

A thermally self-sustained micro solid-oxide fuel-cell stack with high power density

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High energy efficiency and energy density, together with rapid refuelling capability, render fuel cells highly attractive for portable power generation^{1,2}. Accordingly, polymer-electrolyte direct-methanol fuel cells are of increasing interest as possible alternatives to Li ion batteries³. However, such fuel cells face several design challenges and cannot operate with hydrocarbon fuels of higher energy density. Solid-oxide fuel cells (SOFCs) enable direct use of higher hydrocarbons⁴⁻⁶, but have not been seriously considered for portable applications because of thermal management difficulties at small scales, slow start-up and poor thermal cyclability. Here we demonstrate a thermally self-sustaining micro-SOFC stack with high power output and rapid start-up by using single chamber operation on propane fuel. The catalytic oxidation reactions supply sufficient thermal energy to maintain the fuel cells at 500–600 °C. A power output of ~350 mW (at 1.0 V) was obtained from a device with a total cathode area of only 1.42 cm².

Single-chamber fuel cells (SCFCs) are a type of fuel cell, which utilize a fuel + O₂ mixture gas (diluted) as the same gas atmosphere

for both the anode and cathode⁷⁻¹¹. The performance of single-chamber SOFCs is based on the highly selective anode and cathode towards the gas mixture. In addition to its role as the electrochemical catalyst for H₂ and CO oxidation, the anode also acts as the non-electrochemical catalyst for partial oxidation of the hydrocarbon fuel to form these more electrochemically active species. The oxidation reaction is exothermic in nature (for example, C₃H₈(g) + 3/2O₂(g) = 3CO(g) + 4H₂(g), $\Delta H_{550\text{ }^\circ\text{C}} = -206.96\text{ kJ mol}^{-1}$); the heat released raises the temperature of the fuel cells beyond that of the furnace in which they are placed^{12,13}. We used this heat to sustain the fuel-cell temperature in the absence of external heating. Of the fuel choices available for portable power applications, propane is particularly attractive because, as a gas at temperatures down to -42 °C at ambient pressure, it can be easily supplied to a power-generation device, and as liquid phase under moderate pressure (~10 atm at 25 °C), it can readily be stored with high energy density (6.3 kW h l⁻¹ at 25 °C, about twice that of methanol).

Anode-supported, thin-film electrolyte fuel cells were fabricated as reported elsewhere using samaria-doped ceria (Sm_{0.15}Ce_{0.85}O_{1.925},

