Enhancing Hybrid Direct Carbon Fuel Cell anode performance using Ag₂O

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Abstract

A hybrid-direct carbon fuel cell (HDCFC), consisting of a molten slurry of solid carbon black and (Li-K)₂CO₃ added to the anode chamber of a solid oxide fuel cell, was characterized using current-potential-power density curves, electrochemical impedance spectroscopy, and cyclic voltammetry. Two types of experimental setups were employed in this study, an anode-supported full cell configuration (two electrodes, two atmospheres setup) and a 3-electrode electrolyte-supported half-cell setup (single atmosphere). Anode processes with and without catalysts were investigated as a function of temperature (700-800°C) and anode sweep gas (N₂, 4-100 % CO₂ in N₂-CO₂). It was shown that the addition of silver based catalysts (Ag, Ag₂O, Ag₂CO₃) into the carbon-carbonate slurry enhanced the performance of the HDCFC.

Keywords: Direct carbon fuel cell (DCFC), carbon black, silver oxide, electrochemical performance, cyclic voltammetry (CV)

1 Introduction

Direct carbon fuel cells (DCFCs) include a range of different fuel cell types but all include the oxidation of solid carbon in the anode chamber without combustion. DCFCs represent a one-step transformation of solid coal to electricity at a much higher potential efficiency than coal combustion [1-9]. At the anode of a DCFC, in the absence of air, solid carbon is oxidized by a variety of oxidants depending on the fuel cell type, including, hydroxide (OH^- , molten hydroxide fuel cell (MHFC)), carbonate (CO_3^{2-} , molten carbonate fuel cell (MCFC)) and oxygen anions (O^{2-} , solid oxide fuel cell (SOFC)).

Hybrid DCFCs (HDCFCs), which combine elements of MCFCs and SOFCs, were first proposed by Peelen et al. (1998) [10]. This design consists of a SOFC cathode and electrolyte and a molten alkali carbonate-solid carbon slurry in the anode chamber, maintaining the enhanced fuel contact of the molten media while eliminating the need for re-circulation of CO_2 to the cathode, both features of MCFCs. HDCFCs have been investigated at Contained Energy [11], Korea Institute of Energy Research [12], Stanford Research Institute (SRI International) [4, 13], the University of Queensland [14], University of Western Macedonia [15], West Virginia University [16], and the University of St. Andrews [17]. The planar HDCFC developed at the University of St. Andrews (Scotland) is employed here.

Anode chamber processes have been found to be limiting to full-cell HDCFCs [9], hence catalysts are sought to improve performance. Transition metals introduced into the carbon-carbonate melt have been shown to increase electrochemical activity in MCFC-type DCFCs [18]. Loading metals, including silver or nickel, onto the carbon introduced into the anode chamber of SOFC-type DCFCs have also shown enhanced power densities, with 2 wt% Ag showing the greatest enhancement [19]. Silver loaded on gadolinium-oxide doped ceria (GDC) has been shown to enhance anode reactions, through the promotion of CO oxidation, in SOFC-type DCFCs [20]. Further, molten silver has been

employed as both a fuel and oxidant electrode medium and catalyst for molten metal anode SOFC-type DCFCs [21-22]. These DCFC studies, and other investigations of its chemical catalytic activity, drew our attention to the use of silver-based catalysts. Additionally, we recently tested a wide variety of single and mixed materials as carbon oxidation catalyst in air (non-electrochemical activity) by thermo-gravimetric analysis (TGA) [23]; Ag₂O showed the highest catalytic enhancement. Hence, silver oxide was selected for electrochemical testing as a catalyst at the anode of a HDCFC.

In this work we investigated the use of Ag₂O introduced to the HDCFC as part of the carbon-carbonate mixture in the anode chamber. Catalytic enhancement was investigated using two set-ups, as a full-cell and in a single atmosphere 3-electrode half-cell (3E), which allowed examination of the anode processes versus a reference electrode without the contribution of cathode processes, contributions which are unavoidable in full-cell measurements. Electrochemical performance was investigated using electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and current-potential-power density (I-V-P) curves as a function of temperature (700-800°C) and anode sweep gas composition (4-100 % CO₂ in N₂-CO₂). These investigations build on those reported under un-catalyzed conditions for a full-cell HDCFC set-up [24], and seek to determine the catalytic activity of Ag₂O in both 3E half-cell and full-cell setups.

2 Experimental

2.1 Thermo-gravimetric analysis

Carbon oxidation (in air) and gasification (in N₂) temperatures were determined for blank samples, with and without SiC (≥ 97.5 %, Sigma-Aldrich), and in the presence of a catalyst, Ag₂O (99+ %, Alfa Aesar). Additionally, carbon was loaded with a 5 wt% (metal basis) AgNO₃ aqueous solution. As AgNO₃ solution is light sensitive, a new batch was prepared immediately prior to use. The pH of

de-ionized water was first adjusted (pH = 3) with nitric acid, then a 1 M solution was prepared by dissolving solid AgNO_3 (Alfa Aesar) with vigorous stirring in a brown glass bottle. Carbon was first suspended in water, requiring rapid stirring, the aqueous nitrate solution was added, followed by 2-propanol. After heating to 80°C , the metal was reduced by adding a 2.5 times excess of NaBH_4 suspended in ether. After further heating, the solution was filtered with water and heated overnight at 100°C , followed by grinding with an agate mortar and pestle. Pure and Ag-loaded carbon were introduced into the TGA instrument without further mixing.

Catalysts were combined with carbon black acetylene (99.9+ %, Alfa Aesar) in a 96:4 wt% catalyst:carbon ratio, and were manually ground together in an agate mortar and pestle. A known mass was introduced into an alumina crucible, and TGA and differential thermal analysis (DTA) were acquired using simultaneously using a Seiko TG/DTA 320U and Netzsch STA 409CD. Data was acquired between 25 and 1000°C (5°C min^{-1}) in air, N_2 , and 96-4 $\text{N}_2\text{-CO}_2$ (100 mL min^{-1}), and analyzed by using Netzsch Proteus software [23].

2.2 Single-atmosphere setup

Yttria-stabilized zirconia (YSZ, 8 mol% Y_2O_3) powder was pressed (0.6 T/ 15 s, then isostatically at 60 T/ 30 s) and shaped into a 3-electrode pellet and sintered ($1600^\circ\text{C}/ 2 \text{ hrs}$). The working electrode (WE) was depositing by making a slurry of 55:45 wt% NiO:YSZ (YSZ calcined, $1350^\circ\text{C}/ 2 \text{ hrs}$) with an organic solvent, a cellulose-type binder and a phthalate-type dispersant, followed by screen-printing and sintering ($1250^\circ\text{C}/ 2 \text{ hrs}$). The counter (CE) and reference electrodes (RE) were applied by painting Pt paste followed by sintering ($900^\circ\text{C}/ 2 \text{ hrs}$). A zirconia cylinder was employed as a carbon-carbonate reservoir by sealing the cylinder (60 mm height) around the WE, on to the YSZ pellet, using Ceramabond 552 (Aremco, sealing: $90^\circ\text{C}/ 2 \text{ hrs}$; $260^\circ\text{C}/ 1 \text{ hr}$, followed by slow cooling

to room temperature). Various sealants were investigated, including the use of alumino-silicate glasses and gold, all of which proved inadequate in the presence of molten carbonates. Further, the use of an alumina cylinder was ruled out due to difficulties in sealing alumina to the YSZ pellet.

