

EXPRESS ARTICLE

Metallic foam supported electrodes for molten carbonate fuel cells

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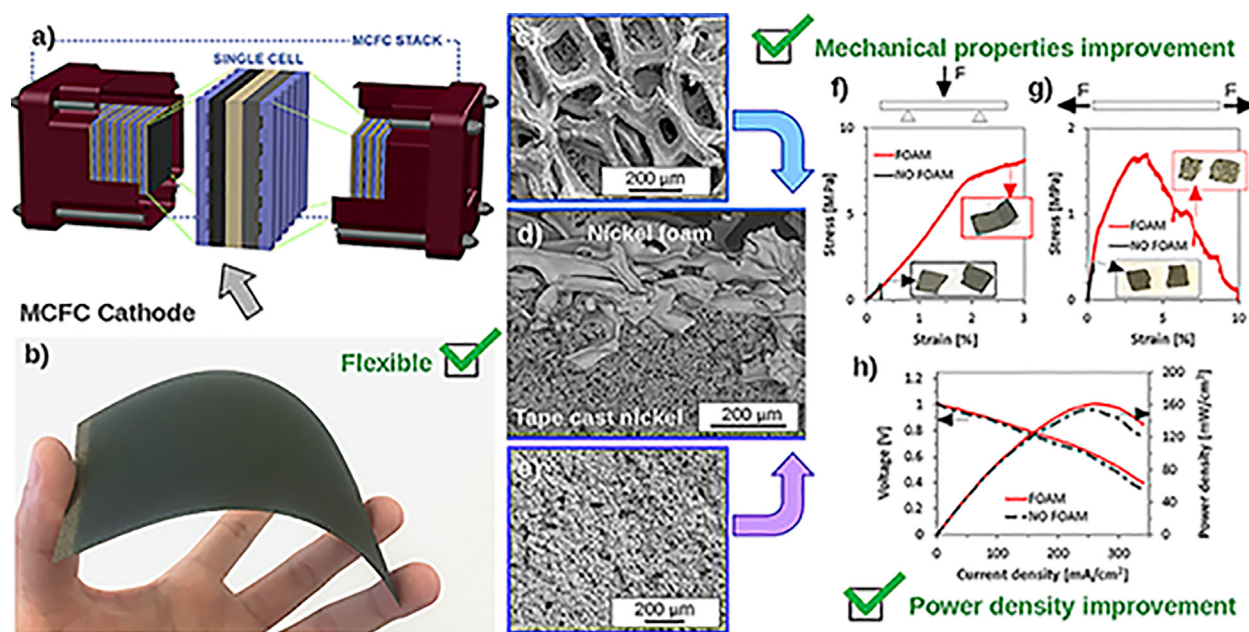
Foam supported electrodes

ABSTRACT

This paper demonstrates the benefits of using a metallic foam support within molten carbonate fuel cell (MCFC) cathodes. A state-of-the-art fabrication process based on tape casting has been developed to produce microporous electrodes with a nickel foam scaffold. Surfactant was added to control the depth to which the slurry infiltrated the foam. New cathodes were used as an alternative to the traditional cathode in the single cell assembly and were tested for power density. Mechanical properties were compared with the current state-of-the-art. The results show that the use of metallic foams for high temperature fuel cell electrodes is beneficial from the technological point of view, especially in larger scale production. It was also found that the resultant continuous metallic structure of the microporous electrodes delivered a slight enhancement to fuel cell power density.

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GRAPHICAL ABSTRACT



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A molten carbonate fuel cell consists of a nickel-based anode and cathode separated by a ceramic matrix (made of LiAlO_2) which immobilizes molten carbonate (eutectic mixture of $\text{Li}_2\text{CO}_3/\text{K}_2\text{CO}_3$ or $\text{Li}_2\text{CO}_3/\text{Na}_2\text{CO}_3$) electrolyte during operation [1,2] – see Fig. 1a. The electrodes within a single cell are characterized by open porous microstructures designed specifically to facilitate phenomena such as gas diffusion, surface reactions, capillary action and ion transport. Electrochemical processes taking place in high temperature fuel cells are complex and depend to a great extent on the microstructure and chemical composition of materials [3,4]. The MCFC cathode catalyzes oxygen reduction (ORR) and its reaction with carbon dioxide towards the formation of carbonate ions. According to the generally accepted theory, electrochemical reactions in an MCFC occur at the triple phase boundary (TPB) between the catalyst surface (electronic conductor), electrolyte (ionic conductor) and pore space (transport of reactants). The TPB perimeter is an active site for the cathode reaction, resulting in the formation of carbonate ions and their desorption/transport to electrolyte melt [5]. Therefore, the total length of the TPB within the electrode – together with the access of the supplied gases to the interface between the electrode and electrolyte – should be optimized to maximize electrode performance [6,7].

