture and Separation Technology for CO₂
Sequestration to Enhance Utilization and Reduce Emissions from Wyoming
Coal**

A Final Executive Report to the Legislature of the State of Wyoming

Clean Coal Technologies Research Program

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Advanced Solvent for CO₂ Capture and Separation Technology for CO₂ Sequestration to Enhance Utilization and Reduce Emissions from Wyoming Coal

The long-term sequestration of carbon dioxide is a technical issue demanding prompt attention which must be addressed for successful carbon capture and sequestration (CCS). The resulting effects of CO₂ injection in relation to saline aquifers is of particular interest in this project as it relates to possible sequestration in saline aquifers located in Wyoming. The goal is the economic removal and treatment of brine streams resulting from CO₂ injection-displaced saline aquifer fluid using advanced separation technologies.

Currently, reverse osmosis (RO) or a combination of nanofiltration (NF) and RO is the treatment method of choice for fresh water production from brackish-level TDS water sources. However, the energy requirements for these processes can be somewhat substantial even if lower than for fresh water purification from seawater-level TDS sources. Capacitive deionization (CDI) offers the possibility of treating lower TDS streams around 10,000 ppm salt or lower more efficiently than RO with energy costs being substantially lower the more dilute the salt concentration becomes. In addition, CDI may be capable of reducing the capital equipment cost of water treatment equipment. When assessing CDI as an energy efficient technology, it was also found that power consumption numbers can be decreased for CDI by over 20% through energy recovery mechanisms. Many aquifers do exist at these lower concentrations which would strongly benefit from the use of CDI over RO processes. With targeted carbon development to

minimize device size and lower energy consumption, CDI can compete and surpass pressure-driven membrane separation processes.

The ultimate goal of this project was to demonstrate the use of a capacitive deionization process capable of treating produced water from carbon dioxide injection sites. To accomplish this, three areas were investigated including (1) carbon surface chemistry to enhance salt capacity, (2) the addition of ion exchange membranes to increase the lifetime of the separation cell, and (3) the development and implementation of a new dc-dc converter capable of significantly lowering the energy cost of the water treatment process.

As an initial proof of concept, the CDI system was applied for the treatment of flue gas desulfurization (FGD) blowdown wastewater stream containing mixed salts, similar to those found in various brine aquifers. Samples were taken from the charge and discharge phases of the treatment process to correlate changes in concentration in the salt stream with use of the CDI cell. The CDI cell formed from UKy-CAER synthesized carbon xerogel (CX) electrodes was operated at 1.2 V and the solution was recirculated at 5 ml/min. The CDI cell showed salt adsorption via changes in conductivity upon the application of this small applied potential. The collected samples were ex-situ analyzed for changes to the comprising salt species using inductively coupled plasma (ICP). Resulting changes in concentration showed that the CDI process could remove a range of salt content including Na^+ , K^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} , Cl^- , and others.

To increase the salt removal capability of these cells and increase the lifetime operation of the device, new surface chemistries were investigated for the carbon electrodes including oxidation

and acid treatments. These surface functionalizations were found to have minimal to moderate impact on the resulting carbon pore structures and porosity meaning the electrode structure could be mostly maintained through the devised treatment processes. Fourier transform infrared spectroscopy (FTIR) was used to confirm the presence of new surface groups including carboxylic and sulfur groups demonstrating successful functionalization. CX electrodes, both functionalized and pristine, were examined in a 3-electrode cell to determine their specific capacitance in 10 mM NaCl solution at a scan rate of 1 mV/s. Specific capacitance curves for acid treated, oxidized, and pristine samples showed modest capacitive improvements. However, prominent shifting of the potential of zero charge (PZC) towards more positive values for the treated samples was observed which can be used to operate a CDI cell in a beneficial asymmetric manner. The PZC's were located between ~ -0.15 and 0 V vs. SCE for the pristine CX electrode, but ~ -0.12 to 0.22 V vs. SCE for the treated electrodes. It should be noted that extended treatment leads to continued shifting in the PZC values making this a viable controlled treatment process to develop user-defined PZC-modified carbon electrodes.

These treated carbon electrodes were subsequently incorporated into asymmetric CDI and membrane capacitive deionization (MCDI) cells to investigate device dependence on the PZC location. When the CDI and MCDI cells are assembled with a pristine electrode at the anode and an oxidized electrode at the cathode, the counterion excess within the voltage operation window is maximized, leading to improved performance over the other configurations. Conversely, when the CDI cell was assembled with an oxidized electrode at the anode and a pristine electrode at the cathode, thereby having coion excess within the anode and cathode operation windows, then an inverted profile can be observed, such that the conductivity when charging is larger than

during discharge, meaning salt desorption occurs when salt separation was intended. This inversion profile is not mirrored by the MCDI system, as the presence of the membrane prevents full expulsion of the coions into the bulk solution and salt separation is still maintained. Amongst all the tested cells, the MCDI cell with the oxidized cathode and pristine anode configuration had the largest capacity with a value of 7.4 mg NaCl / g CX at 1.2 V.