A gold mesh was used as WE current collector, which was fitted prior to tube-pellet sealing; contact was made to the WE current collector using a Au wire. Fuel (~ 1 g) was packed into the tube as 4:1:1 wt% carbon black:(62-38 wt% Li-K)₂CO₃:SiC (no catalyst) or Ag₂O. Pt wire was wrapped around the CE with a fresh coat of Pt paste to serve as current collector, additionally, a Pt wire provided contact to the RE. Two 3-electrode half-cells loaded with solid carbon were simultaneously mounted into a ceramic cell holder, and sealed inside a alumina vessel, which was placed inside a furnace. The half-cell setup is shown schematically in Figure 1. The ceramic cell holder was equipped with a Pt oxygen partial pressure sensor supplied with air, which reported P_{O2} (in mV) of the working atmosphere (CO-CO₂) vs. Pt/air.

(Figure 1)

Half-cells were heated to 800°C (180°C hr⁻¹) in N₂ (5.76 L hr⁻¹). Following reduction of NiO, a mixture of 96-4 vol% N₂-CO₂ (2.3 or 6 L hr⁻¹ total flow) was introduced, and temperature was ramped to operating temperature (700-800°C). Cyclic voltametry (CV) data was acquired by varying the potential against the internal reference electrode (Pt in the working atmosphere, CO-CO₂), which is referred to here as potential difference (ΔE, mV vs. Pt/CO-CO₂). Potential difference was scanned between ± 500 mV vs. Pt/CO-CO₂, at a rate 1-20 mV s⁻¹. OCP was monitored galvanostatically (I = 0) vs. Pt/CO-CO₂, and OCP vs. Pt/air was calculating using P_{O2} sensor data. OCP (mV vs. Pt/air) values are reported as the absolute value of the potential measured with respect to a Pt electrode in air at atmospheric pressure. EIS data was obtained using a Solartron 1250/1287 potentiostat/frequency response analyzer combination. Data was acquired without applied DC potential (ΔE = 0), over the frequency range 65,000 to 0.05 Hz (descending, 6 pts

decade⁻¹), and at an amplitude of 30 mV. Cell performance was measured as a function of temperature (700-800°C) and working atmosphere (4-100 vol% CO₂ in N₂, 2.3 L hr⁻¹ total flow). It was felt that active surface area was poorly defined due to the dynamic nature of the C-CO₃ melt in the WE chamber [25], hence, currents and resistances are reported without area correction.

2.3 Full-cell setup

HDCFC planar full-cells are setup as described in Deleebeeck and Hansen (2014) [24] and shown in Figure 2. Briefly, the anode-supported cells consisted of a NiO-YSZ (YSZ) cermet anode, YSZ electrolyte (10 μm, Topsoe Fuel Cell A/S, Denmark), a La_{1-x}Sr_xMnO₃ (LSM)-YSZ cathode, and LSM current collector layer (NiO-YSZ|YSZ|LSM-YSZ/LSM). Carbon was introduced to the anode chamber as 4:1:1 wt% C:CO₃:SiC (blank), Ag₂O, Ag (≥ 99.9 %, Sigma-Aldrich), or Ag₂CO₃ (99 %, Sigma-Aldrich). Cells were heated to 800°C (180°C hr⁻¹) with N₂ (5 L hr⁻¹) at the anode, and air at the cathode (19 L hr⁻¹). Following reduction of NiO, a mixture of 96-4 vol% N₂-CO₂ (22.5 L hr⁻¹ total flow) or 80-20 vol% N₂-CO₂ (6 L hr⁻¹ total flow) was introduced at the anode, and temperature was ramped to operating temperature (700-800°C). Anode and cathode potential and current were monitored; EIS data was obtained using a Solartron 1260 Impedance/Gain-phase Analyzer (50 Ω internal resistor). Data was acquired at open circuit voltage (OCV), defined as the potential difference between anode and cathode, over the frequency range 82540 to 0.1 Hz (descending, 6 pts/decade), and an amplitude of 3 V, which is a perturbation of ≤ 40 mV to the cell. EIS data was analyzed using the Elchemea program developed at DTU Risø (www.elchemea.com). I-V curves were acquired as current was varied between OCV and ~ 600 mA-2 A (increasing then decreasing). Overall resistance was calculated by applying a linear fit, to determine the slope, to the return (decreasing current) leg of the measurement. Power density and current density were calculated based on the geometric surface area of the cathode.

(Figure 2)

3 Results

3.1 TGA

The catalytic promotion of carbon oxidation in air and gasification in mixed N₂-CO₂ environments by silver-based catalysts was investigated by TGA-DTA. Figure 3(a) shows the DTA and first derivative of TGA measurements (dTGA/dt) acquired, between 25 and 1000°C (5°C min⁻¹) in air, for carbon black acetylene and 5 wt% silver loaded on carbon black. Temperatures of carbon oxidation in air are included in Figure 3, where materials with lower oxidation temperatures were considered better catalysts towards the oxidation of carbon (combustion).

(Figure 3)

Figure 3(b) shows the TGA-DTA measurements for C-SiC and C-Ag₂O in air. SiC is an inert (non-catalytically active) material commonly [26] used in TGA measurements to ensure thermal distribution within the sample holder (alumina crucible). The presence of SiC allowed better heat penetration/dissipation to the carbon, thus lowering the measured oxidation temperature [27-28].

Figure 4 shows the TGA measurements acquired in 96-4 N₂-CO₂ for carbon black and silver loaded carbon, and acquired in N₂ for carbon mixed with SiC and Ag₂O. Mass loss due to gasification was promoted at lower temperatures, vs. C black alone, through the inclusion of silver-based catalysts, suggesting silver and silver oxide are both carbon oxidation (in air) and gasification (in N₂-CO₂) catalysts. In N₂ or mixed N₂-CO₂ environments, carbon mass was lost (Figure 4) through a variety of gasification processes [9], including the reverse Boudouard reaction (Reaction 1).

(Figure 4)

3.2 Half-Cell

3.2.1 ELECTROCHEMICAL RESULTS

Electrochemical performance at the WE was measured by EIS, acquired between 700 and 800°C in a 96-4 N₂-CO₂ atmosphere. Representative Nyquist plots for SiC (no catalyst, a) and Ag₂O (b) at

800°C are shown in Figure 5. At these temperatures, both CO and CO₂ are present under OCP conditions. Although CO was not supplied to the setup as part of the sweep gas, CO was formed chemically through the Boudouard reaction (Reaction 1) and/or gasification of carbon [9], or electrochemically through the reduction of CO₂ (Reaction 2) at the CE (Pt) or the partial oxidation of carbon (Reaction 3) at the WE. Hence, when referring to the internal Pt RE, potential differences (ΔE) are given in mV vs. Pt in a CO-CO₂ atmosphere, termed Pt/CO-CO₂. Using P_{O2} sensor data (Figure 1), potentials were calculated and are given as absolute values in mV vs. Pt/air.

