SPOUTED BED ELECTRODES (SBE) FOR DIRECT UTILIZATION OF CARBON IN FUEL CELLS

FINAL REPORT

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ABSTRACT

This Phase I project was focused on an investigation of spouted bed particulate electrodes for the direct utilization of solid carbon in fuel cells. This approach involves the use of a circulating carbon particle/molten carbonate slurry in the cell that provides a few critical functions: it (1) fuels the cell continuously with entrained carbon particles; (2) brings particles to the anode surfaces hydrodynamically; (3) removes ash from the anode surfaces and the cell hydrodynamically; (4) provides a facile means of cell temperature control due to its large thermal capacitance; (5) provides for electrolyte maintenance and control in the electrode separator(s); and (6) can (potentially) improve carbon conversion rates by “pre-activating” carbon particle surfaces *via* formation of intermediate oxygen surface complexes in the bulk molten carbonate.

The approach of this scoping project was twofold: (1) adaptation and application of a CFD code, originally developed to simulate particle circulation in spouted bed electrolytic reactors, to carbon particle circulation in DCFC systems; and (2) experimental investigation of the hydrodynamics of carbon slurry circulation in DCFC systems using simulated slurry mixtures.

The CFD model results demonstrated that slurry recirculation can be used to hydrodynamically feed carbon particles to anode surfaces. Variations of internal configurations were investigated in order to explore effects on contacting. It was shown that good contacting with inclined surfaces could be achieved even when the particles are of the same density as the molten carbonate. The use of CO₂ product gas from the fuel cell as a “lift-gas” to circulate the slurry was also investigated with the model. The results showed that this is an effective method of slurry circulation; it entrains carbon particles more effectively in the draft duct and produces a somewhat slower recirculation rate, and thus higher residence times on anode surfaces, and can be controlled completely *via* pressure balance.

Experimental investigations in a rectangular spouted vessel hydrodynamics apparatus (SVHA) showed that hydrodynamics can be used to control the circulation, residence time, and distribution of carbon within the spouted bed, as well as provide good particle contact with anode surfaces. This was shown to be a function of viscosity, carbon loading, and particle size, as well as relative densities. Higher viscosities and smaller particle sizes favor more efficient particle entrainment in the draft duct, and particle recirculation.

Both the computational and experimental results are consistent with each another and exhibit the same general qualitative behavior.

Based upon this work, a design of a prototype SBE/DCFC cell was developed and is presented.

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EXECUTIVE SUMMARY

This Phase I project was directed at the application of spouted bed particulate electrodes to the direct utilization of carbon in fuel cells. This involves the use of a circulating carbon particle/molten carbonate slurry in the cell that serves a number of important functions: it (1) fuels the cell continuously with entrained carbon particles; (2) brings particles to the anode surfaces hydrodynamically; (3) removes ash from the anode surfaces and the cell hydrodynamically; (4) provides a facile means of cell temperature control due to its large thermal capacitance; (5) provides a facile means of electrolyte maintenance and control in the electrode separator(s); and (6) can (potentially) improve carbon conversion rates by “pre-activating” carbon particle surfaces *via* formation of intermediate oxygen surface complexes by the carbonate.

The approach taken in this scoping project was twofold: (1) adapt and apply a CFD code originally developed to simulate particle circulation in spouted bed electrolytic reactors, to carbon particle circulation in candidate geometries for DCFC systems; and (2) experimentally investigate the hydrodynamics of carbon slurry circulation in DCFC systems using simulated slurry mixtures.

The CFD model results showed that slurry recirculation can be used to hydrodynamically feed carbon particles to anode surfaces. Variations of internal configurations were investigated in order to explore effects on contacting. It was shown that good contacting with inclined surfaces could be achieved even when the particles are of the same density as the molten carbonate.

Another potentially important mode of operation investigated with the CFD model was the use of CO₂ product gas from the fuel cell as a “lift-gas” to circulate the slurry. This method is preferable to using a mechanical pump to handle the corrosive slurry. In order to investigate this possibility, the CFD model was extended to three phases: carbon particles, molten carbonate, and CO₂, while retaining the Eulerian formulation. The results showed that this was an effective method of slurry circulation, which is superior in some ways to pumping; it entrains carbon particles more effectively in the draft duct and produces a somewhat slower recirculation rate, and thus higher residence times on anode surfaces, and can be controlled *via* pressure balance.

The experimental results in the rectangular spouted vessel hydrodynamics apparatus (SVHA) showed that hydrodynamics can be used to control the circulation, residence time, and

distribution of carbon within the spouted bed, as well as provide good particle contact with anode surfaces. This was shown to be a function of viscosity, carbon loading, and particle size, as well as relative densities. Higher viscosities and smaller particle sizes favor more efficient particle entrainment in the draft duct, and particle recirculation.

Carbon slurry circulation in the SVHA was achieved by entrainment with an inlet liquid jet, and also with CO₂ “gas-lift.” However, as concluded from the computational results, the latter method is preferable since there are no moving or mechanical parts to be in contact with the high temperature, corrosive slurry, and the generally lower circulation rates are good for maintaining high particle residence times on anode surfaces.

Both the computational and experimental results are consistent with each another and exhibit the same general qualitative behavior.

Based upon this work, a design of a prototype SBE/DCFC cell was developed and is presented.

1.0. INTRODUCTION AND BACKGROUND

The production of electricity directly from coal appears to date back to the late 19th century, when William Jacques, a Boston entrepreneur, produced a coal fuel battery that used coke electrodes in a molten sodium hydroxide electrolyte. The most recent breakthrough in this regard is the work of Cooper and co-workers at LLNL who have successfully demonstrated a carbon-oxygen fuel cell that operates on very fine particles (10-1000 nm) of low-ash, turbostratic carbon.¹ Test cells have delivered up to 100 mW/cm^2 , with 80% efficiency at 80 mW/cm^2 . As impressive as this device is, however, a number of problems remain to be solved before this technology can successfully operate on many different carbon sources on a large scale. The use of coal and biomass-derived carbons, for example, requires a fuel cell design that can handle high amounts of ash, and larger particles. It is proposed here to proceed in this direction by investigating the adaptation of a spouted bed electrode (SBE) to the carbon-oxygen fuel cell.

Figure 1. SBER system for electrolytic recovery.

Figure 2. Image of 12" SBER apparatus.