From the manufacturing point of view, controlling the microstructure of the MCFC cathode is challenging, particularly in terms of sintering conditions. The catalyst powder must be well sintered to form a continuous structure with proper contact between the particles providing high electrical conductivity and mechanical strength. The electrode should be elastic to prevent cracking when the pressure is applied during the fuel cell assembling procedure. Therefore, the higher the sintering temperature the better the sintering quality but the smaller the porosity, pore size and specific surface area, which together decreases the reaction rate [8].

In the present paper, an approach is demonstrated, that solves the problem of achieving the required mechanical strength and ductility of MCFC cathodes (Fig. 1b) without reducing their performance. The novel approach used involves a two-layer structure of the cathode, consisting of a gas-diffusion and a catalytic layer. Each layer is specifically designed for the predominant physio-chemical processes taking place during the fuel cell operation. Commercial nickel foam is used

for the gas-diffusion layer, serving also as a support for manufacturing the catalytic layer via the tape casting method, this additionally improves the mechanical properties and crack resistance of the electrodes during assembly, start-up and long-term operation. Additionally, the layered cathodes, manufactured as a result, are dimensionally repeatable, lending themselves to easy-to-assemble fuel cell parts with set structural and utility parameters.

All cathodes were fabricated by the casting of green tapes, which were then fired. The tape casting slurry contained nickel powder, polymeric binder, porogen and other additives, which provide the desired viscosity (i.e. defoamer, dispersant). In order to fabricate foam-supported electrodes, commercial nickel foam has been used as the substrate with a thickness of 0.5 mm, density of 250 g m^{-2} , porosity of around 90% and pore number per inch equal to 100 ppi (~40 pores per cm, which gives average pore intercept length of ~250 μm). The green tape was subjected to a three-step heat treatment in a reducing atmosphere of a $\text{N}_2/5\% \text{ H}_2$ mixture: annealing at 200 °C for 2 h in order to remove the volatile components, heating at 400 °C for 2 h to burn out the organic compounds, and sintering at 800 °C for 1 h.

Analysis of the microstructure of the cathodes was performed by Scanning Electron Microscopy (SEM). Specimens were studied using a Hitachi SU8000 with accelerating voltage in the range of 5–25 kV in the scattered electrons (SE) mode. Bending and tensile tests were used to characterize the mechanical strength of the materials. For each test 5 samples of size $10 \times 5 \times 0.6 \text{ mm}$ were cut from the larger tape. Mechanical testing was carried out using an MTS Tytron 250 system. Stress-strain curves were produced for static bending and tensile deformation.

The cathodes fabricated within these studies were analyzed in a single-cell testing rig, where current, voltage and power density were measured for real operation conditions. Single MCFC cells were assembled by stacking the green sheets of electrolyte and matrix between the electrodes (with an effective electrode area of 20.25 cm^2) covered with current collectors. An assembly pressure of 1.2 bar was applied to the single cell to produce solid contact between the components. Afterwards cell conditioning was conducted for 21 h in air at temperatures ranging from 25 to 450 °C, during which thermal decomposition of the organic binders occurred. Then, heating for 13 h in a H_2/CO_2 rich atmosphere at temperatures ranging from 450 to 650 °C was conducted in