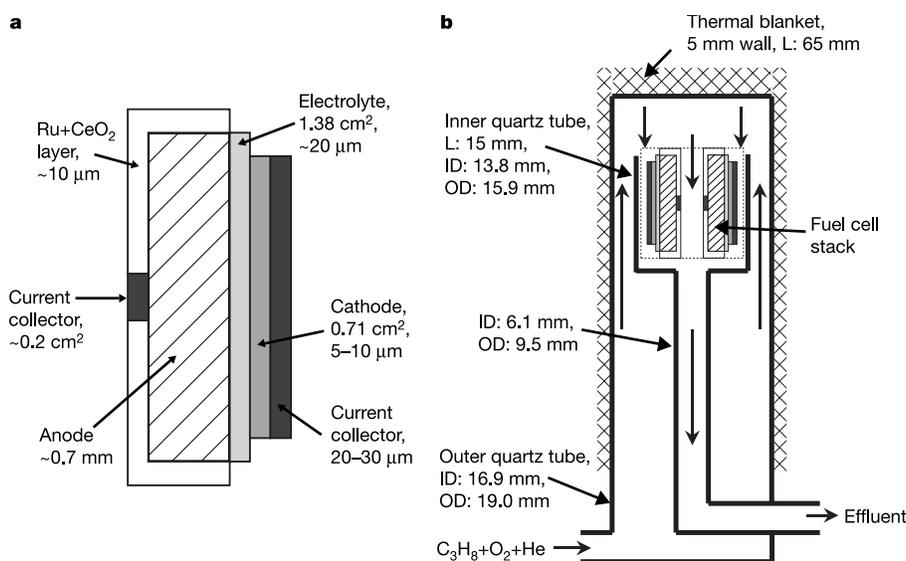


Figure 1 | Schematic diagram of the cell configuration and reactor system used in the thermally self-sustaining micro-SOFCs. **a**, The disc-shaped fuel cell comprises an SDC electrolyte (~20 μm) supported on an Ni + SDC anode (0.7 mm) with BSCF + SDC (70:30 wt%) as the cathode (5–10 μm); a ~10-μm-thick Ru + CeO₂ catalyst layer was coated onto the entire anode surface, with the exception of about 0.2 cm² at the centre, over which the

current collector (Ag paste) was placed; the entire cathode surface was covered with a layer of BSCF + Ag which served as the current collector (20–30 μm). **b**, The fuel-cell reactor comprises a removable ceramic thermal insulator or blanket, an inner quartz tube, and an outer quartz tube for introducing the gas mixture for the fuel cell. Component dimensions (L, width; ID, inner diameter; OD, outer diameter) are as indicated.

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SDC) as the electrolyte, Ni + SDC as the anode (SDC:NiO = 40:60 by weight), and a mixture of Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF) 70 wt% + SDC 30 wt% as the cathode¹⁴. Here, an additional ~10 μm of a porous layer of Ru + CeO₂, ~7 wt% Ru (crystalline, ~500-nm particles) physically mixed with CeO₂, was coated onto the anode surface (with the exception of a small centre region for making electrical contact) to enhance catalysis of propane partial oxidation at lower temperatures. Silver net and gold wires were attached to the electrode surfaces for current collection. The cell so fabricated (Fig. 1a) was placed in a quartz tube reactor for thermal and electrochemical evaluation (Fig. 1b). We first investigated the feasibility of thermally self-sustained micro-SOFCs by measuring the thermal behaviour of anode-supported structures, both with and without the Ru + CeO₂ catalyst layer. Half cells (thin ceria electrolyte supported on porous Ni + SDC) were placed in a furnace, parallel to the gas flow direction; the cell temperature was monitored using a thermocouple protected with a thin-walled (0.4 mm) quartz tube and placed in direct contact with the centre of the anode surface. The feed gas was composed of 40 ml min⁻¹ C₃H₈, 90 ml min⁻¹ O₂ and 360 ml min⁻¹ He (all at standard temperature and pressure, STP, 298 K, 1 atm); this mixture has a fuel-to-oxygen ratio found elsewhere¹⁴ to be optimal for high fuel-cell power output, and an inert-to-oxygen ratio similar to air, so it is representative of fuel-air mixtures envisioned for practical applications. The furnace temperature was raised or lowered in 25 °C increments, and the cell temperature recorded at each step after both the furnace and cell reached steady-state conditions.

Ignition of the partial oxidation reaction for the cell containing no additional catalyst layer occurred only when the furnace temperature was raised to 461 °C ($T_{\text{cell}} = 680$ °C); see Fig. 2a. The reaction was sustained to somewhat lower temperatures on cooling, but was nevertheless extinguished below a furnace temperature of 361 °C ($T_{\text{cell}} = 621$ °C). The application of a Ru + CeO₂ catalyst layer had a significant impact on the thermal behaviour of the cells; see Fig. 2a. Initiation of the partial oxidation reaction occurred at a furnace temperature of 311 °C (cell temperature, 618 °C), as compared to 461 °C without the catalyst. Moreover, upon cooling the furnace to room temperature, partial oxidation was not extinguished even in the absence of external heating. The cell maintained a temperature of 504 °C with the furnace turned off and left in the open position. When the reactor was better insulated by covering with a thermal blanket, the cell temperature increased to around 580 °C. This temperature was maintained with excellent stability over the course of a 200-h test (Fig. 2b). An existing model of heat-recirculating reactors¹⁵ including heat losses to ambient and heat conduction along the tube walls was adapted to simulate the current apparatus. Model results show that the heat recirculation contributes about 280 °C of temperature rise. Thus, heat recirculation, along with thermal insulation and the Ru + CeO₂ catalyst, which is highly active at low temperatures, are all important ingredients for thermal sustainability in these small fuel cells (Supplementary Fig. S1). The temperature of a two-cell stack (described further below) exposed to similar conditions was ~575 °C, almost identical to that of the single cell.