We have developed spouted bed electrolytic reactors (SBER) for point source metals recovery (supported by the EPA and Lucent Technologies).² A schematic and image of our 12" cylindrical SBER are presented in Figures 1 and 2. As shown, the aqueous solution containing metal ions is introduced as a high velocity jet at the bottom of a conical vessel *via* a central draft tube. This liquid jet entrains particles that disengage from the jet in a region above the draft tube known as the "fountain." The particles are then distributed radially to the bed periphery by the distributor, where they fall onto the cathodic "feeder cone" at the reactor bottom, and are directed back to the inlet of the draft tube for re-entrainment. Metal is deposited on the particles when they are in contact with the cathodic bottom cone. The metallic mesh anode is supported under

the particle distributor, above the cathodic cone. The "pumping action" of the spout continually circulates the particles through the vessel; upwards in the spout, and downwards in the annular region. We have successfully recovered Ag, Au, Cu, Ni, Sn, and Cd from various aqueous solutions with this system at high current densities and high current efficiencies.³

2.0. The Spouted Bed Electrode/Direct Carbon Fuel Cell (SBE/DCFC) Concept.

A few different concepts have been proposed or used as DCFCs. Of these, however, two in particular are currently receiving significant attention – the molten carbonate fuel cell (MCFC) and the solid oxide fuel cell (SOFC).⁴ The MCFC typically uses mixed alkali carbonate electrolytes, and carbonate ions are the current carriers. These electrolytes are well-suited for carbon cells due to their high conductivity and stability in the presence of CO₂. The anode and cathode half-cell reactions for a carbon fuel are:

The overall reaction is, of course, $\text{C(s)} + \text{O}_2 \rightarrow \text{CO}_2$; $\Delta G_{800^\circ\text{C}}^\circ = -396.7 \text{ kJ/mol}$, or $E^\circ = +2.05\text{V}$. In the SOFC O²⁻ is the current carrier in a solid oxide (defect zirconia) matrix. The corresponding SOFC anode and cathode half-cell reactions are:

which results in the same overall carbon conversion reaction.

One possible conceptual schematic of the SBE/DCFC is presented in Figure 1. Carbon/molten carbonate slurry flows continuously through the system in a toroidal fashion – upwards in the draft tube and then centripetally back down along inclined, bipolar anode/cathode stacks. Two such stacks are shown in Figure 1 (one at the vessel bottom and the other serves as a slurry distributor); however, it is anticipated that a number of these stacks will be arranged in a single spouted vessel in chevron-like arrangements. The slurry can be circulated through the fuel cell either mechanically or by gas-lift created by injecting CO₂ produced in the carbon oxidation reaction into the slurry below the draft tube entrainment region (e.g., as in a gas-lift riser). Fuel cell operation requires continuous carbon feed and removal of spent, ash-rich particles. The flow in the SBE/DCFC provides a few possibilities for accomplishing these objectives. For example, the slurry can be circulated in an external circuit to remove spent, ash-rich particles (e.g., by

filtration with metallic or ceramic media), and to feed fresh carbon particles to the SBE/DCFC. These operations can also be performed within the cell either at the draft tube inlet or outlet.

Figure 3. Schematic of spouted bed direct carbon fuel cell (SBE/DCFC).

Both of these types of fuel cells are well established and much is known about their operation with gaseous fuels.^{5,6} DCFCs can be operated with either type of electrode. In both cases, however, the solid carbon particles must be transported to and maintained in contact with the anode(s), and the resultant ash must be continually removed. Direct gravity feed of pulverized carbon fuel onto anodes, and the removal of the resultant ash becomes difficult to control on a large scale. Although these issues may be relatively minor in a small-scale laboratory system, problems like particle mounding, broad residence time distributions of carbons particles on anodes, and fouling by accumulated ash, become much more critical for larger-scale systems.

The SBE/DCFC concept addresses a number of these problems by employing a circulating carbon particle/molten carbonate slurry. The circulating slurry continuously transports particles to the anode surfaces, cleans them by removing and transporting ash particles, manages the electrolyte (in the case of the molten carbonate fuel cell approach), and may also facilitate the electrochemical oxidation reaction at the anode. Since a molten carbonate slurry vehicle is used,

the MCFC approach has a number of advantages. Thus, the current proposal focuses specifically on the MCFC version of the DCFC, as has been described by Cooper and co-workers.^{14,7}

For the carbon fuel cell application, the SBE would be operated in reverse from that in metal electrowinning; that is the particulate slurry will be the anode at which oxidation occurs. The carbonaceous feedstock would be provided by the pyrolysis/hydropyrolysis of solid fuels, such as coal and biomass. The particulate carbon is slurried with molten (sodium, lithium, or potassium) carbonate.

In order to be a viable system, the SBE/DCFC must be capable of operation on a large scale. The SBE/DCFC has some significant advantages in this regard: (1) it is readily scalable (e.g., by “stacking” units and inclined bipolar elements); and (2) continuous flow provides the means for performing removal and recovery of spent particles; continuous “self-cleaning” of electrodes, that can be easily fouled in other systems; and facile temperature control *via* convective heat removal. In particular, the “self-cleaning” nature of the electrodes tends to minimize the effects of contaminants on performance and aging. In addition, the continuous feed of carbonaceous material tends to reduce electrode sintering that can be a problem for fixed solid electrodes.

The objectives of this project are to explore the extension/application of SBE-like systems to direct carbon fuel cells. More specifically: (1) to adapt SBE CFD codes to simulate the expected hydrodynamics of DCFC; and (2) to perform simulated experiments of fluid-particle circulation in a rectangular spouted vessel hydrodynamics apparatus (SVHA).

3.0. Computational Investigations

3.1. Numerical Model

As a result of our SBER work, we have developed numerical Eulerian CFD models for simulating the performance of SBE systems. For electrowinning, these models were validated with hydrodynamic data from a rectangular spouted vessel hydrodynamics apparatus (SVHA). We are pursuing a similar approach for the SBE/DCFC concept. That is, simulation of carbon slurry flows with the CFD model, and hydrodynamics experiments with simulated carbon/molten carbonate slurries in the SVHA.

A “two-fluid” (fluid and solid phases), Eulerian-Eulerian model was developed to simulate the hydrodynamics of a rectangular spouted bed, operated with draft duct. Following the

approach of workers such as Chapman and Cowling,⁸ Ding and Gidaspow,⁹ Jenkins and Savage,¹⁰ and Savage and Jeffrey,¹¹ the solid-phase stresses are based on an analogy between the random particle motion arising from particle-particle collisions and the thermal motion of molecules in a gas, taking into account the inelasticity of the granular phase. The intensity of the particle velocity fluctuations determines the stresses, viscosity, and pressure of the solid phase. The kinetic energy associated with the particle velocity fluctuations is represented by a “pseudothermal” or granular temperature that is proportional to the mean square of the random motion of the particles.

3.2. Model Summary

Syamlal *et al.*,¹² Drew and Passman,¹³ Drew,¹⁴ and Enwald *et al.*¹⁵ used spatial, time, and ensemble averages were used in developing the equations of motion for two-phase flow systems. Assuming no interphase mass transfer, the continuity equations for the liquid and particulate phase ($q = s$ for solid, and l for liquid) are:

$$\frac{\partial}{\partial t} \alpha_q \rho_q + \nabla \cdot \alpha_q \rho_q \vec{u}_q = 0, \quad (1)$$

where α_q , ρ_q and u_q are volume fraction, averaged density, and averaged velocity vector associate with phase q , respectively. The volume fraction of the solid and liquid are related through the constraint, $\alpha_s + \alpha_l = 1$. The momentum conservation equations for the liquid and solid phases are given by the following expressions:

$$\frac{\partial}{\partial t} (\alpha_f \rho_f \vec{u}_f) + \nabla \cdot (\alpha_f \rho_f \vec{u}_f \otimes \vec{u}_f) = -\alpha_f \nabla p + \nabla \cdot \overline{\overline{\tau}}_f + \alpha_f \rho_f \vec{g} + K_{sf} (\vec{u}_s - \vec{u}_f), \quad (2)$$

$$\frac{\partial}{\partial t} (\alpha_s \rho_s \vec{u}_s) + \nabla \cdot (\alpha_s \rho_s \vec{u}_s \otimes \vec{u}_s) = -\alpha_s \nabla p - \nabla p_s + \nabla \cdot \overline{\overline{\tau}}_s + \alpha_s \rho_s \vec{g} + K_{fs} (\vec{u}_f - \vec{u}_s), \quad (3)$$

where p_s is the solids pressure and $K_{fs} = K_{sf}$ are the fluid-solid momentum exchange coefficients or two-phase drag coefficients. The particle or solids pressure, p_s , is caused by particle interactions (collisions). This pressure transmits a force both by short-duration collisional impacts, as well as by longer-duration particle-particle contact. The particle pressure gradient term serves to keep the particles apart so that the calculated particle volume fraction cannot exceed the maximum concentration attainable for a given size distribution of particles. A value of 0.64 (see Huilin *et al.*¹⁶) was assumed for this maximum particle volume fraction, which is close to the packing limit of a BCC crystal structure (0.68).