EIS data was fitted using a model circuit consisting of a resistor (series resistance, R_s) in series with two (or three) resistor-constant phase element units (RQ, in parallel) (Figure 5, inset). High frequency (HF) processes were associated with the charge transfer reaction(s) at the WE, while low frequency (LF) processes were related to the supply of reactants or the rate of initial chemical processes in the WE chamber. Polarization resistances (R_p) were calculated from the addition of resistances for RQ units in series ($R_p = R(\text{HF}) + R(\text{LF})$). It should be noted that the 3E cell was electrolyte supported (vs. anode supported full-cell) and so gave relatively high resistance values.

(Figure 5)

Catalytic activity of Ag₂O included at the WE was investigated under load (applied potential difference vs. Pt/CO-CO₂ RE) by acquiring CVs as a function of temperature (700 - 800°C) and working atmosphere (4-100 % CO₂ in N₂-CO₂). A representative CV curve acquired for carbon black-CO₃-SiC (no catalyst present) at 700°C in 96-4 N₂-CO₂ is shown in Figure 6. Similar CVs were acquired in the presence of Ag₂O (Figure 6(b)). Various current and potential values were recorded, as illustrated in Figure 6, including current when no potential difference was applied (ΔE

= 0), peak currents and potentials, and current measured at fixed overpotential ($\eta = + 400\text{-}500\text{ mV}$ vs. OCP).

(Figure 6)

3.2.2 Effect of Temperature

Figure 7(a) shows EIS Nyquist plots acquired in 96-4 $\text{N}_2\text{-CO}_2$ as temperature was increased between 730 and 800°C. Overall R_p decreased with increasing temperature, with the LF feature dominating the changing impedance response, such that the LF contribution was larger than the HF contribution over the temperature range investigated. Figure 7(b) shows CVs ($\pm 500\text{ mV}$ vs. Pt/CO- CO_2 RE) acquired in a 96-4 $\text{N}_2\text{-CO}_2$ atmosphere at a high flow rate (6 L hr^{-1} total flow). The currents at which the forward (anodic) sweep of the CV crosses the current-axis ($\Delta E = 0$) and at fixed overpotential ($\eta = + 500\text{ mV}$) were measured at each temperature and are tabulated in Table 1. Further, the potential at which the CVs crossed the potential-axis ($I = 0$) were measured independently by holding the cell at OCP (galvanostatic, $I = 0$) for a length of time sufficient to stabilize the acquired potential values ($> 2\text{ min}$) and are given in Table 1.

(Figure 7)

(Table 1)

For SiC (no catalyst) and Ag_2O (Table 1), OCP (a) and currents measured at $\Delta E = 0$ (b) and $\eta = 500\text{ mV}$ (c) in 96-4 $\text{N}_2\text{-CO}_2$, plotted as a function of temperature in Figure 8, were seen to increase as temperature was increased between 700 and 800°C. OCP values tended to increase linearly, while currents appeared to increase exponentially.

(Figure 8)

3.2.3 EFFECT OF CO₂

In addition to using CVs to investigate 3E half-cell performance as a function of temperature (Figures 7-8), performance was investigated as a function of atmosphere composition (N₂-CO₂, 2.3 L hr⁻¹ total flow) at 700 and 770°C. In the presence of Ag₂O, CVs were acquired at 700 °C and in the presence of SiC and Ag₂O at 770°C at various N₂:CO₂ ratios. The OCP values determined from galvanostatic ($I = 0$) and P_{O₂} sensor data as a function of % CO₂ (balance of N₂) at 700 (Table 2) and 770°C (Table 3) for Ag₂O are shown in Figure 9(a). At 700°C, OCP values showed a slight peak between 10-15 vol% CO₂ followed by a logarithmic decay with further increases in CO₂ content, while at 770°C, OCP values decreased logarithmically over the CO₂ composition range tested (4-100 % CO₂) in the presence of both SiC and Ag₂O. A steady decrease in OCP values with increasing CO₂ concentration was seen in full-cell tests in the absence of catalyst [24], and is predicated by the Nernst equation as a function of P_{CO₂} [29].

(Figure 9)

Table 2 tabulates the current at fixed overpotential ($\eta = + 500$ mV), and forward sweep peak currents, as well as OCP and peak potentials (vs. Pt/air) acquired at 700°C in the presence of Ag₂O. Similarly, Table 3 tabulates data acquired at 770°C, where peaks in the forward sweep of the CVs were only observed at high CO₂ concentrations (75-100 % CO₂ in N₂). As illustrated in Figure 9(b), in the presence (Ag₂O) and absence (SiC) of catalyst, current at fixed overpotential increased with % CO₂ at 770°C. Performance in the presence of Ag₂O was found to increase slightly ($\sim 9 \mu\text{A} (\% \text{CO}_2)^{-1}$) with increasing CO₂ concentration at 700°C, with less relative change seen at 770°C ($6 \mu\text{A} (\% \text{CO}_2)^{-1}$). Forward sweep peak currents increased with CO₂ content, mirroring the increase in current at $\eta = + 500$ mV. This indicated that greater 3E half-cell performance could be achieved at higher temperatures and CO₂ concentrations.

(Table 2)

(Table 3)

3.2.4 RELATIVE PERFORMANCE

Relative performance of fresh (immediately following ramp up to operating temperature and allowing ~ 30 min for WE layer NiO reduction) 3E half-cells was determined by CV in 96-4 N₂-CO₂ (6 L hr⁻¹) at 800°C in the presence (Ag₂O) and absence (SiC) of catalyst (Figure 10). With Ag₂O, the magnitude of the OCP was slightly decreased (1114 mV vs. Pt/air) compared to the uncatalyzed system (SiC, 1161 mV vs. Pt/air). However, Ag₂O catalyzed a higher performance under load (as applied overpotential, $\eta > 0$), and so was selected for scale-up to a full-cell test setup.

(Figure 10)

3.3 Full-Cell

3.3.1 ELECTROCHEMICAL RESULTS

Electrochemical performance of the catalyzed (Ag₂O) and un-catalyzed (SiC) carbon black fueled systems were measured in a full-cell setup using EIS acquired at OCV between 700 and 800°C with mixed N₂-CO₂ sweep gas introduced at the anode. Representative Nyquist plots for SiC (a, 800°C) and Ag₂O (b, 755°C) are shown in Figure 11. EIS data was fitted using a model circuit consisting of Rs-RQ-RQ-RQ (Figure 11, inset). Rs was related to supply of oxygen anions (O²⁻) through the YSZ electrolyte and anode support layer (ASL), and was expected to depend on electrolyte thickness and temperature. The high frequency (HF, ~ 500 Hz) process was ascribed to the charge transfer reaction at the anode, the oxidation of CO (2), while the low frequency (LF, ~ 0.3 Hz) process(es) were more complex to assign. As discussed elsewhere [24], these processes were suspected to be related to the chemical formation of CO according to the Boudouard equilibrium (Reaction 1) and were limited by either the rate of supply of CO₂ to the solid carbon surface, or the rate of this chemical reaction. Intermediate frequency (IF, ~ 10 Hz) features are related to cathode processes [24].