The difference in thermal behaviour between the untreated and Ru + CeO₂-treated half-cells can be understood in terms of the catalytic activity of Ni + SDC versus that of Ru + CeO₂ towards propane oxidation (Fig. 3), as measured using powder samples in a standard catalytic reactor¹⁶. At temperatures below 400 °C (Fig. 3a, c), Ni + SDC is essentially inert, whereas Ru + CeO₂ becomes active at temperatures just above 300 °C (Fig. 3b, d). This greater degree of activity towards propane oxidation results in greater heat release at low temperatures (300–500 °C; Fig. 3e), as calculated from the propane conversion data (Fig. 3c, d) and the known enthalpies of the partial and total oxidation reactions (with total oxidation releasing more heat than partial oxidation). It is this heat release that sustains the Ru + CeO₂-treated cells at a temperature (500–580 °C) suitable for

fuel-cell operation in the absence of external heating. Furthermore, while both catalysts produce, at temperatures below 650 °C, greater quantities of the deep oxidation products (H₂O and CO₂), than the partial oxidation products (H₂ and CO), Ru + CeO₂ shows somewhat better selectivity for partial oxidation at the lower temperatures (Fig. 3f). This feature is an additional advantage of Ru + CeO₂ for fuel-cell operation.

A complete fuel-cell structure with BSCF + SDC as the cathode and a Ru + CeO₂-treated anode was then examined for power output under thermally self-sustaining conditions. A C₃H₈ + O₂ + He gas mixture with a fixed volumetric ratio of 4:9:36 and a total flow rate of 368–490 ml min⁻¹ (at STP) was supplied to the fuel cell. Start-up was initiated by placing the cell directly into a preheated furnace (500 °C). The cell temperature rose rapidly, and after a short equilibration, the fuel cell was removed from the furnace and the thermal blanket applied. In the self-sustaining mode, an open circuit voltage (OCV) of ~0.7 V was obtained with peak power densities of 182 to 247 mW cm⁻² and short-circuit current densities of 0.8–1.1 A cm⁻² (Fig. 4). The latter two properties increased with increasing propane flow rate, although the OCV remained roughly constant (Fig. 4a). The increase in power output was accompanied by an increase of the fuel-cell temperature, from 535 to 580 °C for a corresponding propane flow rate increase from 32 to 40 ml min⁻¹. The OCVs measured here are lower than can be obtained from conventional dual-chamber fuel cells, but are typical of SOFCs in which imperfect selectivity of the electrodes results in some fuel oxidation at the cathode¹⁴. Furthermore, the power densities are lower than reported previously for identical fuel cells because of the