The solid pressure, p_s , is determined from an equation of state similar to the van der Waals equation of state for fluids, as discussed by Chapman and Cowling¹⁷ and Gidaspow¹⁸:

$$p_s = \alpha_s \rho_s \Theta_s + 2 \rho_s (1 + e_{ss}) \alpha_s^2 g_{oss} \Theta_s \quad (4)$$

where e_{ss} is the coefficient of restitution, Θ_s is the “granular temperature,” and g_{oss} is the radial distribution function. The latter is a correction factor that modifies the probability of collisions between particles when the mixture becomes dense and is obtained from the theory of non-uniform gases.⁸ The radial distribution function is equal to unity when the particles are loosely packed, and becomes infinite when the particles are so closely packed that relative motion is impossible. The radial distribution function given by Ding and Gidaspow⁹ was used in the current work:

$$g_o = \frac{3}{5} \left[1 - \left(\frac{\alpha_s}{\alpha_{s,\max}} \right)^{\frac{1}{3}} \right]^{-1} \quad (5)$$

Closure of the governing mass and momentum balances is provided by constitutive equations. The stress tensor for both phases is given by the Newtonian stress-strain relation. The solid stress-strain tensor is given by:

$$\tau_{s,ij} = \alpha_s \mu_s \left(\frac{\partial u_{s,i}}{\partial x_j} + \frac{\partial u_{s,j}}{\partial x_i} \right) + \left(\alpha_s \lambda_s - \frac{2}{3} \alpha_s \mu_s \right) \delta_{ij} \frac{\partial u_{s,l}}{\partial x_l} \quad (6)$$

Non-Newtonian properties of the particulate phase can be taken into account by modeling the particle viscosity as a function of the fluid volume fraction, as discussed further below.

The solids shear stress tensor contains shear and bulk viscosities arising from particle momentum exchange due to translation and collision. A frictional component of viscosity was been included to account for the viscous-plastic transition that occurs when particles of a solid phase reach the maximum solid volume fraction. Thus, the total solid shear stress is given by:

$$\mu_s = \mu_{s,col} + \mu_{s,kin} + \mu_{s,fric} \quad (7)$$

The collisional and kinetic viscosities of the solid phase are given by Syamlal *et al.*¹² as:

$$\mu_{s,col} = \frac{4}{5} \alpha_s \rho_s d_s g_{oss} (1 + e_{ss}) \left(\frac{\Theta_s}{\pi} \right)^{1/2} \quad (8)$$

$$\mu_{s,kin} = \frac{\alpha_s \rho_s d_s \sqrt{\Theta_s \pi}}{6(3 - e_{ss})} \left[1 + \frac{2}{5} (1 + e_{ss}) (3e_{ss} - 1) \alpha_s g_{oss} \right] \quad (9)$$

The solids bulk viscosity accounts for the resistance of the granular particles to compression and expansion, and has the following form, according to Lun *et al.*¹⁹:

$$\lambda_s = \frac{4}{3} \alpha_s \rho_s d_s g_{oss} (1 + e_{ss}) \sqrt{\frac{\Theta_s}{\pi}} \quad (10)$$

Frictional viscosity generation due to friction between particles, and between particles and walls, becomes especially significant as the solids volume fraction approaches the packing limit. The following expression derived by Schaeffer²⁰ was used to estimate the frictional viscosity:

$$\mu_{s,fr} = \frac{p_s \sin \phi}{2 \sqrt{I_{2D}}} \quad (11)$$

where ϕ is the angle of internal friction, and I_{2D} is the second invariant of the deviatoric stress tensor.²⁰

The fluid-solid exchange coefficient used here is given by Syamlal *et al.*¹² and is based on the measurement of the terminal velocities of particles in fluidized beds. These correlations give exchange coefficients in terms of the volume fraction and relative Reynolds number as:

$$K_{sf} = \frac{3\alpha_s \alpha_f \rho_f}{4v_{rs}^2 d_s} C_D \left(\frac{\text{Re}_s}{v_{rs}} \right) |\vec{u}_s - \vec{u}_f| \quad (12)$$

in which the relative Reynolds number is defined as:

$$\text{Re}_s = \frac{\rho_f d_s |\vec{u}_s - \vec{u}_f|}{\mu_f} \quad (13)$$

The terminal velocity correlation for the solid phase was obtained experimentally by Garside and Al-Dibouni²¹:

$$u_{rs} = 0.5(A - 0.06\text{Re}_s + \sqrt{(0.06\text{Re}_s)^2 + 0.12\text{Re}_s(2B - A) + A^2}) \quad (14)$$

where the coefficients of A and B are specified as functions of the liquid volume fraction:

$$\begin{aligned} A &= \alpha_l^{4.14} \\ B &= 0.8\alpha_l^{1.28} \quad \text{for } \alpha_l \leq 0.85 \\ B &= \alpha_l^{2.65} \quad \text{for } \alpha_l > 0.85 \end{aligned} \quad (15)$$

The drag coefficient used was derived by Dalla Valle²²:

$$C_D = (0.63 + \frac{4.8}{\sqrt{\text{Re}_s / u_{rs}}})^2 \quad (16)$$

The granular temperature for the solid phase is proportional to the kinetic energy of the random motion of the particles. Ding and Gidaspow⁹ derived a transport equation from kinetic theory that has the form:

$$\frac{3}{2} \left[\frac{\partial}{\partial t} (\rho_s \alpha_s \Theta_s) + \nabla \cdot (\rho_s \alpha_s \bar{u}_s \Theta_s) \right] = -(\bar{p}_s \bar{\mathbf{I}} + \bar{\bar{\tau}}_s) : \nabla \bar{u}_s + \nabla \cdot (k_{\Theta_s} \nabla \Theta_s) - \gamma_{\Theta_s} + \phi_{sl} \quad (17)$$

where:

$$-(\bar{p}_s \bar{\mathbf{I}} + \bar{\bar{\tau}}_s) : \nabla \bar{u}_s = \text{generation of energy by the solid stress tensor}$$

$$\nabla \cdot (k_{\Theta_s} \nabla \Theta_s) = \text{diffusion of energy, with } k_{\Theta_s} \text{ as diffusion coefficient}$$

$$\gamma_{\Theta_s} = \text{collisional dissipation of energy}$$

$$\phi_{sl} = \text{energy exchange between fluid and solid phase}$$

The rate of energy dissipation within the solid phase due to interparticle collisions, as derived by Lun *et al.*,¹⁹ is given by:

$$\gamma_{\Theta_s} = \frac{12(1 - e_{ss}^2) g_{0,ss}}{d_s \sqrt{\pi}} \rho_s \alpha_s^2 \Theta_s^{3/2} \quad (18)$$