(Figure 11)

Full-cell activity with Ag_2O in the anode chamber was measured under load (applied current) by acquiring I-V-P curves as a function of temperature (700 - 800°C) in 96-4 $\text{N}_2\text{-CO}_2$ (22.5 L hr^{-1} total flow) and 80-20 $\text{N}_2\text{-CO}_2$ (6 L hr^{-1} total flow). A representative set of I-V-P data, acquired at 755°C with 80-20 $\text{N}_2\text{-CO}_2$ (6 L hr^{-1} total flow) at the anode, is shown in Figure 12. Various values were recorded, as illustrated, including OCV, I-V curve slope at low current densities, and power density at fixed current density (e.g., 35 mA cm^{-2}).

(Figure 12)

3.3.2 EFFECT OF TEMPERATURE

For SiC (no catalyst) and Ag_2O , area-specific R_p values calculated from EIS data recorded between 700 and 800°C in 96-4 $\text{N}_2\text{-CO}_2$ were seen to decrease as temperature was increased (Figure 13(a)). R_p values decreased more rapidly between 700 and 755°C than at higher temperatures, indicating that full-cell processes were more strongly activated by increased temperature over this range.

(Figure 13)

For Ag_2O , I-V curves acquired from 800 to 700°C and I-P curves calculated from data acquired at 700 and 800°C are shown in Figure 13(b). Maximum achieved power densities ($i = 52 \text{ mA cm}^{-2}$) were 31 and 48 mW cm^{-2} at 700 and 800°C, respectively. OCV and power densities calculated at 35 mA cm^{-2} in the presence of SiC and Ag_2O are shown in Table 4. As illustrated in Figure 14, for both systems, OCV (a) and power densities (b) increased with temperature, as expected [24].

(Table 4)

Low temperature (700-730°C) I-V curves underwent transitions (slope change) at a cell voltage ~ 725 mV, which are indicated by asterisks in Figures 12-13. As temperature increased, this transition was no longer observed (755-800°C), and I-V curves appeared linear. Linear fitting of I-V curves allowed the determination of slope and calculation of overall resistance for the full-cells in the

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5 presence of SiC and Ag₂O. This resistance was seen to decrease as temperature was increase
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7 (Figure 14(c)), and showed an activation energy of 1.1 ± 0.5 eV.
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10 (Figure 14)

11 **3.3.3 DURABILITY**

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13 Batches (~ 2 g) of carbon black with (Ag₂O) and without catalyst were placed in the anode chamber
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15 of a full-cell HDCFC. These were tested at OCV for up to 24 hrs with (flow conditions) and without
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17 (no anode flow conditions) 80-20 N₂-CO₂ (6 L hr⁻¹) at 755°C, with I-V curves acquired every 30 to
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19 60 min. OCV and power density at 19 mA cm⁻² values were recorded as a function of operation
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21 time, as show in Figure 15. Both systems showed the capacity to operate with (80-20 N₂-CO₂) and
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23 without sweep gas flowing at the anode, as we have demonstrated previously for un-catalyzed
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25 systems (SiC) [24]. Un-catalyzed and Ag₂O systems showed an average OCV decrease of 10 and 18
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27 mV hr⁻¹, respectively. In the presence of the Ag₂O catalyst, higher power densities, which showed
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29 an average decline of 0.74 mW hr⁻¹ cm⁻² over 16 hrs, were achieved than in the absence of catalyst
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31 (Figure 15(a)).
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37 (Figure 15)

38 **3.3.4 RELATIVE PERFORMANCE**

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40 Various silver-based catalysts were tested for activity towards HDCFC anode processes in a full-
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42 cell configuration. The performance of catalyzed (Ag and Ag₂O) and un-catalyzed carbon black was
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44 determined at 800°C with pure N₂ at the anode (Figure 16(a)). Similarly, SiC (non-catalyzed), Ag,
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46 Ag₂O and Ag₂CO₃ systems were examined at 755°C in 96-4 N₂-CO₂ (Figure 16(b)). Ag and
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48 Ag₂CO₃ showed lower OCV values at 755 and 800°C, while all silver-based catalysts (Ag, Ag₂O
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50 and Ag₂CO₃) were found to promote the processes occurring at the anode (higher power densities)
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52 when compared to the un-catalyzed systems tested under identical conditions. However, Ag₂O was
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54 consistently found to promote higher activity. Indeed, Ag₂O was found to be one of the most active
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catalysts towards carbon oxidation reactions. The relative catalytic activity in carbon black fueled HDCFCs of a variety of catalysts, including Ag-, Mn-, Ce-, and doped ceria-based materials, is the subject of an ongoing investigation [23].

(Figure 16)

4 Discussion

4.1 TGA

Aneggi et al. (2009) propose two carbon (as soot) oxidation mechanisms depending on catalyst material employed, including redox-active species (e.g., CeO₂) and materials which promote the formation of activated surface oxygen intermediates (e.g., Ag). Ag promotes carbon oxidation through the transfer (spillover) of these intermediates from the catalyst to the carbon surface. This promotion has been likened to its catalysis of CO oxidation [30], recently reviewed by Zhang et al. (2013) [31]. There within, the activated silver surface oxygen species, intermediate in CO oxidation [32], was proposed to be superoxide (O₂⁻) molecularly adsorbed in a bent end-on geometry [33]. Determining the rate determining step (RDS) of CO and carbon oxidation mechanisms on Ag was, however, complicated by its dependence on (1) catalyst support materials (active vs. inert) and (2) temperature [31].

Ag₂O showed high catalytic activity towards carbon oxidation (Figure 3). The oxidation temperature of Ag₂O-C (240-243°C) fell within the temperature range of Ag₂O reduction to Ag metal (217-257°C [34]). Ag₂O has been suggested to promote carbon oxidation through reduction to silver [33]. Once metallic silver (Ag) was formed, this acted as the catalyst through the formation of adsorbed surface oxides (e.g., Ag-O₂⁻). Investigations of silver supported on SiO₂ have allowed the determination of relative catalytic activity of Ag₂O (T = 350°C, 50 % efficiency) vs. Ag (T = 250°C, 71 % efficiency). Following soot oxidation up to 600°C in air, analysis of a 3 mol% Ag₂O-SiO₂ catalyst revealed only the presence of metallic silver (on SiO₂), suggesting Ag₂O was complete reduced to Ag during carbon oxidation [33]. More detailed TGA investigations of 5 wt%

Ag-ZrO₂ suggested there exist two oxygen surface species on silver, a strong oxidative capacity species which cleaved C-C bonds directly, and a lower oxidative capacity species which reacted with intermediate species on the soot surface following their formation. These species could not be positively identified but were suggested to be peroxide and/or superoxide species [30, 35].