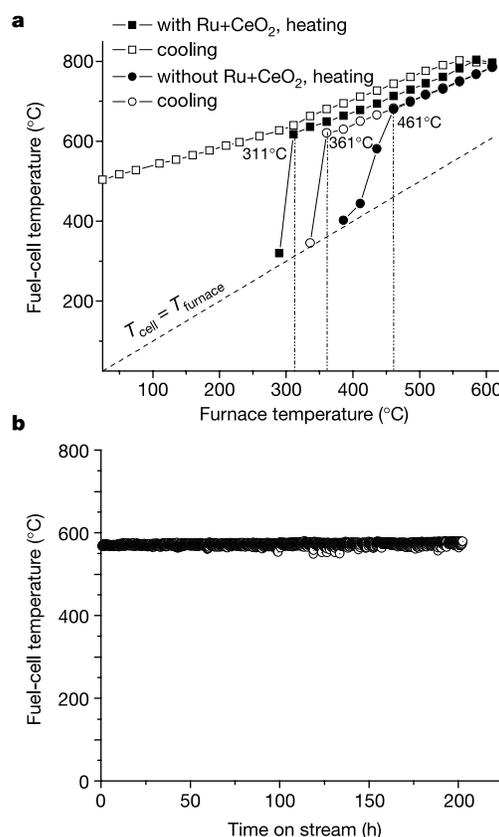


Figure 2 | The temperature recorded for the half-cells, both with and without a Ru + CeO₂ catalyst layer. The feed gas composition was 40 ml min⁻¹ C₃H₈ + 90 ml min⁻¹ O₂ + 360 ml min⁻¹ He (all at STP). **a**, Steady-state fuel-cell temperature as a function of furnace temperature; **b**, temperature of the self-sustaining Ru + CeO₂-treated cell, showing excellent long-term stability.