Transfer of the kinetic energy of random fluctuations in particle velocity from the solid phase to the fluid phase is represented by the expression derived by Gidaspow *et al.*²³ as:

$$\phi_{ls} = -3K_{ls} \Theta_s \quad (19)$$

3.3. Solution Procedure

The governing set of partial differential equations was discretized using a finite volume technique, as given by Patankar.²⁴ The discretized equations along with the initial and boundary conditions were solved using FLUENTTM. The conservation equations were integrated using power law differencing in space, and implicit differencing in time, in such a manner that the integral conservation is satisfied over the calculation domain, over a time interval. Discretization of the convection terms using a power law interpolation scheme provides formal local accuracy between first and second order.²⁴ The power law scheme provides a better approximation to the

exact solution of steady one-dimensional convection and diffusion equations and has been adopted for three-dimensional problems. It is more robust and less computationally intensive than higher order schemes, and provides an extremely good representation of the exponential behavior of the exact solution of one-dimensional convection-diffusion equations.²⁴ The SIMPLE algorithm²⁴ was used to relate the velocity and pressure corrections and to reformulate the continuity equation in terms of a pressure correction equation. The set of linearized algebraic equations was solved using a tridiagonal matrix algorithm.

The system simulated was a rectangular spouted vessel with a central draft duct (*cf.*

Figure 13, and description below) that was constructed to provide validation data for the simulations. In order to reduce computational time, only one quadrant of the rectangular vessel, as defined by its two vertical planes of symmetry, was modeled. This computational domain was divided into a finite number of non-overlapping control volumes, each surrounding a grid point. Scalar variables such as pressure, phase volume fractions, and turbulence properties were stored at the grid points. A staggered grid arrangement was used, and the velocity components were stored in the control volume surfaces.²⁴ The entire computational domain was represented with a set of computational control volumes consisting of 2288 structured cells; i.e., (22, 26, 4) sections in the (x, y, z) directions, with corresponding physical dimensions (to the rectangular spouted vessel) of (0.12, 0.36, 0.0127)m. The computational grid system is presented in Figure 4. A grid independence study was performed in previous work²⁵ that indicated this domain size was adequate to capture the physical behavior of the system.

Figure 4. Computational grid schematic.

The boundary conditions include the two planes of symmetry since only one quadrant of the physical domain was simulated. The inlet liquid velocity and the outlet pressure (1 atm) were specified. “No-slip” boundary conditions were assumed at the walls for the liquid phase.

Interactions of particles with the walls were modeled with the same formulation used for solids pressure and granular viscosity for the particle-particle interactions, except that the walls were conceptually treated as very “large” particles. Therefore, in the solid phase the particles can move tangentially while in contact with the wall; i.e., they can exhibit some “slip” as determined by wall friction (which was assumed to be the same as between particles).

The solids volume fraction in a domain of known volume was specified at the beginning of each simulation to correspond to the desired solids loading (defined as the total mass of particles in the bed). Due to lack of other data, values of the coefficient of restitution and the friction coefficient for these particles were estimated to be 0.97 and 0.092, respectively, according to the measurements of Foerster *et al.*²⁶ for soda lime glass spheres. The same coefficient of friction was also assumed for interactions between the walls and the particles.

Zero velocity initial conditions were used for both the liquid and solid phases everywhere in the computational domain. The time step selected for the simulations was 0.001 s. Simulation of a total real time of 20s required between 24 to 72 hours to run on Pentium III computers, depending on the solids loading.

3.4. Results

Some sample results obtained with the CFD model are presented below. In these cases, the transient development to steady-state of the carbon particle volume fraction in a carbon/Li₂CO₃ slurry in the SBE/DCFC quadrant is presented in (a), and the corresponding velocity vector map of the particles at steady-state in (b).

In Figure 5(a) is presented the development of the carbon particle volume fraction in a carbon/Li₂CO₃ slurry for a configuration with only the draft duct and the particle distributor in place (molten carbonate: 810°C, 0.2 m/s inlet velocity; carbon particles: 200 g, 1 mm particles; the density for both molten carbonate and carbon particles is 1.8 g/cc.). As shown, under these conditions at steady-state (30 s), there is a large inventory of particles in the freeboard that are not in contact with any surfaces that may serve as an anode. There is also relatively poor contact of the carbon particles with the inclined vessel bottom, which in some designs may serve as the primary inclined anode. This is more clearly evident in the velocity vector field plot in Figure 5(b) where considerable bypassing of the inclined vessel bottom by the carbon particles is evident. As shown in Figure 6(a,b), this behavior is exacerbated by increasing the molten carbonate inlet flow velocity to 0.5 m/s. The behavior is improved by increasing the particle

density to 2.1 g/cc, such that they are heavier than the molten carbonate, as shown in Figures 7(a,b).

In order to keep most of the particles out of the freeboard and improve the contact between the carbon particles and the inclined surfaces, the SBE/DCFC computational quadrant was modified to include a “cap,” as shown in Figure 8(a) (molten carbonate: 810°C, 0.5 m/s inlet velocity, 1.8 g/cc. Carbon particles: 200 g, 0.1 mm particles, 1.8 g/cc). As indicated in Figures 8(a,b), this improves the situation significantly. Much higher particle volume fractions are maintained on the inclined bottom at steady-state, and there is a heavy recirculation of particles low on the bottom towards the particle entrainment point. However, it was found that it is not necessary that the carbon particles be heavier than the molten carbonate in order to maintain good contact with the vessel bottom. As shown in Figures 9(a,b), reducing the molten carbonate inlet velocity to 0.3 m/s, with both carbon and molten carbonate at the same density, improves the contact with the inclined bottom significantly. Particle size does not seem to have much of an effect on the slurry behavior at the sizes investigated, as is evident in a comparison of the results in Figures 8(a,b) and 10(a,b) that differ in conditions only in that the former is for 0.1 mm particles, while the latter is for 0.5 mm particles (0.3 m/s molten carbonate inlet velocity). Decreasing the inlet molten carbonate velocity also improves the slurry behavior, as is evident in a comparison between Figures 10(a,b) and 11(a,b) that differ only in inlet velocity; 0.3 m/s in the former case, and 0.1 mm/s in the latter for 0.5 mm particles.

Another potentially important mode of operation investigated was the use of CO₂ “lift-gas” to circulate the slurry. This method of circulating the molten carbonate slurry in the SBE/DCFC is preferable to using a mechanical pump to handle the corrosive slurry. As indicated above in Section 2, the essential idea is to make use of the CO₂ generated by the SBE/DCFC to circulate the molten carbonate slurry. In order to explore this possibility, the model had to be extended to three phases: carbon particles, molten carbonate, and CO₂, while retaining the Eulerian formulation described above in Section 3.2. A sample result from this model is shown in Figure 12. In this calculation, CO₂ gas was admitted at atmospheric pressure and zero velocity at the inlet, in lieu of molten carbonate. This can be accomplished by using a check valve, as was done in the experimental studies in the spouted vessel hydrodynamics apparatus (SVHA) (see Section 4 below).