4.2 Half-Cell

4.2.1 CV PEAKS

A peak seen in the forward ($\Delta E = 0 \rightarrow 400$ mV vs. Pt/CO-CO₂) sweep of the CVs is illustrated in Figure 6 at 700°C in 96-4 N₂-CO₂, and is seen at both low and high flow rates (2.3 and 6 L/hr). The peak in the reverse sweep ($\Delta E = 400 \rightarrow -200$ mV vs. Pt/CO-CO₂) is seen near $\Delta E = 0$. The currents of both peaks (forward and reverse scans) were determined as a function of CV scan rate (v), and were found to depend on the $v^{1/2}$. This relationship, according to the Randles-Sevcik equation (Equation 4), indicated diffusion control of a reversible reaction gave rise to these peaks. While reversible, this reaction was likely kinetically slow in the reverse (reduction) direction, as the peak in the reverse sweep of the CV was not always observed (e.g., Figure 7(b)).

$$I_p = 0.4463nFAC(nFvD/RT)^{1/2} \quad (4)$$

In Equation 4, I_p is peak current (amperes, A), n is the number of electrons transferred in the RDS ($n = 1$), A is the reactive surface area, C is the concentration of diffusing species, v is the scan rate (V/s), D is the diffusivity of the species, and F , R and T (in K) have their typical meanings. The diffusing species may exist in a liquid (molten) or gaseous medium. It should be noted that this relationship (Figure 6) indicating diffusion control of peaks in the forward sweep of these CVs was only seen after several dozen hours (~ 48 hrs) at high temperatures in a reducing environment (N₂-CO₂-CO). Similar data acquired on a fresh 3E half-cell revealed the presence of CV peaks of comparable current and potential difference (vs. Figure 6) when tested in 100 % CO₂ (2.3 L hr⁻¹) at

700°C. However, these measurements revealed no relationship between forward scan peak current and CV scan rate (Equation 4). As a result, we postulate that the same reduction/oxidation (redox) couple occurred in both cases (fresh vs. aged cells). Redox occurred in the anode layer for fresh cells but predominately in the carbonate melt for aged cells. Species from the anode were gradually dissolved into the molten media, giving rise to the change in diffusion control of the CV peaks as a function of contact time with molten carbonate under CO₂ at elevated temperatures (testing time). Additionally, these peaks were seen with (Figure 7) and without (SiC, Figure 6) the presence of Ag₂O. Similar CV data acquired for silver in (32-68 wt% Li-K)₂CO₃ at 650°C in N₂ did not reveal any peaks [36]. Therefore, the peaks observed in Figures 6-7 are suggested to be related the 3E half-cell and not to the presence of the catalyst (Ag₂O).

Based on the chemical species present in the WE chamber, a thermodynamic calculation program (FactSage 6.4 [37]) was employed to determine the redox potentials of electrochemical reactions which could potentially give rise to these peaks. In Table 5, reactions are written in order to give negative Gibbs free energies (ΔG), meaning these equilibria are thermodynamically favored to proceed left to right. For each of these 4-electron reactions, the redox potential was calculated at 700°C using Gibbs free energy minimization, results are shown in Table 5. Reactions 13-15 are the carbon oxidation reactions, which are suggested to give rise to the OCP values, values which depended on both temperature and CO₂ concentration.

(Table 5)

A CV of a Ni metal electrode in contact with NiCO₃ dissolved in (Li-K-Na)₂CO₃ under 1 atm pure CO₂ at 650°C showed similarity to the CVs shown in Figure 7(b), with a peak seen in the anodic sweep ($\Delta E > 0$), but a relatively flat (absence of peak) response in the cathodic sweep. Literature reports of the potential of the Ni/NiO redox couple (Reaction 6) include 763 mV (vs. Li₂O/O₂ RE), where potential is given as an absolute value, at 750°C in (Li-K-Na)₂CO₃ [38], and 695 mV (vs.

standard reference electrode in 66-33 CO₂-O₂) at 650°C in (62-38 Li-K)₂CO₃ [39], both acquired under 1 atm pure CO₂. Based on the potentials (mV vs. Pt/air) at which the forward sweep peaks (Figure 7(b)) were observed at 700 and 770°C (Tables 2-3) and literature values for similar redox couples [38-39], these peaks were ascribed to Reaction 6. Where Ni (or NiO) dissolved into the alkali carbonate melt, such that these peaks were controlled by the diffusion of species in the melt in aged cells (48 hrs contact time).

The solubility of NiO was reported as 0.9-1.1 μmol cm⁻³ in (62-38 Li-K)₂CO₃ at 650°C and 0.8 μmol cm⁻³ (4x10⁻⁴ mol kg⁻¹ alkali carbonate) in the ternary (Li-K-Na)₂CO₃ eutectic melt at 750°C in 1 atm CO₂, with the dissolution process having an activation energy of 0.47 eV (Reaction 16) [39]. Solubility of this species has been shown to depend on potential [38], temperature, P_{CO2}, and alkali carbonate melt composition [40]. Under high P_{CO2} conditions, NiO solubility (acidic dissociation) increased with increasing P_{CO2} but decreased with increasing temperature. Decreased solubility at higher temperatures was due to the decreased stability of complexes (Ni(CO₃)₂²⁻ and Ni(CO₃)₃⁴⁻) formed upon reaction of NiO with CO₂ and carbonate anions (CO₃²⁻) [40]. The solubility of metallic nickel (Reaction 17) was also reported to decrease with increasing temperature but to increase with P_{CO2} at higher CO₂ concentrations (> 50 % CO₂, (52-48 Li-Na)₂CO₃, 570°C, Ni-Al alloy) [41].

Forward sweep peak currents increased with CO₂ concentration at 700°C (Table 2), while peaks were only apparent under 75-100 % CO₂ when examined at 770°C (Table 3). The temperature and P_{CO2} dependence of these peaks was suggested to be related to the solubility of NiO, formed through Reaction 6, in the alkali carbonate melt. Here, we propose that the electrochemical oxidation of Ni (Reaction 6) was coupled with the subsequent dissolution of NiO (Reaction 16), and

that the combination of these reactions gave rise to the peaks seen in the forward sweep of CVs acquired on a Ni-YSZ WE in contact with a (Li-K)₂CO₃ melt at 700 and 770°C.

4.2.2 EFFECT OF TEMPERATURE

As seen in Figure 7 for Ag₂O and illustrated in Figure 8(b) for SiC and Ag₂O as a function of temperature, CVs did not pass through the origin ($\Delta E = 0$, $I = 0$) as temperature was increased ($T \geq 755^\circ\text{C}$). When the reactions were balanced between the RE and the WE (Reaction 2), CO₂ was reduced at the RE, while CO was oxidized at the WE, which was seen when mixed CO-CO₂ was introduced into the half-cell test setup [42], and zero net current was measured when no potential was applied to the WE ($\Delta E = 0$). Non-zero current values at $\Delta E = 0$ may be observed when the reactant and product concentrations are significantly different at the WE vs. RE and/or when multiple electrochemical reactions occur at the WE, leading to mixed potentials. In addition to CO oxidation, other possible WE reactions include the complete (Reaction 18) or partial oxidation (Reaction 2) of carbon by O²⁻ or CO₃²⁻ [9].

Further, as summarized in Table 1, forward sweep ($\Delta E = 0$ and $\eta = + 500$ mV) currents showed an exponential increase with temperature (Figure 8(b) and (c)). The natural logarithm of currents at fixed overpotential ($\eta = + 500$ mV) were plotted as a function of inverse temperature according to the Arrhenius relationship (Figure 17). From the slope, activation energies (E_a) of 1.1 eV for SiC (no catalyst) and between 0.97 and 1.3 eV for Ag₂O were calculated. Similarity in E_a values suggested inclusion of Ag₂O did not significantly alter the RDS of the processes occurring at the WE. E_a values calculated for the 3E half-cell were expected to be dominated by limiting rate of

transfer either of O^{2-} through the electrolyte support layer (Figure 1), or diffusion of dissolved species (CO and/or CO_2) in the carbonate melt.

