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ORIGINAL PAPER

Current status of proton-conducting solid oxide fuel cells development

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Abstract Solid oxide fuel cells (SOFC) are promising devices for high efficiency cogeneration. The most widely used and studied ones have an anion conducting electrolyte that requires high operating temperatures to limit ohmic losses across this electrolyte; temperatures typically range between 800 and 1,000 °C. This temperature is associated with undesirable phenomena such as material interaction and insulating phase formation that result in unsatisfactory durability and high cost for market entry. Proton conducting solid oxide fuel cells (PCFC) constitutes a promising alternative since they allow a significant decrease in operating temperature. The Ba(Zr,Ce,Ln)$O_{3-\delta}$ perovskite family exhibits ionic conductivities reaching 10^{-2} to 10^{-1} S cm^{-1} at temperatures as low as 600–700 °C, these values being obtained with anion conducting SOFC between 700 and 1,000 °C. On the basis of a review of work on half cells and complete cells, this paper addresses the main parameters that control and limit PCFC behaviour. This analysis aims at proposing recommendations for designing and testing proton conducting fuel cells.

Keywords Proton conducting solid oxide fuel cell · PCFC · Fuel cell operation · Proton conducting ceramic material

1 Introduction

Solid oxide fuel cells (SOFC) have been widely developed for their capability to produce Combined Heat and Power based on natural gas or biomass gas operation. From material development to demonstration programs, a significant spectrum of research and development activities is being covered worldwide [1–3].

Main current limitations of SOFCs lie in their reliability and durability, directly linked to the high operating temperature needed to limit ohmic losses across the electrolyte and ranging typically between 800 and 1,000 °C. This high temperature allows fuel flexibility, particularly direct hydrocarbon fuel reforming, but is also associated with undesirable phenomena such as material interaction and insulating phase formation that result in both unsatisfactory durability and high cost for market entry.

Proton conducting solid oxide fuel cells (PCFC), based on a proton conducting oxide electrolyte, should allow a significant decrease in operating temperature and constitute a promising alternative. Indeed the Ba(Zr,Ce,Ln)$O_{3-\delta}$ perovskite family for example exhibits ionic conductivities reaching 10^{-2} to 10^{-1} S cm^{-1} at temperatures as low as 600–700 °C, these values being obtained on 8% Yttria stabilized Zirconia (YSZ) between 800 and 1,000 °C.

On the basis of a review of current work on PCFC half cells and complete cells, the main parameters that control their behaviour are listed and major issues to be addressed are reviewed.

2 Current status of regular SOFC operation

Solid oxide fuel cells (SOFC) are fabricated as a solid electrochemical chain (Atm1 | electrode | electrolyte | electrode | Atm2) that allows charge carrier transport and charge transfer at interfaces, resulting in the conversion of chemical energy into electrical energy (Fig. 1). The SOFC most commonly used nowadays has an anion conducting

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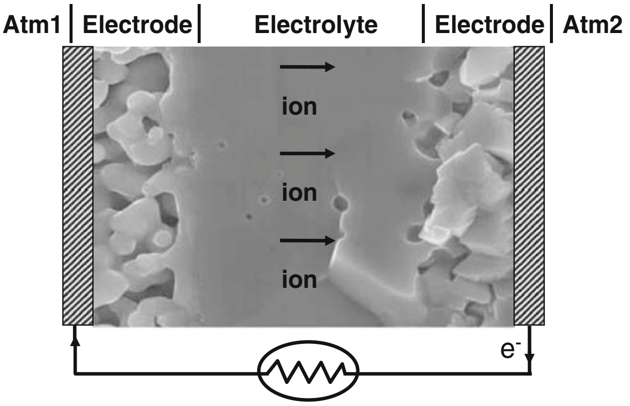


Fig. 1 Structure of Solid oxide fuel cells (SOFC). The solid electrochemical chain (Atm1 | electrode | electrolyte | electrode | Atm2) allows charge carrier transport and electricity production

electrolyte such as YSZ and porous electronic conductors as electrodes.

To minimise electric losses within the fuel cell, high conductivities are required for all constituent materials: exclusively ionic in the electrolyte, exclusively electronic in the current collection circuit, including interconnects, and essentially electronic in the electrodes. Mixed electronic and ionic conduction is found to be even better in the electrodes because it allows the electrochemical reaction to occur in an enlarged active volume instead of the active surface at the interface between electrode and electrolyte where three phase boundaries are located. In addition to these bulk material properties, all interfaces have to be fully optimised with Area Specific Resistance (ASR) ranging around 0.1 Ω cm^2. Material specifications for SOFCs are gathered in Table 1.

Good reproducibility regarding cell performance is now obtained with current materials such as Ni-8YSZ Cermet as anode, 8YSZ as electrolyte and perovskite cathodes such as YSZ–LSM (Strontium doped Lanthanum Manganite) or more recently LSCF (Strontium doped Lanthanum cobalto-ferrite) and with fabrication technologies such as tape-casting and serigraphy. At 800 °C, nominal power outputs as high as 0.7 W cm^{-2} are classically obtained with an acceptable fuel utilisation rate (higher than 40%) as illustrated in Fig. 2 with some results from the Real-SOFC European program [4]. On single cells, these performances are even better, frequently exceeding 1 W cm^{-2} in similar operating conditions. However, as shown on Fig. 2, decreasing the operating temperature causes major nominal power output decrease and excludes these operating temperature ranges.