Figure 5(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.2 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g , 1 mm particles, 1.8 g/cm^3 .

Figure 5(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C , 0.2 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 1 mm particles, 1.8 g/cm^3 .

Figure 6(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.5 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g , 1 mm particles, 1.8 g/cm^3 .

Figure 6(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C , 0.5 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 1 mm particles, 1.8 g/cm^3 .

Figure 7(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.5 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 1 mm particles, 2.1 g/cm^3 .

Figure 7(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C, 0.5 m/s inlet velocity, 1.8 g/cm³. Carbon particles: 200 g, 1 mm particles, 2.1 g/cm³.

Figure 8(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.3 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g , 0.1 mm particles, 1.8 g/cm^3 .

Figure 8(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C , 0.3 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 0.1 mm particles, 1.8 g/cm^3 .

Figure 9(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.5 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g , 0.1 mm particles, 1.8 g/cm^3 .

Figure 9(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C , 0.5 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 0.1 mm particles, 1.8 g/cm^3 .

Figure 10(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C, 0.3 m/s inlet velocity, 1.8 g/cm³. Carbon particles: 200 g, 0.5 mm particles, 1.8 g/cm³.

Figure 10(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s after start-up (steady-state). Molten carbonate: 810°C , 0.3 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 0.5 mm particles, 1.8 g/cm^3 .

Figure 11(a). Carbon particle volume fraction in carbon/ Li_2CO_3 slurry in spouted bed quadrant. Molten carbonate: 810°C , 0.1 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g , 0.5 mm particles, 1.8 g/cm^3 .

Figure 11(b). Carbon particle velocity vector map in carbon/ Li_2CO_3 slurry in spouted bed quadrant at 30s (steady-state) after start-up. Molten carbonate: 810°C , 0.1 m/s inlet velocity, 1.8 g/cm^3 . Carbon particles: 200 g, 0.5 mm particles, 1.8 g/cm^3 .

Figure 12. Three-phase (carbon particles/molten carbonate/CO₂ gas) CFD calculation of volume fractions of carbon particles (left) and CO₂ (right) in carbon/Li₂CO₃ slurry in SBE/DCFC quadrant operating under gas-lift with CO₂, 30 s after start-up. Molten carbonate: 810°C, 1.8 g/cm³. Carbon particles: 200 g, 0.5 mm particles, 1.8 g/cm³.

4.0. Experimental Investigations

4.1. Apparatus and Procedures

Simulated carbon slurry experiments were conducted in the Spouted Vessel Hydrodynamics Apparatus (SVHA) shown in Figure 13. Carbon particles slurried in water solutions of varying viscosity at ambient temperature were used to model carbon/molten carbonate slurries at elevated operating temperatures.

The rectangular SVHA shown in Figure 13, was constructed from two 40.6 cm x 40.6 cm x 35.6 cm plexiglassTM sheets that served as the front and back of the spouted vessel. The rectangular draft duct and distributor were also made of plexiglass.TM The draft duct was rectangular in cross section, 1.90 cm (0.75”) x 2.54 cm (1.0”) inner dimensions. The liquid jet inlet was of the same cross section. A “hot glue gun” was used to attach all the vessel internals to the front and back plates. Hard rubber strips were used to form the sides of the vessel, and to serve as a water seal when clamped between the front and back plates of the spouted vessel. The top of the spouted vessel was open to the atmosphere.

The SVHA system consisted of the solution reservoir from which an IwakiTM magnetic pump was used to feed the solution to a T-connection, one branch of which connected to the bed, while the other was a bypass back to the reservoir. A ball valve was placed in each of these branches to control the flow rate. The PVC tubing making up the bypass line was 1.27 cm (0.5 in.) inside diameter, while the rest of the tubing was 1.90 cm (0.75 in.) inner diameter. The reduction of the tubing diameter in the bypass line was necessary to obtain a more precise control of the flow rate at the elevated solution viscosities that were used in this work. The flow rate was varied by adjusting the two ball valves. A SignetTM flow meter was placed below the entrance to the spouted bed to measure the flow rate. The solution exited the vessel at the top over two overflow weirs that emptied back into the reservoir tank in order to provide continuous circulation. Two mesh screens were installed over the overflow weirs to retain the carbon particles in the vessel.

A micro-pitot tube, constructed by Aeroprobe Corp., was used to measure pressure and the three velocity components in the spouted vessel. This system consisted of five probes of 0.508 mm (0.02”) in diameter, mounted on a conical tip of 0.3175 cm (0.125”) in diameter. Each port was connected with flexible tygon tubing to a pressure transducer, capable of measuring 0-6895

Pa (0-1psig). The electrical signal from each pressure transducer was fed to a pressure scanner device. In this manner, the five holes in the probe communicated with the five transducers of the scanner. The scanner was interfaced *via* a laboratory computer through a CIO-DAS08 data acquisition board and signal conditioning software provided by the manufacturer.

Figure 13. Schematic of Spouted Vessel Hydrodynamics Apparatus (SVHA).

An x-z translator was used to position the probe at selected coordinate locations. It employed two stepper motors controlled through the GPIB port. The *Aeroacquire* program and calibration data for the sensors supplied by Aeroprobe Corp., were used to resolve the pressure

data into velocity vectors. The presence of the 0.3175 cm diameter probe in the 2.54 cm thick vessel was not observed to produce any observable perturbations on the operation/behavior of the spouted vessel.

Four properties of the slurries were varied: carbon particle size, carbon particle loading, solution viscosity, and volumetric flow rate. The carbon particles selected for the experiments were Sigma™ activated charcoal. The particles were sieved to two nominal sizes: 0.5 mm and 1.0 mm. The particles were then soaked in water. A surfactant (3M Fluorad FC-135™) was added to aid in the removal of air trapped in the particle pores and to prevent fine air bubbles from attaching to the particles.

Three particle loadings were investigated: 25, 50, and 75 cm³. Below 25 cm³, the particles were highly dispersed throughout the vessel, while above 75 cm³ the particles tended to clog at the ends of the distributor and at the inlet to the entrainment zone, which disrupted smooth circulation.

The viscosity of molten carbonates at elevated temperatures tends to vary over the range of 2-5 cp,^{27,28,29} so solution viscosities of 1, 2, 3, 4, and 5 cp were investigated. The higher viscosity values were achieved by adding carboxymethylcellulose (CMC) to the water in the solution reservoir. The viscosities of the resultant solutions were measured in a Brookfield viscometer. However, the density of the liquid still remained close to that of water. It was found that both viscosity and density could not varied independently in a simple fashion, while retaining the essential slurry characteristics. Therefore, the investigations focused on viscosity variation.

4.2. Experimental Results

A summary of the experiments in which the liquid was recirculated *via* the inlet jet is presented in Table 1. The flow in the draft duct was laminar in all these cases.

Some images of the behavior of the slurries in the SVHA for these experiments are presented in Figures 14-17. It can be concluded from these figures that the best contact of the carbon particles with the inclined surfaces in the vessel (i.e., bottom and distributor) is achieved at low flow rates and low loadings. However, as indicated by the computational results, good contacting can also be achieved at higher flow rates if the vessel internals are modified to retain the particles in the region below the freeboard; by employing “cap” for example (see Figures 6-11).