(Figure 17)

4.2.3 EFFECT OF CO_2

Reactions at the WE are suggested to include several physical and chemical steps in addition to the electrochemical oxidation of CO (Reaction 2) [24]. Physical processes may include dissolution of CO_2 into the carbonate melt, ad- and de-sorption of reactant and product species, transport processes of various species, including O^{2-} through the electrolyte, as well as CO and/or CO_2 through the carbonate melt. Chemical processes may include (a) carbonate decomposition (Reaction 19) and carbon gasification reactions leading to the forming CO_2 , and (b) the Boudouard reaction (Reaction 1) and other carbon gasification reactions leading to the formation of CO [9].

Increased performance at higher CO_2 content and temperature indicated reactions at the WE were limited by physical and/or chemical processes occurring prior to the electrochemical oxidation of CO. Increased temperature has the effect of increasing the rate of physical and (electro)chemical processes, including the formation rate of CO through the inverse Boudouard reaction [5] and movement of CO and/or CO_2 species dissolved in the melt. While increased introduced CO_2 content (% CO_2 increased) has the potential to increase CO_2 dissolution rate into the carbonate melt (higher P_{CO_2} pressure in the gas phase) and supply of reactant to the Boudouard reaction, and so supply of CO to the WE catalyst layer. Although it should be noted that increased temperature decreases the rate of CO_2 dissolution from the gas phase into the melt. As performance was seen to increase with increasing temperature, this suggested CO_2 dissolution rate was unlikely to be the rate limiting process.

4.3 Full-Cell

4.3.1 EIS

Fitting parameters, taken from EIS data (Figure 11), were tabulated as a function of temperature (700-800°C) in 96-4 N₂-CO₂. As shown in Figure 13(a), R_p values were seen to decrease as temperature was increased with SiC and Ag₂O included in the carbon-carbonate slurry at the anode of the full-cell. The natural logarithm of inverse resistances (R_s and R_p) were plotted as a function of inverse temperature according to the Arrhenius relationship (Figure 18). Both SiC and Ag₂O R_s values ($0.10 \pm 0.3 \Omega \text{ cm}^2$ at 700°C) had an activation energy of $\sim 0.50 \text{ eV}$, and thus showed no dependence on presence of catalyst in the anode chamber. This confirmed that R_s represented a process present in all full-cells, independent of catalytic species, but dependent on temperature. The YSZ (10 μm) electrolyte was calculated to contributed a R_s value of $0.07 \Omega \text{ cm}^2$ at 700°C (ionic conductivity = 0.015 S cm^{-1} [43]) and an activation energy of 0.9-1 eV [44]. This discrepancy between calculated and measured values suggested that R_s was not only limited by ionic conductivity through the thin electrolyte, but was dominated by another transport process, such as, the percolation of charged species through the anode-support layer or the carbon-molten carbonate medium.

R_p, consisting of contributions from the anode and cathode processes, displayed activation energies of 1.23 and 1.14 eV for SiC and Ag₂O, respectively, similar to those calculated from overall cell resistances ($1.1 \pm 0.5 \text{ eV}$). R(HF) values decreased as temperature increased, as expected, as the rate of CO oxidation increases as temperature increases. Interestingly, R(LF) showed no dependence on temperature, although the nature of the controlling process(es) was uncertain. However, these are unlikely to be gas phase diffusion in the anode chamber, although gas diffusion is a temperature independent process [25].

(Figure 18)

4.3.2 I-V CURVES

A change in slope, marked by an asterisk, was observed for I-V curves acquired at low temperature (700-755°C) and CO₂ concentrations (< 20 vol% CO₂) in the presence of Ag₂O (Figures 12-13) and SiC [24]. As we have remarked previously [9], similar transitions have been observed by others [45-49] and have been proposed to be related to a change in mechanism and reaction locus by Cooper and Selman (2012) [50]. An alternative explanation has been proposed by Allen et al. (2014), who suggested these transitions, which they observed for coal and graphite in (Li-Na-K)₂CO₃ under CO₂ at 500°C, are related to a change in RDS in the same reaction mechanism (complete oxidation of carbon by CO₃²⁻, Reaction 18) [49].

For carbon black in (Li-K)₂CO₃, we have observed the slope change in I-V curves to occur at cell voltages between 650 and 750 mV (e.g., Figures 12-13, [24]), a voltage relatively close to that of the Ni/NiO redox couple (Reaction 6). Hence, in the HDCFC full-cell tested here, the transitions in I-V curve slope may be related to changes in the resistance of the anode support layer, due to reduction/oxidation of Ni/NiO in this layer and accompanying change in conductivity. NiO shows electronic conductivity at elevated temperatures (550-900°C) with an activation energy of $5500 \pm 1000 \text{ cal mol}^{-1}$ (0.23 eV) [51].

4.4 Half-cell and full-cell

From half-cell and full-cell HDCFC investigations of carbon black systems containing SiC and Ag₂O, the following was observed:

- OCP and current measured at fixed overpotential for half-cells and OCV and power density calculated at fixed current density for full-cells were found to increase as temperature was increased.

- OCP and OCV values decreased as % CO₂ was increased in mixed N₂-CO₂,
- Current measured at fixed overpotential increased as % CO₂ was increased from 4 to 100 % CO₂, while R_p values measured at OCV were found to decrease (full-cell activation) between 4 and 20 % CO₂, without further variation at > 20 % CO₂ [24]. The variability in the effect of % CO₂ on performance may be related to the differences in gas flow rate and configurations (Figures 1-2) and/or working atmosphere composition at the WE (half-cell) vs. anode (full-cell).
- R_p and R_T activation energies (~ 1.1 eV) showed similarity to those calculated from half-cells (0.95-1.2 eV). While this may be co-incidental, this may indicate the RDS processes, giving rise to E_a, are similar in both setups. Suggesting RDS is associated with molten carbonate-carbon processes or a Ni-YSZ related process, independent of anode/WE microstructure. Tests in the absence of the Ni-YSZ WE are being undertaken to investigate the latter possibility.
- Effects of the Ni/NiO redox couple may be observed in both experimental setups, as CV peaks in half-cells (Figures 6-7) and changing slope of I-V curves in full-cells (Figures 12-13).
- Ag₂O promotes HDCFC WE/anode processes relative to the inclusion of SiC (inert filler).
- The addition of Ag₂O increased the OCV value relative to the un-catalyzed system when investigated in a full-cell configuration, but decreased the magnitude of the OCP in the half-cell configuration. This may be related to differences arising from measuring cell voltage versus a cathode (LSM-YSZ) while calculating the WE potential versus a Pt RE. Unfortunately, the reasons for this could not be ascertained from the present experiments.

5 Conclusions

Silver oxide (Ag_2O) was tested as a catalysts in a molten medium composed of solid carbon black and $(\text{Li-K})_2\text{CO}_3$ placed in contact with the Ni-yttria stabilized zirconia (YSZ) anode of a solid oxide fuel cell (SOFC), thus acting as an anode chamber catalyst for a hybrid direct carbon fuel cell (HDCFC). Ag_2O was shown to have high catalytic activity between 700 and 800°C in a mixed N_2 - CO_2 anode atmosphere (activation energy $\sim 1.1 \pm 0.5$ eV). This catalyst showed greater electrochemical performance enhancement, measured as current-potential-power density (I-V-P) curves, in a full-cell configuration when compared to identical mass loadings (4:1 carbon: catalyst) of powdered metallic silver metal (Ag), Ag_2CO_3 and a blank cell (using an inert material, SiC). Ag_2O was shown to have, by thermo-gravimetric-differential thermal analysis (TGA-DTA), catalytic activity towards carbon oxidation in air and gasification in mixed N_2 - CO_2 environment. Further, it had been reported as a CO oxidation catalyst, such that this material may have enhanced HDCFC anode reactivity through promotion of carbon gasification and CO oxidation.

