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Enhancing Hybrid Direct Carbon Fuel Cell anode performance using Ag_2O

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ABSTRACT

A hybrid-direct carbon fuel cell (HDCFC), consisting of a molten slurry of solid carbon black and $(Li-K)_2CO_3$ 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 (N_2, 4–100% CO_2 in N_2-CO_2). It was shown that the addition of silver based catalysts (Ag, Ag_2O, Ag_2CO_3) into the carbon-carbonate slurry enhanced the performance of the HDCFC.

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] Ag_2O 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 Ag_2O introduced to the HDCFC as part of the carbon-carbonate mixture in the anode chamber. Catalytic enhancement was investigated using two setups, as a full-cell and in a single atmosphere 3-electrode half-cell (3 E), which allowed examination of the anode processes versus a reference electrode without the contribution of cathode processes,

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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% CO_2 in N_2-CO_2). 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 Ag_2O in both 3 E half-cell and full-cell setups.

2. Experimental

2.1. Thermo-gravimetric analysis

Carbon oxidation (in air) and gasification (in N_2) temperatures were determined for blank samples, with and without SiC ($\geq$ 97.5%, Sigma-Aldrich), and in the presence of a catalyst, Ag_2O (99+ %, Alfa Aesar). Additionally, carbon was loaded with a 5 wt% (metal basis) $AgNO_3$ aqueous solution. As $AgNO_3$ 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 N_2-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 °C/2 hrs). The working electrode (WE) was depositing by making a slurry of 55:45 wt% NiO:YSZ (YSZ calcined, 1350 °C/2 hrs) with an organic solvent, a cellulose-type binder and a phthalate-type dispersant, followed by screen-printing and sintering (1250 °C/2 hrs). The counter (CE) and reference electrodes (RE) were applied by painting Pt paste followed by sintereing (900 °C/2 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 °C/2 hrs; 260 °C/1 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 inadaquate 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 ($\sim$ 1 g) was packed into the tube as 4:1:1 wt% carbon black:(62–38 wt% Li-K$)_2CO_3$:SiC (no catalyst) or Ag_2O. 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 Fig. 1. The ceramic cell holder was equiped with a Pt oxygen partial pressure sensor supplied with air, which reported P_{O2} (in mV) of the working atmosphere (CO-CO_2) vs. Pt/air.

Half-cells were heated to 800 °C (180 °C hr^{-1}) in N_2 (5.76 L hr^{-1}). Following reduction of NiO, a mixture of 96–4 vol% N_2-CO_2 (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-CO_2), which is referred to here as potential difference (ΔE, mV vs. Pt/CO-CO_2). Potential difference was scanned between ± 500 mV vs. Pt/CO-CO_2,

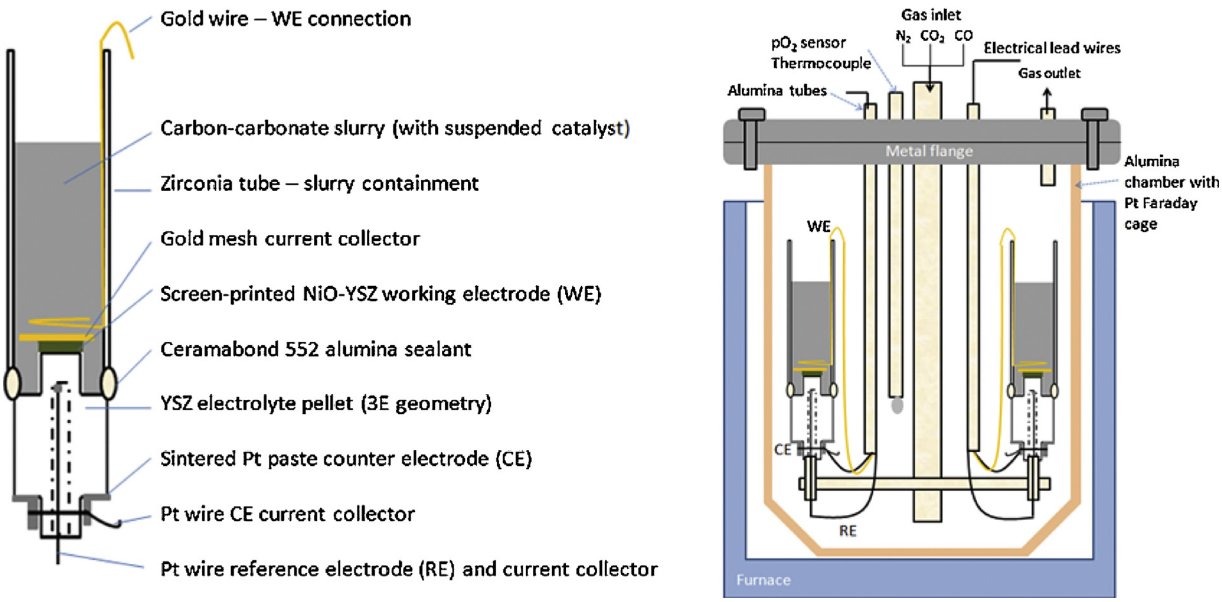

Fig. 1. HDCFC 3-electrode half-cell setup–Schemic illustrating single atmosphere 3-electrode (3 E) HDCFC half-cell setup.