Table 1. Summary of experimental runs.

	1 mm Particles			0.5 mm Particles		
	1	1	1	1	1	1
Viscosity (cp)						
Loading (cm³)	25	50	75	25	50	75
		Volumetric Flow Rate (cm³/s)				
				37.8	37.8	37.8
	63.1	63.1	63.1	63.1	63.1	63.1
	88.3	88.3	88.3	88.3	88.3	88.3
	107.2	107.2	107.2	107.2	107.2	107.2
Viscosity (cp)		2		2		
Loading (cm³)	25	50	75	25	50	75
		Volumetric Flow Rate (cm³/s)				
				37.8	37.8	37.8
	1	1	1	37.8	37.8	37.8
	1.4	1.4	1.4	63.1	63.1	63.1
	1.7	1.7	1.7	88.3	88.3	88.3
	107.2	107.2	107.2	107.2	107.2	107.2
Viscosity (cp)		3		3		
Loading (cm³)	25	50	75	25	50	75
		Volumetric Flow Rate (cm³/s)				
				37.8	37.8	37.8
	63.1	63.1	63.1	63.1	63.1	63.1
	88.3	88.3	88.3	88.3	88.3	88.3
	107.2	107.2	107.2	107.2	107.2	107.2
	132.5	132.5	132.5			
Viscosity (cp)		4		4		
Loading (cm³)	25	50	75	25	50	75
		Volumetric Flow Rate (cm³/s)				
				37.8	37.8	37.8
	63.1	63.1	63.1	63.1	63.1	63.1
	88.3	88.3	88.3	88.3	88.3	88.3
	107.2	107.2	107.2	107.2	107.2	107.2
	132.5	132.5	132.5			
	157.7	157.7	157.7			
Viscosity (cp)		5		5		
Loading (cm³)	25	50	75	25	50	75
		Volumetric Flow Rate (cm³/s)				
				37.8	37.8	37.8
	63.1	63.1	63.1	63.1	63.1	63.1
	88.3	88.3	88.3	88.3	88.3	88.3
	107.2	107.2	107.2			
	132.5	132.5	132.5			
	157.7	157.7	157.7			

The apparatus was also modified by installing a check valve at the vessel jet inlet to introduce carbon dioxide gas instead of slurry liquid *via* the vessel inlet, while retraining the slurry in the vessel. The introduction of carbon dioxide provides “gas-lift” of the slurry up through the draft duct. This is potentially the most desirable slurry circulation technique, since it does not require a mechanical pump. The carbon dioxide is conveniently provided as the fuel cell product gas. The experimental conditions used for these experiments were: a viscosity of 2 cp, 75 cm³ carbon loading, and 0.5 mm particles. The CO₂ flow rate was varied from 0.1 - 0.4 liters/min. Images from these experiments are presented in Figure 18. As shown, introduction of carbon dioxide produced good slurry recirculation and contact with the inclined vessel surfaces (i.e., bottom and distributor) in all cases. The observed behavior was consistent with the computation results that showed good slurry entrainment produced by the introduction of carbon dioxide gas *via* the jet inlet. However, at the higher flow rates, the particle inventory in the freeboard increased considerably. This can be avoided, by installation of a “cap,” as demonstrated in the computational results (*cf.* Figures 6-11).

Data obtained with the Aeroprobe micro-pitot tube assembly allowed measurements of the split in the volumetric flow rate between the draft duct and the upward flow through the peripheral particle bed (i.e., the “bypass” flow). The velocity measurements under fully developed laminar flow near the top of the draft duct were used to calculate the draft duct flow rate, and the bypass flow was determined by difference.

Although a significant amount of data is presented in Figures 19 and 20, the overall trends are clear. For the 1 mm particle slurries, at low viscosities and low total volumetric flow rates (i.e., low inlet jet velocities), the two flows are about the same. Increasing total flow rate causes the bed bypassing to increase. As the solution viscosity increases, the two flows become more nearly similar, and they both increase proportionately with total flow rate. At the highest viscosity, the draft duct flow rate becomes larger than the bypass flow at low total flow rates, while still remaining similar at higher flow rates. Particle loading appears to have a second order effect, at least over the parameter region examined.

Similar trends are evident in the 0.5 mm particle data. However, the effect of viscosity appears to be more pronounced, since the draft duct flow becomes larger than the bypass flow over the entire flow rate range by 4 cp, and this difference widens at 5 cp.

Much of this behavior can be explained in terms of the drag force on the particles versus the gravity force. Since the smaller particles have a greater surface area-to-volume ratio, drag force has a more marked effect on smaller particles, which makes them easier to entrain in the draft duct flow. Thus, better circulation can be achieved with smaller particles at higher viscosities. Both of these are characteristics that are expected in direct carbon fuel cells. Consequently, the SBE/DCFC approach appears to be well-suited for this application.

(a)

(b)

(c)

Figure 14. 0.5 gpm, 1 cp, 1 mm particles. Carbon loading: (a) 25 cm³; (b) 50 cm³; (c) 75 cm³.

(a)

(b)

(c)

Figure 15. 0.7 gpm, 1 cp, 1 mm particles. Carbon loading: (a) 25 cm³; (b) 50 cm³; (c) 75 cm³.

(a)

(b)

Figure 16. 0.5 gpm, 1 cp, 0.5 mm particles. Carbon loading: (a) 25 cm^3 ; (b) 50 cm^3 .

(a)

(b)

Figure 17. 0.7 gpm, 1 cp, 0.5 mm particles. Carbon loading: (a) 25 cm^3 ; (b) 50 cm^3 .

(a)

(b)

(c)

(d)

Figure 18. “Gas-lift” with CO₂. 75 cm³ carbon particle loading, 2 cp. CO₂ flow rate: (a) 0.1 l/min; (b) 0.2 l/min; (c) 0.3 l/min; (d) 0.4 l/min.

Figure 19. Volumetric flow rates in the draft duct and peripheral bed region as a function of carbon loading (25, 50, and 75 cm³) for 1 mm particles. (a) 1 cp; (b) 2 cp; (c) 3 cp; (d) 4 cp; and (e) 5 cp.

Figure 20. Volumetric flow rates in the draft duct and peripheral bed region as a function of carbon loading (25, 50, and 75 cm³) for 0.5 mm particles. (a) 1 cp; (b) 2 cp; (c) 3 cp; (d) 4 cp; and (e) 5 cp.

5.0. Spouted Bed Electrode/Direct Carbon Fuel Cell (SBE/DCFC) Prototype Design.

Our original SBER designs were of cylindrical geometry with conical vessel bottoms to accommodate the cathode current feeder for electrolytic recovery (*cf.* Figure 2). In this Phase I project, we investigated a rectangular SBE geometry with inclined anodes that could be ordered in chevron-like arrangements of bipolar elements (*cf.* Figure 3). Based upon this work, we have developed an improved SBE/DCFC design. The basic approach is to employ materials, electrodes and separators that have already been demonstrated to be effective for MCFC/DCFC applications, and to add the important feature of carbon/molten carbonate slurry recirculation. The essentials of this design are presented below.