The anode of the planar HDCFCs developed at the University of St. Andrews was investigated in a novel single atmosphere 3-electrode (3E) half-cell configuration. The technique permitted the following findings:

- The Ag_2O catalyst showed enhanced performance, as shown by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS), as temperature (700-800°C) and CO_2 content of the mixed N_2 - CO_2 atmosphere were increased.
- When isolating for the anode chamber reactivity (vs. full cell contributions), CVs revealed the presence of mixed potentials, which may have arisen from multiple electrochemical reactions. This was indicated by the measured current when potential was set to zero, currents which increased as temperature increased. The appearance of these features renews

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5 the question of whether complete solid carbon oxidation occurs in addition to CO oxidation,
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7 requiring further investigations to better understand the combination of processes occurring
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9 in an HDCFC anode chamber.
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- CV measurements also showed the presence of peaks in the forward sweep (potential, $\Delta E > 0$), both current and potential of which depended on temperature (700 and 770°C) and CO₂ content of the mixed N₂-CO₂ atmosphere (4-100 % CO₂ in N₂). These arose from a combination of the Ni/NiO reduction/oxidation (redox) couple and the solubility of NiO in molten carbonate, and so are independent of the presence of Ag₂O. The solubility of NiO increased with P_{CO2}, but decreased as temperature increased, giving rise to the temperature and atmosphere dependence of these CV peaks. Finally, these processes were suggested to occur in the anode layer of fresh cells, but increasingly in the melt for cells held in contact with molten alkali carbonate media under CO₂ at 700°C (aged cells) as Ni (or NiO) progressively dissolved from the anode layer into the melt. Hence, the CV peaks were under diffusion control after ~ 48 hrs, as determined from the relationship of peak current with CV scan rate.
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Figure Captions

Figure 1. HDCFC 3-electrode half-cell setup - Schematic illustrating single atmosphere 3-electrode (3E) HDCFC half-cell setup.

Figure 2. HDCFC 2-electrode setup - Schematic illustrating full-cell 2-electrode (2G) HDCFC setup [24].

Figure 3. TGA and DTA in air – DTA and first derivative of TGA ($dTGA/dt$), in air, for (a) carbon black acetylene (C black) and Ag-loaded carbon (Ag-C), and (b) carbon black mixed with SiC (C-SiC) and Ag_2O (C- Ag_2O). Temperatures of maximum rate of mass loss ($dTGA/dt$) and of temperature change (DTA) are indicated.

Figure 4. TGA in the absence of air – TGA curves (a) carbon black acetylene (C black) and Ag-loaded carbon (Ag-C) in 96-4 N_2 - CO_2 , and (b) carbon black mixed with SiC (C-SiC) and Ag_2O (C- Ag_2O) in N_2 . Onset temperatures of majority of mass losses are indicated.

Figure 5. 3-electrode EIS – Typical Nyquist plots acquired at 800°C in 96-4 N_2 - CO_2 (6 L hr^{-1}) in the presence of carbon mixed with (a) SiC, and (b) Ag_2O . Points represent acquired data, while line and arcs are generated by fitting with the model circuit (inset). Frequencies are given in Hz.

Figure 6. 3-electrode CV – Typical CV acquired in 96-4 N₂-CO₂ (2.3 L hr⁻¹) at 700°C for carbon black-(Li-K)₂CO₃-SiC (no catalyst present), with potential difference (ΔE) scanned between + 400 and – 200 mV (vs. Pt/CO-CO₂) at 15 mV s⁻¹, plotted as a function of potential (mV vs. Pt/air). Various tabulated (see text) values are illustrated, including OCP, currents at $\Delta E = 0$, of the forward sweep ($\Delta E = 0 \rightarrow 400$ mV vs. Pt/CO-CO₂) peak, at fixed overpotential ($\eta = + 400$ mV vs. Pt/air) and reverse sweep ($\Delta E = 400 \rightarrow -200$ mV vs. Pt/CO-CO₂) peak. Inset: forward sweep peak current plotted as a function of (scan rate)^{1/2} to determine diffusion-control of CV peaks, according to the Randles-Sevcik Equation.

Figure 7. Effect of temperature on 3-electrode performance – Data, acquired with Ag₂O in 96-4 N₂-CO₂ (6 L hr⁻¹) between 700 and 800°C, including (a) EIS, and (b) CV ($\Delta E = \pm 500$ mV, 10 mV s⁻¹) plotted as a function of potential difference (vs. Pt/CO-CO₂).

Figure 8. Effect of temperature on CVs – From CVs acquired in 96-4 N₂-CO₂ (6 L hr⁻¹) between 700 and 800°C in the presence of SiC (+) and Ag₂O ($\diamond$, 2 replicates shown), (a) OCP (mV vs. Pt/air), (b) current at $\Delta E = 0$ and (c) current at fixed overpotential ($\eta = + 500$ mV) as a function of temperature.

Figure 9. Effects of test atmosphere composition on 3-electrode results – For SiC (+) and Ag₂O ($\diamond$, 2 replicates shown), effect of atmosphere composition, given as % CO₂ in N₂-CO₂ on (a) OCP and (b) current at fixed overpotential ($\eta = + 500$ mV) values determined from CV at 700°C (filled symbols) and 770°C (open symbols).

Figure 10. Catalysis by Ag₂O – CV illustrating half-cell performance for carbon mixed SiC and Ag₂O, acquired in 96-4 N₂-CO₂ (6 L hr⁻¹) at 800°C (± 500 mV, 10 mV s⁻¹), shown as a function of potential (mV vs. Pt/air) calculated from P_{O2} sensor data. OCP values given vs. Pt/air.

Figure 11. Full-cell EIS – Typical Nyquist plots acquired at OCV for (a) SiC (no catalyst) in 96-4 N₂-CO₂ (22.5 L hr⁻¹) at 800°C, and (b) Ag₂O in 80-20 N₂-CO₂ (6 L hr⁻¹) at 755°C. Points represent acquired data, while line and arcs are generated by the model circuit employed (inset). Data shown is not corrected by the geometric surface area of the cathode (12 cm²), such that impedance values are in Ω, while frequency values are given in Hz.

Figure 12. Full-cell I-V-P data – A representative current density-potential-power density (I-V-P) curves acquired in 80-20 N₂-CO₂ (6 L hr⁻¹) at 755°C in the presence of Ag₂O. Various tabulated (see text) values are illustrated, including OCV, overall cell resistance (R_T), power density at fixed current density and maximum power density. Current density and power density are area-corrected for the geometric surface area of the cathode. Inflection point in the I-V curve is marked (*).

Figure 13. Effect of temperature on full-cell performance – (a) R_p values calculated from EIS data acquired at OCV in 96-4 N₂-CO₂ (22.5 L hr⁻¹) between 700 and 800°C for SiC (+, 2 replicates shown) and Ag₂O (◇, 3 replicates shown). (b) I-V-P curves for Ag₂O. Inflection points in the I-V curves are marked (*).