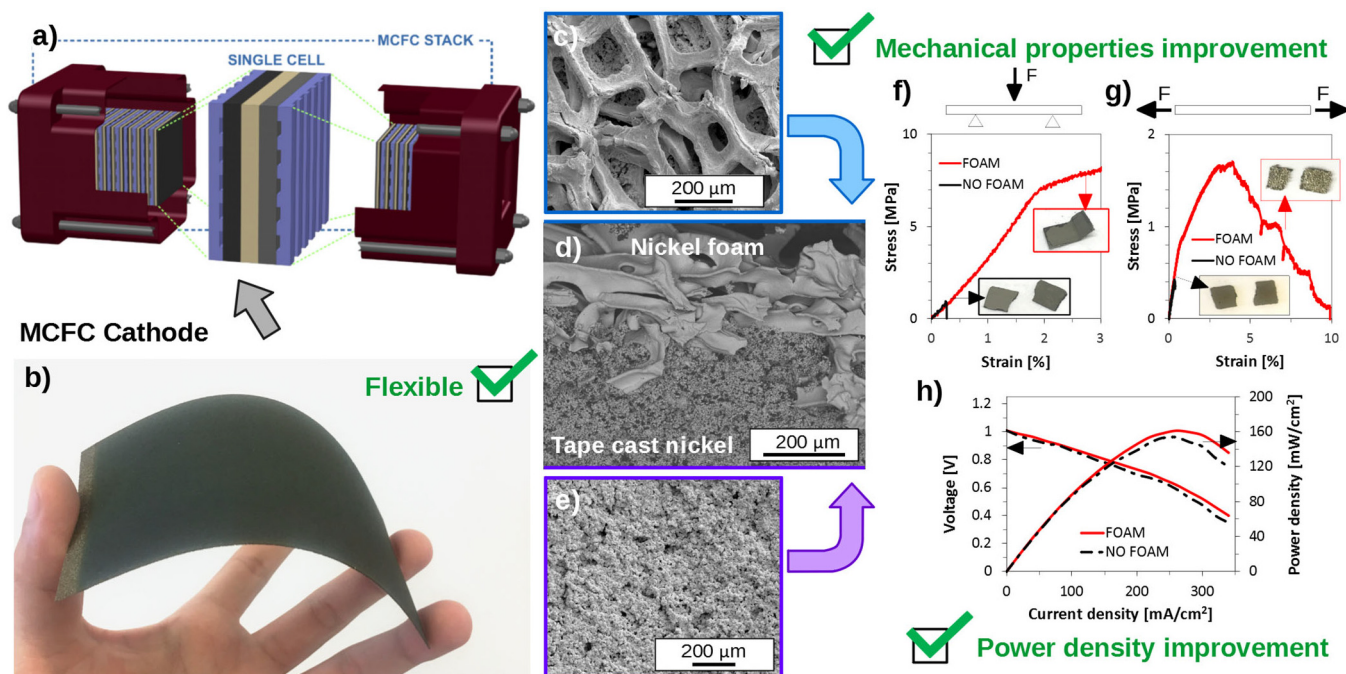


Fig. 1. Metallic foam supported MCFC cathode: microstructure and properties.

order to fully melt the carbonates. After cell conditioning, four measurements for each sample were performed at 650 °C, during which the fuel gas (H₂)80/(CO₂)20%, as well as the oxidant gas (Air)70/(CO₂)30% were fed, and cell voltage and current density were analyzed.

The microscopic image of the example foam supported cathode is presented in the Fig. 1c–e. It can be seen that the surface of the cathode is homogenous and free of macroscopic defects (Fig. 1e). The cross-sections of the cathode (Fig. 1d) show that the foam is partly infiltrated with microporous catalytic layer. The total thickness of the cathode is 0.6–0.7 mm. The gas-side of the cathode (Fig. 1c) is highly porous due to the presence of a layer of continuous nickel foam, not infiltrated by the slurry, of thickness 0.2–0.3 mm. The mechanical tests indicate that the cathodes with foam support have superior strength (both, ultimate bending and tensile stress) when compared to the reference materials (without foam support). The results of the static bending tests (Fig. 1f) show that the reference cathode behaves as a brittle material and cracks at very low stress and strain. Samples with foam exhibit a larger linear region (elastic part) and did not break during the bending test. The results of tensile tests (Fig. 1g) confirmed that ultimate tensile stress and strain-to-failure of the new cathodes are significantly enhanced due to the application of foam support.

The results of the single-cell performance test (Fig. 1h) show that a slightly higher maximum power density (about 10% increase) can be expected when a typical cathode is replaced with a foam-supported one. The explanation of this finding requires more detailed studies using electrochemical impedance spectroscopy. The enhancement of fuel cell performance can be attributed to gas transport being facilitated by the presence of the highly porous foam layer and/or increased electronic transport through the continuous foam structure.

These studies present a new concept of an MCFC cathode where commercial nickel foam is used as a mechanical support embedded into the catalytic layer. The results of mechanical tests show that this approach greatly reduces the brittleness of the materials typically used. Superior mechanical properties combine with a slight increase in the maximum power density of the fuel cell that can be obtained through application of the novel material. The proposed solution is especially important in the case of the cathode due to the higher porosity and in-situ oxidation compared with the anode. Furthermore, the concept

can be applied to both MCFC anode and matrix materials [9,10] and also to other fuel cell electrodes.

CRediT authorship contribution statement

T. Wejrzanowski: Funding acquisition, Conceptualization, Investigation, Supervision, Formal analysis, Writing - original draft, Writing - review & editing. **K. Cwieka:** Investigation, Visualization. **J. Skibinski:** Investigation. **T. Brynk:** Investigation. **S. Haj Ibrahim:** Validation, Visualization. **J. Milewski:** Funding acquisition, Investigation. **W. Xing:** Formal analysis, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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