The performance attributes from combining ion-exchange membranes with pristine CX electrodes were also examined as a function of applied potential. MCDI tests were carried out in de-aerated 5 mM NaCl at applied potentials ranging from 1.2 to 2.6 V with membranes sandwiching CX electrodes in a CDI setup. Stable deionization response was observed at all the tested potentials. The electrosorption capacity increased with increasing applied potential, and at a terminal voltage of 2.6 V, the capacity was as high as 12 mg NaCl/ g CX. Increasing the charging potential increases the electrosorption capacity by amplifying the attractive force between the ions in solution and the polarized electrodes, which ultimately leads to increased charge storage and electrode utilization. Long-term cycling of these CDI and MCDI cells was also carried out to determine if stable performance would be possible for use at remote locations such as Wyoming brine aquifers. MCDI cells were found to have stable performance over the course of 50 hours of operation while CDI cells were found to degrade over similar time periods. Management of carbon oxidation in these CDI cells will be crucial to maintaining their salt separation performance.

Finally, energy recovery operations were investigated to lower the cost of the separation beyond that possible with RO. The CDI process was integrated with a new multi-input bi-directional dc-

dc converter towards achieving these lower energy requirements. The converter's electronic board controls energy input from the power supply and the transfer of energy from a discharging CDI cell to the one that is charging. The experiments proceeded in several stages to transfer energy: Firstly, cell 1 (C1) was charged at 1.2 V, then C1 was used to charge a secondary cell, C2, with the aid of the converter electronics. The potential, current, and conductivity profiles were recorded during this operation. During the recovery process, the converter first instantaneously drops the potential of the discharging cell (C1) to precipitate a reciprocal jump in the charging potential of the charging cell (C2). This is then followed by linear voltage ramping until the end of the experimental period. During operation, the converter tries to discharge cell 1 completely in 300 s, after which C2 is completely powered by the power supply. An energy recovery of ~35% and utilization of over 54% was observed with the use of this new dc-dc converter. Further optimization of this converter and integration with CDI cell operation could increase these energy recovery values further and make CDI a more efficient technology for a variety of brine aquifers, even above 10,000 ppm.

In this project, capacitive deionization of saline species in CDI and MCDI cells was examined. Deionization operation was augmented with energy recovery to improve the applicability of the technology. Carbon electrodes were functionalized with acid and electrochemical treatments to boost electrode capacitance. The treatments resulted in a marginal increase in capacitance but a significant relocation of the potential of zero charge which greatly influenced the consequent performance of both the CDI and MCDI cells. The performance of CDI and MCDI single cells configured symmetrically with a pair of pristine CX electrodes, and asymmetrically with pristine CX and treated CX electrodes were evaluated. The asymmetric MCDI-CX cell with PZCs

outside the working domain displayed the best performance result of all the 1.2 V tested CX cells due to having PZCs located to enhance the appropriate ion excess, and the membranes in-place to reject expelled co-ions from accessing the bulk as well as mitigating electrochemical side-reactions. An electrosorption capacity of 7.4 mg NaCl/ g Carbon electrode at 1.2 V was realized for the PZC modified cell versus 4.3 mg NaCl/g Carbon for the pristine only cell. Increasing the applied potential on the pristine only MCDI cell to 2.6 V amplified the deionization performance to 12 mg NaCl/g Carbon. Furthermore, operation with the membrane significantly extended the operation lifetime of the deionization system, due to its ability to mitigate the electrochemical degradation of the electrodes. CDI cells were interfaced with a dc-dc converter to recover energy from the discharge operation. Converter variables including extent of potential drop and charging time were explored, and a recovery of ~ 35 % of the energy input to the cell was demonstrated.

In assessing the practicality of this technology, the proposed study constitutes critical work on advancing capacitive deionization as a viable separation process. CDI already compares favorably with RO, especially for lower salt concentration streams, but increased sorption capacity, lifetime, and energy recovery will make the technology even-more attractive to potential users. CDI can be integral not only to saline aquifer sequestration as proposed in this study, but also to other related industries such as the food, nuclear, and electric utilities that produce some amount of liquid waste or wastewater. Systems to treat wastewater account for ~4% of the total energy used in the United States, and the current treatment options available can be quite expensive. The dc-dc integrated CDI cell technology proposed can be coupled with other deionization systems to target much more concentrated streams and is primed to deliver a

superior and cost-effective solution. In addition, the proposed device will be significantly smaller than prior CDI/MCDI cells requiring less land and initial capital investment, and operate at considerably lower energy demands.