5.1. Design Overview

A conceptual schematic of the prototype cell design is presented in Figure 21. As shown, the cell is rectangular with an inclined bottom to facilitate carbon particle slurry entrainment and recirculation. Unlike the concept shown in Figure 3, however, the electrodes in this design are rectangular and arranged vertically, rather than inclined. This geometry simplifies construction of the cell by employing flat, rectangular elements to form a “sandwich” of the electrodes, current collectors, and the separator, thereby facilitating the arrangement of cells in stacks in a fashion that is quite similar to bipolar plates in conventional fuel cells. Details of this design, and the functioning of the SBE/SCFC element are discussed in more detail below.

Vertical Anodes. The use of vertical anodes was suggested by some spouted bed electrode designs that have been used to bring conductive bed media particles in direct contact with vertically oriented cathodic current feeders to reduce metal cations in solution to metal on the surfaces of the circulating cathodic bed particles. Copper^{30,31,32,33} and zinc³⁴ electrowinning have been successfully conducted in rectangular spouted bed cells in which the vertical front and back walls serve as the electrodes.

The anode current carriers in the design in Figure 21 are the vertical front and back walls of the upcomer draft duct and the two outside downcomers. In all our experimental and modeling work with SBERs, the particle volume fraction at the walls of the draft duct is always observed to be significantly greater than in the bulk phase. This is a well-known phenomenon in fluid-particle flows. The viscous drag at the boundary slows the fluid, such that particles tend to concentrate in the region near the wall. This effect has been substantiated in numerous experimental and simulation investigations in a number of similar and related systems. For

example, Kwauk³⁵ showed experimentally that the radial solids fraction of FCC catalyst particles in a 90 mm diameter riser decreased from the wall to the axis. This was also observed by He *et al.*^{36,37} who measured particle velocity and solids concentration in a spouted bed with a fiber optic probe; and also by Samuelsberg and Hjertager³⁸ who investigated the flow patterns in a circulating fluidized bed reactor, both numerically and experimentally using laser Doppler anemometry (LDA). In both of these latter studies it was also shown that the particle flux in the axial direction also decreases from the axis to the walls, which means that particles near the wall experience a greater residence time than particles in the bulk phase. This latter effect is also consistent with other related observations in the literature.^{39,40} This effect can be used to feed vertical anodes in the spout (upward flow) and downcomer flow regions. The particle volume fraction at the wall can be controlled and optimized *via* the hydrodynamics and the particle loading. The continuous flow and concomitant particle movement will also prevent electrode fouling due to the accumulation of ash contaminants (see below).

Carbon/Molten Carbonate Slurry Recirculation. As indicated above, the major improvement in the SBE/DCFC approach is the addition of a recirculating molten carbonate slurry containing the carbon particle fuel. The recirculating slurry serves a number of important functions. More specifically, it provides facile means for:

- (1) bringing carbon particles in contact with the vertical anode surface, as described above.
- (2) preventing the anode surfaces from becoming contaminated with ash. The resultant ash will be convected away by the slurry flow. Entrainment in the flowing molten carbonate allows for continuous removal of ash from the cell *via* a purge stream. The carbonate salt can be separated from the ash in this stream by aqueous techniques. Cooper⁴ has suggested that the sodium-potassium carbonate eutectic mixture (710°C melting point) is especially useful for this purpose, due to its high solubility in water.
- (3) fueling the cell. As shown in Figure 21, solid carbon particles can be entrained in a CO₂ stream derived from the cell product gas, and then used as part of the CO₂ “lift-gas” stream to drive the slurry circulation. In this manner, fresh carbon particles are injected directly at the slurry entrainment point. Another method for fueling the cell would be to introduce carbon particles into the fresh molten carbonate recycle stream produced following removal of the ash in an external process. The fresh recycle stream is shown entering at the top of the cell in Figure 21.

Figure 21. Schematic of SBE/DCFC.

- (4) temperature control of the cell. Due to the very large thermal capacitance of the circulating slurry, cell temperatures can be precisely controlled.
- (5) electrolyte maintenance and control in the separator. Fresh, ash-free and carbon particle-free molten carbonate, following external ash cleaning, can be used to maintain the electrolyte in the separator. Vertical orientation of the separator allows the electrolyte to flow and drain so that it does not collect in locations that would seal off oxygen transport to reactive cathode sites. The approach shown in Figure 21 introduces fresh molten carbonate into a reservoir at the top of the separator. A metal screen or filter prevents contamination of the fresh electrolyte with carbon and ash from the recirculating slurry. This method also provides a means of introducing make-up carbonate to the recirculating slurry through the filter. Electrolyte from the separator drains at the bottom where it mixes with the recirculating slurry. The flow rate of fresh electrolyte to the separator and for the make-up is controlled by pressure balance.
- (6) (potentially) improving carbon conversion rates. That is, the recirculating carbonate slurry may serve to “activate” the carbon particles for electrochemical oxidation. Molten carbonates at high temperatures are well known catalysts for coal gasification. The first step in this conversion process is the formation of oxygen surface complexes which upon further reaction desorb as oxides of carbon to gasify the carbon. Cooper and co-workers^{41,42} have suggested that the mechanism of oxidation of carbon at the anode may be similar to that of the carbon anode in the cryolite/alumina electrolyte used in aluminum smelting. In this latter case, the carbon electrode produces nearly pure CO₂ at temperatures as high as 1100°C.⁴³ The accepted mechanism involves initiation by thermal decomposition of an aluminum-fluoride species to form O²⁻ that adsorbs on the surface of the carbon electrode. Upon discharge, the adsorbed ion forms strongly bound –C(O) surface functional groups. A second adsorption of O²⁻ at these sites and its discharge requires polarization, such as would occur at an anode surface, and results in –C₂O₃ surface functional groups that readily decompose to CO₂.⁴⁴ Mixed carbonate electrolytes readily decompose into CO₂ and O²⁻ at temperatures in the operating range of DCFCs.⁴⁵ Thus, the mechanisms for anodic oxidation of carbon by O²⁻ and CO₃²⁻ anions may be somewhat similar. In the case of oxidation by carbonate anions, the anodic mechanism may proceed according to:

The $-\text{C}_2\text{O}_3$ surface complexes may be similar to the carboxylic anhydride complexes that have been identified as major intermediate species in the air/oxygen gasification of carbons and chars.^{46,47,48}

The carbonate anions in the recirculating slurry may serve as a “catalyst” to “activate” carbon particle surfaces by performing the first oxidation step to form the requisite $-\text{C}(\text{O})$ surface complexes. If the polarization is insufficient at the point of oxidation in the bulk melt phase to release the two electrons, the surface oxygen complex may remain charged, or the charge may be delocalized over the carbon particle. In any case, it will ultimately give up its electrons to the anode upon the second oxidation step to form $-\text{C}_2\text{O}_3$ surface functional groups occurs at the anode. Depending upon which oxidation step is rate-limiting, “activation” or oxidation in the bulk slurry melt might serve to increase the rate of the anode reaction. If this occurs, it could be an important effect, since the kinetics of the overall electrochemical carbon conversion process is known to be relatively slow under typical DCFC conditions.