Figure 14. Effect of temperature on I-V-P curves – From I-V-P curves acquired in the presence of SiC (+) and Ag₂O (◇, 2 replicates shown) in 96-4 N₂-CO₂ (22.5 L hr⁻¹) between 700 and 800°C, (a) OCV, (b) power density at 35 mA cm⁻², and (c) overall cell resistance (R_T) as a function of temperature.

Figure 15. Performance with time – From I-V-P curves acquired in 80-20 N₂-CO₂ (◇, 6 L hr⁻¹) and in the absence of anode sweep gas (□, no anode flow) at 755°C, (a) in the absence of catalyst (4:1 carbon black:carbonate) and (b) in the presence of Ag₂O, OCV (filled symbols) and power density at 19 mA cm⁻² (open symbols) as a function of operation time.

Figure 16. Performance activation by silver-based catalysts – I-V-P curves acquired in (a) N₂ (5 L hr⁻¹) at 800°C in the absence of catalyst (+, C black), in the presence of Ag₂O (◇), and Ag (□), and in (b) 96-4 N₂-CO₂ (22.5 L hr⁻¹) at 755°C in the presence of SiC (non-catalyzed, +), Ag₂O (◇), Ag (□) and Ag₂CO₃ (○).

Figure 17. Arrhenius plot from 3-electrode half-cells – Arrhenius plot of current at fixed overpotential ($\eta = + 500$ mV) determined from CVs acquired in 96-4 N₂-CO₂ (6 L hr⁻¹) between 700 and 800°C in the presence of SiC (+) and Ag₂O (◇, 2 replicates shown). Activation energies given in eV.

Figure 18. Arrhenius plot from full-cell data – Arrhenius plot of R_s and R_p values calculated from EIS data acquired in the presence of SiC (+) and Ag₂O (◇) in 96-4 N₂-CO₂ (22.5 L hr⁻¹) between 700 and 800°C. Activation energies are given in eV.

Table Captions

Table 1. From CVs acquired with C-CO₃-Ag₂O in 96-4 N₂-CO₂ (6 L hr⁻¹ total flow), current at fixed overpotential ($\eta = 500$ mV), current measured when potential difference is zero ($\Delta E = 0$, Figure 7), and OCP values calculated against Pt/air RE using P_{O2} sensor data

Table 2. For Ag₂O, from CVs acquired at 700°C as a function of atmosphere composition (N₂-CO₂, 2.3 L hr⁻¹ total flow), current at fixed overpotential ($\eta = + 500$ mV), current and potential (mV vs. Pt/air) measured at forward sweep peaks (Figure 6), and OCP values calculated against Pt/air RE

Table 3. For Ag₂O, from CVs acquired at 770°C as a function of atmosphere composition (N₂-CO₂, 2.3 L hr⁻¹ total flow), current at fixed overpotential ($\eta = + 500$ mV), current and potential (mV vs. Pt/air) measured at forward sweep peak, and OCP values

Table 4. OCV and power density (calculated at 35 mA cm⁻²) values in the presence of SiC (no catalyst), and Ag₂O (96-4 N₂-CO₂ anode atmosphere)

Table 5. Thermodynamically calculated Gibbs free energy (ΔG) and potential (E) of selected reactions at 700°C [37]

Research Highlights:

- Silver-based catalysts for the anode chamber of a hybrid direct carbon fuel cell (HDCFC) investigated
- Ag_2O is a good catalyst when combined with the carbon-carbonate melt at the anode
- HDCFC anode processes investigated in a single atmosphere 3-electrode half-cell geometry
- Cyclic voltammetry (CV) suggests the presence of Ni/NiO anode layer redox cycling
- Catalyzed performance increased at higher temperature and CO_2 content in mixed $\text{N}_2\text{-CO}_2$ atmosphere

Graphical abstract

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

Figure 17

Figure 18

Table 1

Temperature/ °C	Current/ mA		OCP (vs. Pt/air)/ mV
	$\Delta E = 0$	$\eta = + 500 \text{ mV}$	
700	0.41	1.2	991
715	0.30	1.7	961
730	0.44	1.5	999
755	0.91	2.4	1056
770	1.4	3.1	1085
785	1.9	4.0	1101
800	2.6	5.3	1110

Table 2

Atmosphere/ % CO₂	Current/ mA		Peak Potential (vs. Pt/air)/ mV	OCP (vs. Pt/air)/ mV
	$\eta = + 500 \text{ mV}$	Peak		
4	0.28	0.25	523	913
7	0.29	0.26	544	913
10	0.31	0.26	582	917
15	0.31	0.28	576	916
20	0.32	0.30	592	914
50	0.37	0.37	619	900
75	0.46	0.49	605	889

Table 3

Atmosphere/ % CO ₂	Current/ mA		Peak Potential (vs. Pt/air)/ mV	OCP (vs. Pt/air)/ mV
	$\eta = + 500$ mV	Peak		
4				1036
7				1014
10				
15	0.51			981
20				973
50	0.47			
75	0.61	0.66	627	925
100	0.71	0.76	628	912

Table 4

Temperature/ °C	OCV/ mV		Power density/ mW cm ⁻² i = 35 mA cm ⁻²	
	SiC	Ag ₂ O	SiC	Ag ₂ O
700	910	909		21.4
715	922	952	16.3	25.8
730	929	965	17.3	29.8
755	939	987	20.5	34.2
770	917	1000	22.9	35.7
785	923	1009	22.9	36.9
800	979	1043	22.3	37.9

Table 5

Reaction Number	Reaction	- ΔG^a / kJ	E/ mV
5	$2\text{Ag}_2\text{O} \leftrightarrow 4\text{Ag} + \text{O}_2$	61.7	160
6	$2\text{Ni} + \text{O}_2 \leftrightarrow 2\text{NiO}$	303	785
7	$4\text{Li} + \text{O}_2 \leftrightarrow 2\text{Li}_2\text{O}$	940	2436
8	$4\text{K} + \text{O}_2 \leftrightarrow 2\text{K}_2\text{O}$	456	1182
9	$2\text{Ag}_2\text{CO}_3 \leftrightarrow \text{O}_2 + 2\text{CO}_2 + 4\text{Ag}$	219	567
10	$2\text{Ni} + 2\text{CO}_2 + \text{O}_2 \leftrightarrow 2\text{NiCO}_3$	79.8	207
11	$4\text{Li} + 2\text{CO}_2 + \text{O}_2 \leftrightarrow 2\text{Li}_2\text{CO}_3$	1089	2822
12	$4\text{K} + 2\text{CO}_2 + \text{O}_2 \leftrightarrow 2\text{K}_2\text{CO}_3$	946	2451
13	$2\text{CO} + \text{O}_2 \leftrightarrow 2\text{CO}_2$	396	1026
14	$2\text{C}_{(\text{s})} + \text{O}_2 \leftrightarrow 2\text{CO}$	396	1026
15	$\text{C}_{(\text{s})} + \text{O}_2 \leftrightarrow \text{CO}_2$	396	1026

^a All reactions written such as to be thermodynamically favorable ($\Delta G < 0$), and with an identical number of electrons transferred ($n = 4$)