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Short Communication

Dual ionic conductive membrane for molten carbonate fuel cell

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ABSTRACT

Within this study, the electrochemically inert, molten carbonate fuel cell (MCFC) γ -LiAlO₂ matrix is replaced by oxygen ion conducting ceramics, typical for solid oxide fuel cell (SOFC) application. Such solution leads to synergistic ion transport both by molten carbonate mix (CO₃²⁻) and yttria-stabilized zirconia (YSZ) or samaria-doped ceria (SDC) matrix (O²⁻).

Single unit cell tests confirm that application of hybrid ionic membrane increases the performance (power density) of the MCFC over pure γ -LiAlO₂ for a wide range of operating temperatures (600 °C–750 °C). Cell power density with SDC and YSZ matrices is 2% and 13% higher, respectively, compared to the γ -LiAlO₂ at typical 650 °C operating temperature of MCFC.

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Introduction

In the recent years, many factors have influenced the increase of interest in the field of the fuel cell technology. Limitations regarding the carbon dioxide emission and the reduction of the greenhouse effect became the driving force of progression in the fuel cell field. The efficiency of energy production is of great importance when the operation costs and pollution are considered. Molten carbonate fuel cells (MCFCs) are facing commercialization, mostly as megawatt (MW) scale systems

[1]. MCFC can operate on biofuels and hydrocarbons with negligible pollution and high efficiency of fuel conversion [2]. One way of increasing the performance of these fuel cells is to improve the electrolyte matrix, a component that is exclusive for the cells with a liquid electrolyte, necessary to withhold the carbonate melt in its fine open-porous structure.

Currently, the most widely used matrix material for MCFC is lithium aluminate (LiAlO₂) [3–5]. LiAlO₂ has sufficient stability in both reducing (anode) and oxidizing (cathode) atmospheres to assure long-term electrolyte retention [6], however, it is inert from the electrochemical point of view (as it is not

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ion-conducting). The ion transport (CO_3^{2-}) takes place thanks to the molten mixture of carbonates (most commonly Li and K eutectic [3]). This is where the solid oxide fuel cell (SOFC) approach can be brought up – the use of solid state ion-conductive oxides. Solid oxide fuel cells operate at much higher temperatures than molten carbonate fuel cells (1000 °C compared to 650 °C [7–9]) which increases the ionic (O^{2-}) conductivity of the membranes, but a fraction of this conductivity can be beneficial in the molten carbonate fuel cells when compared to the $\gamma\text{-LiAlO}_2$. Operating temperature is an important factor in the MCFC and SOFC as its increase results in higher system efficiency at a cost of premature material degradation and shorter lifespan [10].

This paper compares the performance of single cell units using the same Ni/NiO electrodes and electrolyte melt (Li/K eutectic) with three different matrices, made from: $\gamma\text{-LiAlO}_2$ (γ -lithium aluminate), 10YSZ (yttria-stabilized zirconia, 10% Y_2O_3), and 20SDC (samaria-doped ceria, 20% Sm_2O_3) to quantify the synergistic effect of hybrid ion conductivity.

Yttria-stabilized zirconia was chosen for its sheer popularity in the SOFC application, being the most common material choice for the electrolyte layer in these cells [11–14]. Another doped oxide – samaria-doped ceria – was selected for its ability to operate at lower temperatures than YSZ, as the ion conductivity characteristics starts to raise from lower temperatures (as in intermediate temperature solid oxide fuel cells – IT-SOFC) [15,16]. This can be beneficial as the MCFC is operated at lower temperatures than the conventional SOFC. Even higher ionic conductivity at lower temperatures is observed for the gadolinia-doped ceria (GDC), but this material was not subject to this study although it can be brought up for future investigations [12,17].