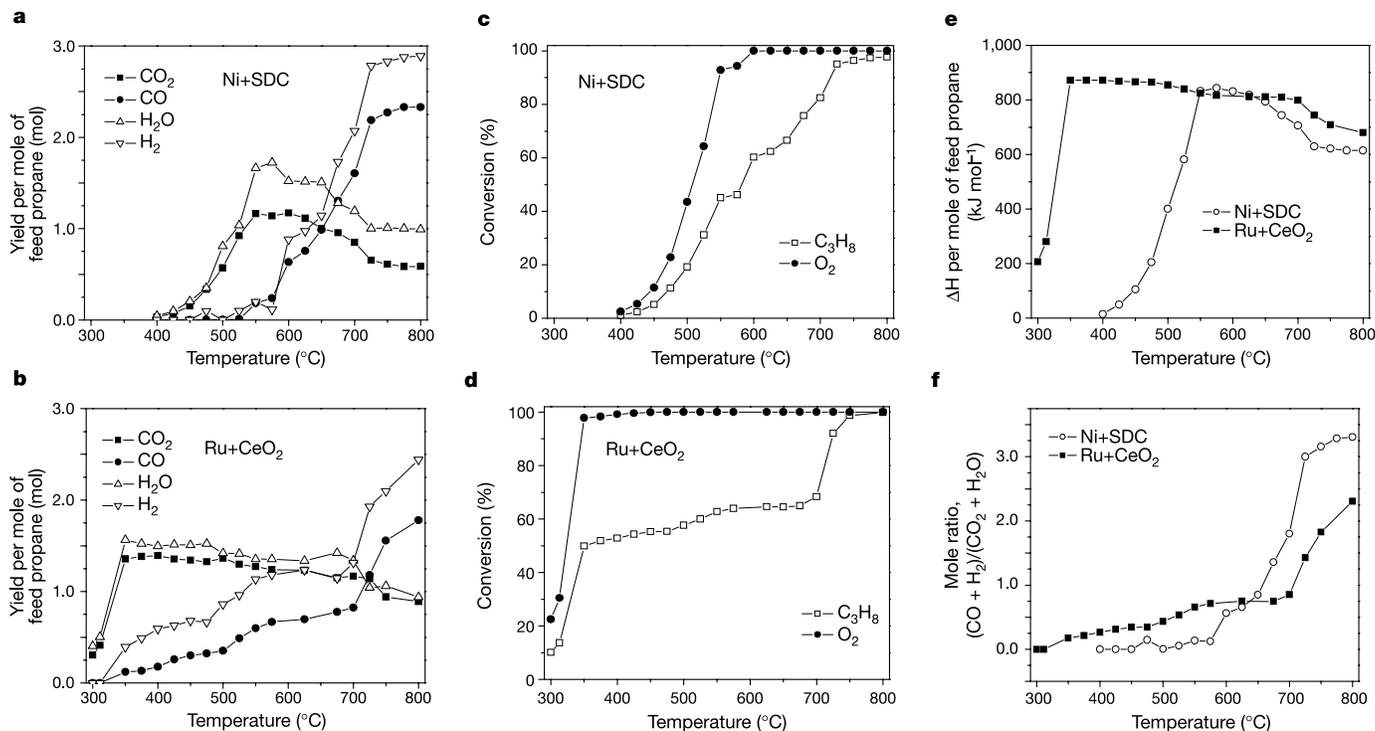


Figure 3 | Catalytic properties of Ni + SDC and Ru + CeO₂ towards propane oxidation. The feed gas composition was 10 ml min⁻¹ C₃H₈ + 22.5 ml min⁻¹ O₂ + 90 ml min⁻¹ He (all at STP). In all cases, the temperature reported is the real catalyst temperature, monitored by an in situ K-type thermocouple. **a**, Oxidation products as a function of temperature over 0.18 g of Ni + SDC powder (calcined at 1,350 °C). **b**, Oxidation products as a function of temperature over 0.18 g Ru + CeO₂ (Ru 7 wt%) catalyst powder reduced and calcined at 950 °C. **c**, **d**, Corresponding temperature dependences of propane and oxygen conversion over the

Ni + SDC and Ru + CeO₂ catalysts, respectively. **e**, Heat released as a function of temperature over the Ni + SDC and Ru + CeO₂ catalysts owing to the exothermic oxidation reactions, as calculated from the measured catalytic activity. **f**, The ratio of partial oxidation products (CO + H₂) to deep oxidation products (CO₂ + H₂O) over Ni + SDC catalyst and Ru + CeO₂ catalyst at various temperatures. Overall, Ru + CeO₂ releases more heat and is more selective for partial oxidation products at temperatures below ~600 °C than Ni + SDC.

lower fuel-cell temperature¹⁴ (which results in higher electrode and electrolyte resistances), but the values are nonetheless higher than those attained from the most advanced DMFCs, typically 100–200 mW cm⁻² (refs 17, 18). Quite significant is the fact that the electrolyte resistance, which is highly dependent on grain size and impurity content (Supplementary Fig. S2), was responsible for ~65% of the fuel-cell polarization losses (Supplementary Fig. S3). Thus, careful control of the fabrication procedures to decrease the electrolyte resistance and improved design of reactor to improve OCV can be anticipated to increase the power output by at least a factor of two. Additional design efforts are also required to improve the overall fuel utilization and thereby the efficiency, which is presently estimated at ~1%.

For practical applications, a voltage greater than 0.70 V is generally required and can be achieved by combining individual fuel cells into a stack. In conventional dual-chamber fuel cells, stacks are arranged in a cathode-facing-anode multilayer configuration, with interconnect layers separating anode and cathode chambers. Here we implement an anode-facing-anode stack configuration. Because the two anodes share the same gas, no interconnect layer is necessary, fabrication is exceedingly simple and the stack can be made very compactly. The stack produced approximately double the voltage (1.44 V) and more than double the power of a single cell (Fig. 4b), enough to operate a 1.5-V MP3 player (Supplementary Fig. S4). The 11% increase in average peak power density from 247 to 275 mW cm⁻² attained in the stacked configuration is due to the favourable gas transport pathways in the anode-facing-anode stack. Here, the partial oxidation products H₂ and CO are hindered from readily transporting to the cathode. In contrast, an anode-facing-

cathode dual-cell stack constructed without an interconnect layer resulted in near-zero OCV. In this configuration the highly reactive partial oxidation products (CO + H₂) are rapidly transported to the cathode, at which chemical oxidation is presumably catalysed. Undesirable gas-phase transport between electrodes apparently also limits the power outputs of fuel cells configured with anode and cathode strips placed on the same side of a supporting electrolyte¹⁹.