Since a significant fraction of the carbon particles in the molten carbonate slurry will be out of electrical contact with the anode surfaces, care must be taken that carbon gasification does not occur to any appreciable extent in the bulk phase. This will be controlled *via* a combination of operating temperature (which can be closely controlled in the SBE/DCFC) and molten carbonate salt composition. Various binary and ternary eutectics of sodium-lithium and sodium-lithium potassium carbonates have been examined as potential electrolytes. However, the preferred MCFC electrolyte has been the binary lithium-potassium carbonate, consisting of 62 mol% lithium carbonate and 32 mol% potassium carbonate (490°C liquidus temperature).⁶ Other eutectics of lithium, potassium, and sodium carbonates exhibit melting points below 400°C. Some experimentation will be required in order to decide upon a suitable carbonate formulation and operating temperature.

Carbon gasification by gaseous CO₂ *via* the Boudouard reaction is not expected to be significant since the bulk of the CO₂ introduced in the lift gas passes through the cell as gas bubbles and thus has poor contact with the carbon particles in the slurry.

Gas Cathode. Air/O₂ mixed with CO₂, obtained from the cell product gas, is introduced *via* the gas cathode. The gas passes through a metal cathode current collector that is a perforated plate or mesh screen, and then through a sintered nickel or compressed nickel foam anode. Cooper⁴ observed that at high temperatures, CO₂ does not have to be added to the cathode air stream because the opposed gradients of carbonate and oxide are sustained by ionic migration and diffusion from sources at the anode and cathode, respectively; i.e.,

He also suggested, however, that it may still be desirable to introduce CO₂ in the cathode gas stream because the accumulation of the heavy and less mobile carbonate anion at the cathode/gas interface is responsible for generating a continuous flux of alkali carbonate from cathode to anode through the separator. This effect might be exploited to offset fouling of the separator by ash impurities.

5.2. SBE/DCFC Scale-Up

In order to become a commercially viable system, the SBE/DCFC must be capable of operation on a large scale. This primarily involves “stacking” the bipolar electrode elements to produce useful voltages, and increasing the surface area of the anodes. The vertical rectangular design of the prototype cell allows for “stacking” cells horizontally in bipolar elements, analogous to bipolar plates. A conceptual schematic of a stack of rectangular SBE/DCFCs is presented below in Figure 22.

Although spouted bed systems have been successfully scaled-up for a wide variety of applications,⁴⁹ for the SBE/DCFC application there are a number of additional constraints. Additional anode surface area can be provided by increasing the length and lateral extent of the rectangular elements, as well as by adding more elements. However, the length of the elements and the width of the slurry flow channels are limited by the hydrodynamics. Increasing length

increases the pressure drop, and beyond some point slurry circulations ceases entirely. Wider flow channels and separator thickness would tend to decrease pressure drop, but would also increase the overall volume of the bipolar elements, as well as the electrical resistance of the separator. The SBE concept, however, is quite flexible and can be modified in a number of ways. For example, a “trough” type design is possible wherein one central, larger rectangular draft duct or elongated slot feeds a few rectangular downcomers on either side that are located and arranged in bipolar stacks. In this manner, a relatively high flow rate in the single large upcomer can be matched by the flow in a few smaller downcomers, allowing for an acceptable pressure balance. The bottom of this “composite cell” (i.e., consisting a few bipolar stacks) would be inclined, as in Figure 21, to facilitate movement of the circulating slurry towards the entrainment point at the center.

Figure 22. Top view of bipolar stack of spouted bed electrodes.

Other design modifications may also be used improve the performance of the SBE//DCFC. For example, the separator can be eliminated by using the molten carbonate slurry as both the fuel transport medium and the electrolyte. A schematic of such a rectangular cell element is shown in Figure 23. In this design a ceramic frit serves as a membrane or diaphragm that passes

the carbonate ion current carriers produced at the cathode, but does not allow carbon particles to come in contact with the cathode. The carbonate ions are transported across the slurry/electrolyte to the anode on the other side where they oxidize the carbon fuel. This arrangement is analogous to that used in our cylindrical SBER and the rectangular SBEs described above³⁰⁻³⁴ for electrowinning metals from aqueous acidic solutions. In this latter case, the aqueous solution serves as both the particle transport medium and the electrolyte. This design is somewhat simpler than that presented in Figures 22 and 23, since it eliminates potential electrolyte maintenance problems in the separator, and may actually reduce the overall cell resistance by elimination of the separator. However, this reduction is also dependent on the width of the electrolyte compartment.⁵⁰ In the SBE/DCFC, the latter also depends on the hydrodynamics (i.e., pressure drop). Therefore, assessment of the relative merit of the approach schematized in Figure 23 must be the subject of experimental validation.

Figure 23. Top view of alternative spouted bed cell arrangement with carbon/molten carbonate slurry serving as the electrolyte.

6.0. Conclusions

This Phase I project was directed at the application of spouted bed particulate electrodes to the direct utilization of carbon in fuel cells. This involves the use of a circulating carbon particle/molten carbonate slurry in the cell that serves a number of important functions: it (1) fuels the cell continuously with entrained carbon particles; (2) brings particles to the anode surfaces hydrodynamically; (3) removes ash from the anode surfaces and the cell hydrodynamically; (4) provides a facile means of cell temperature control due to its large thermal capacitance; (5) provides a facile means of electrolyte maintenance and control in the electrode separator(s); and (6) can (potentially) improve carbon conversion rates by “pre-activating” carbon particle surfaces *via* formation of intermediate oxygen surface complexes by the carbonate.

The approach taken in this scoping project was twofold: (1) adapt and apply a CFD code originally developed to simulate particle circulation in spouted bed electrolytic reactors, to carbon particle circulation in candidate geometries for DCFC systems; and (2) experimentally investigate the hydrodynamics of carbon slurry circulation in DCFC systems using simulated slurry mixtures.

The CFD model results showed that slurry recirculation can be used to hydrodynamically feed carbon particles to anode surfaces. Variations of internal configurations were investigated in order to explore effects on contacting. It was shown that good contacting with inclined surfaces could be achieved even when the particles are of the same density as the molten carbonate.

Another potentially important mode of operation investigated with the CFD model was the use of CO₂ product gas from the fuel cell as a “lift-gas” to circulate the slurry. This method is preferable to using a mechanical pump to handle the corrosive slurry. In order to investigate this possibility, the CFD model was extended to three phases: carbon particles, molten carbonate, and CO₂, while retaining the Eulerian formulation. The results showed that this was an effective method of slurry circulation, which is superior in some ways to pumping; it entrains carbon particles more effectively in the draft duct and produces a somewhat slower recirculation rate, and thus higher residence times on anode surfaces, and can be controlled *via* pressure balance.

The experimental results in the rectangular spouted vessel hydrodynamics apparatus (SVHA) showed that hydrodynamics can be used to control the circulation, residence time, and distribution of carbon within the spouted bed, as well as provide good particle contact with anode surfaces. This was shown to be a function of viscosity, carbon loading, and particle size, as well as relative densities. Higher viscosities and smaller particle sizes favor more efficient particle entrainment in the draft duct, and particle recirculation.

Carbon slurry circulation in the SVHA was achieved by entrainment with an inlet liquid jet, and also with CO₂ “gas-lift.” However, as concluded from the computational results, the latter method is preferable since there are no moving or mechanical parts to be in contact with the high temperature, corrosive slurry, and the generally lower circulation rates are good for maintaining high particle residence times on anode surfaces.

Both the computational and experimental results are consistent with each another and exhibit the same general qualitative behavior.

Based upon this work, a design of a prototype SBE/DCFC cell was developed and is presented.

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