Experimental procedure

Matrices fabrication

The matrices for MCFC unit cell were fabricated by tape casting the ceramic/polymer slurry [18]. Solsperse 20000 (Lubrizol) was used as a dispersant, polyvinyl butyral – Mowital B 60 H (Kuraray) was used as a binder, dibutyl phthalate – DBP (Chempur) as a plasticizer, Agitan DF 311 M (Munzing Chemie) as a defoamer. Ethyl alcohol (96%, Chempur) was used as a solvent in all of the slurries. The ceramic powders used were: $\gamma\text{-LiAlO}_2$ (γ -lithium aluminate, ABCR), 10YSZ (yttria-stabilized zirconia, 10% mol Y_2O_3 , Tosoh) and self-manufactured 20SDC (samaria-doped ceria, 20% mol Sm_2O_3).

The SDC powder was formed by a solid state reaction [19]: the desired amounts of Sm_2O_3 and CeO_2 were ball-milled in ethanol for 12 h. The powder mixture was calcined at 1200 °C for 6 h. The calcined powder was subsequently ball-milled and dried. Finally, the dried powder was sieved through a 200-mesh screen.

The solid content in the slurries was kept at a constant powder volume ratio to total volume of the slurry, based on the densities of the ceramic powders, in order to obtain the same thickness of the green tapes (see Table 1). This assumption allowed collation of cell current (power density) measurements for different matrices eliminating effects other

Table 1 – Composition of slurries used for tape casting of the green tapes.

Comp./wt%	$\gamma\text{-LiAlO}_2$	10YSZ	20SDC
Base powder ^a	40.95	60.06	65.26
Solvent	37.54	25.40	22.09
Binder	6.66	4.50	3.92
Plasticizer	12.29	8.31	7.23
Defoamer	0.85	0.58	0.50
Dispersant	1.71	1.15	1.00

^a Vol% was kept constant for even thickness of the matrices.

than the chemical composition. The slurries were prepared by high-energy milling each ceramic powder in the solvent containing the dispersant for 18 h in Retsch RM400 planetary ball mill using sintered zirconia containers with 5 mm zirconia balls. Milling was conducted in order to obtain a fine particle size for all three powders thus leading to a smaller pore size of the matrix, necessary for proper operation of the cell (e.g. gas leak prevention) [20].

After the first ball-milling, binder and the remaining additives were added for additional 3 h of mixing and then vacuum de-aired (0.1 bar, 30 s) in order to obtain a homogeneous slurry for the tape caster. Subsequently, green tapes of 8 cm width were casted on a polyethylene surface using a moving-blade tape caster device with a doctor blade height set to 0.55 mm. The flowchart of matrices fabrication is presented in Fig. 1, with base powder ($\gamma\text{-LiAlO}_2$, 10YSZ, 20SDC) being the only variable. The composition of the slurries is presented in Table 1.

Characterization and testing

In order to investigate the structure of the matrices, green (as-casted) matrix tapes were heated slowly to 750 °C and kept at this temperature for 18 h in order to burn-out the polymer additives. The porous samples were then vacuum deposited with copper in order to perform scanning electron microscopy on Hitachi SU8000.

Performance tests were conducted in a testing rig with cell working area of 20 cm². Two layers of matrix green tape (2 × 0.30 mm when dried) were used for each cell test assembly. Both electrodes were prepared by tape casting and sintering before the cell assembly. The anode was 1.2 mm thick Ni and the cathode was 0.65 mm thick Ni (oxidized to NiO during the start-up of the stack) [21]. The electrolyte melt was an eutectic mixture of Li and K carbonates (62/38 mol% ratio) prepared as ethanol-based paste. All components were housed in 310 alloy stainless steel endplates with 310 alloy current collectors. A single cell unit was brought up to working temperature of 600 °C (then to 650 °C, 700 °C and 750 °C) with soak times at 310 °C and 460 °C. Gas tightness was confirmed by nitrogen flow. A mixture of air + CO_2 (2.31:1 ratio) was used as an oxidant and H_2 + CO_2 (4:1 ratio) was used as fuel gas. The unit was operated at atmospheric pressure with the same reference point for gas compositions and flow rates for all matrices. Cell voltage was measured directly at the electrodes and its value was processed by a National Instruments board. For load demand, DC electronic load (SAE Electronic Conversion SRL) was used [19].

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