Hydrocarbon-fuelled fuel cells often suffer from carbon deposition at the anode, especially under open-circuit conditions²⁰. Because of the presence of oxygen in the fuel stream, however, SCFCs are much less susceptible to carbon coking (Supplementary Fig. S5). Our Ru + CeO₂-treated half-cell was entirely free of carbon deposits after the 200-h exposure to C₃H₈ + O₂ + He (at essentially OCV conditions). In contrast, a small amount of visible carbon was evident at the anode of our untreated half-cell after only ~24 h of exposure ($T_{\text{cell}} \approx 600$ °C). Not surprisingly, serious carbon coking, which completely destroyed the fuel cell, occurred when the Ni anode was exposed to pure propane (Supplementary Fig. S6). In the case of the Ru + CeO₂-treated cell, no carbon deposition occurred on the Ni beneath the catalyst layer (we peeled off the top layer to inspect the anode), suggesting that Ru + CeO₂ is so active that the partial oxidation was completed within this exterior layer and no propane, in fact, reached the inner Ni + SDC anode.

The ability of the fuel cell to withstand rapid thermal cycling was tested by directly inserting and removing the fuel-cell reactor from the high-temperature furnace (500 °C) multiple times. The fuel cell did not exhibit any mechanical cracks or deterioration in performance. This behaviour is achievable because the otherwise delicate seal of a conventional SOFC has been eliminated, because a thin-film

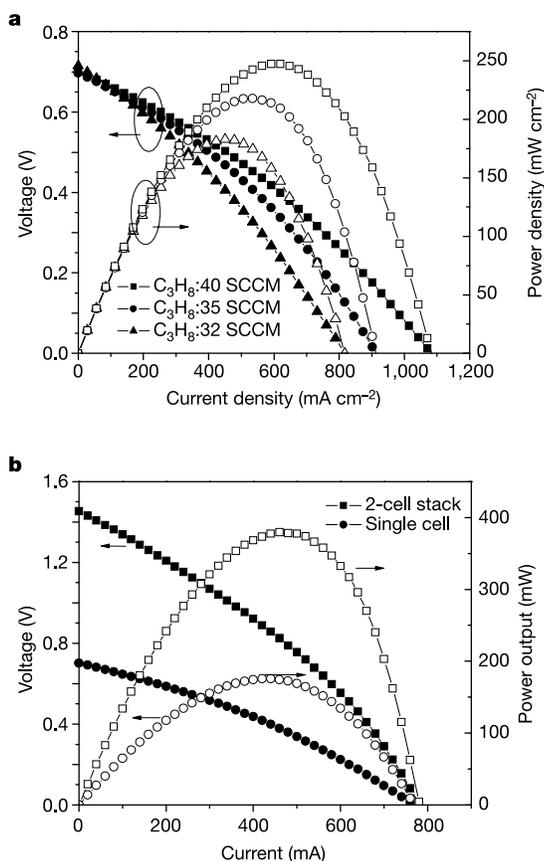


Figure 4 | Performance of the thermally self-sustained fuel cells. **a**, The cell voltage and power output versus current for a single cell at different propane feed rates, but fixed propane to oxygen to helium ratio of 4:9:36; **b**, A comparison of the performance of an anode-facing-anode, two-cell stack and a single cell at a flow composition of 40 ml min⁻¹ C₃H₈ + 90 ml min⁻¹ O₂ + 360 ml min⁻¹ He (all at STP), the cathode surface area for each cell is 0.71 cm².

electrolyte has been implemented, and because the operation temperature has been reduced to 500–600 °C. The time from cold-start to stable power output was typically less than 1 min, a competitive timescale for portable power. Although an external heat source has been employed in the present design for the start-up process, ultimately, self-initiation of the power generator may be possible using improved catalysts and a fuel that ignites on a catalyst at low temperature such as methanol, hydrogen or di-methyl ether. Several technical hurdles remain and the inherently low efficiency of the single chamber design poses additional challenges, but these results demonstrate the viability of high-energy-density hydrocarbon fuels for portable power applications.

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Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

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