Recently major progress has been achieved regarding SOFC degradation and durability. Small stacks exhibit degradation rates as low as 1% per 1,000 h under wet hydrogen and air at 800 °C and 0.3 A cm^{-2} [5]. These

Table 1 Main specifications for SOFC constituting materials

	Anode	Electrolyte	Cathode	Interconnect
Material requirements	Chemical stability under reducing atm. ($p_{O_2} \sim 10^{-18}$ Atm)	Chemical stability under high p_{O_2} gradient (10^{-18} Atm to 1 Atm)	Chemical stability under oxidising atm. ($p_{O_2} \sim 1$ Atm)	Chemical stability and corrosion resistance
Density	Porous (20–40%) Preferably with gradient	Dense (>95%)	Porous (20–40%) Preferably with gradient	Dense (>95%)
Ionic conductivity	Delocalise the electrochemical reaction	Highest (YSZ: 10^{-1} S cm^{-1} at 1,000 °C, 10^{-2} S cm^{-1} at 750 °C)	Delocalise the electrochemical reaction	
Electronic conductivity	Highest (Ni-Cermet 10^3 S cm^{-1} at 800–900 °C)	Negligible compared to ionic conductivity	Highest (LSM ~ 10^2 S cm^{-1} at 800–900 °C)	Highest (including protective coating & oxide layer)

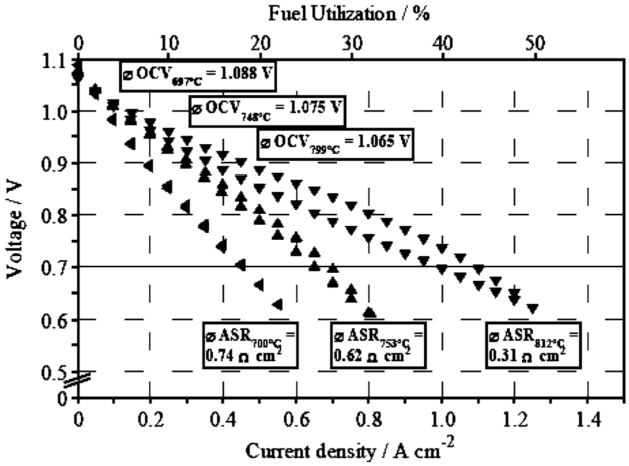


Fig. 2 Polarisation curves at 800, 750, and 700 °C on large single repeat units (cell + interconnects) operated with reformate gas [4]. (Ni-8YSZ anode, 8YSZ electrolyte and LSM/YSZ cathode fabricated at FZ Jülich)

results, though constituting a step forward, remain unsatisfactory in terms of operating atmosphere, operating condition severity and duration.

Among the mechanisms associated with these degradation phenomena, interconnect corrosion and, more specifically, Cr vaporisation, can be mentioned, as well as glass sealing instability and minor alloying element diffusion [6]. All these mechanisms are thermally activated and should be inhibited or at least seriously slowed by decreasing the operation temperature. This is a major issue for next generation SOFCs.

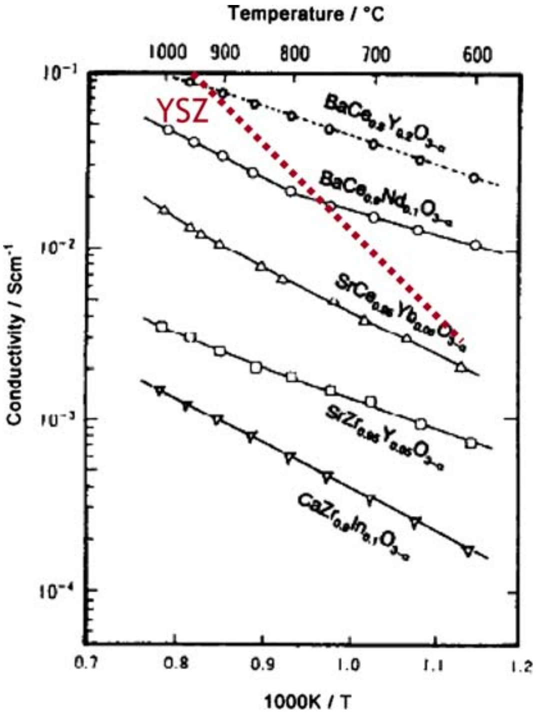
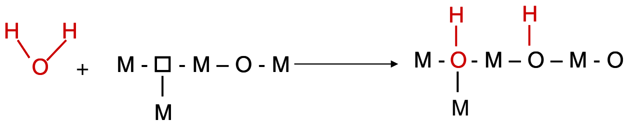


Fig. 3 Conductivity of major proton conducting family after Iwahara [9] and for comparison YSZ classical conductivity

3 Main advantages and specifications of PCFC

Proton conducting materials have been known for many years for their high ionic conductivity at intermediate temperature [7]. Indeed similar conductivities can be expected at 800 °C with a YSZ electrolyte and at 600 °C with a Ba(Ce,Y)$O_{3-\delta}$ one (Fig. 3). This allows significantly decreasing proton conducting SOFC operation without increasing ohmic losses across the electrolyte.

The proton conduction is based on the existence of a proton defect in the oxide that is created when the oxide, containing oxygen vacancies, dissociates and absorbs water from a surrounding wet atmosphere.



The process can be written according to the following equations which are more or less equivalent:

$$O_O^X + V_O^{\bullet\bullet} + H_2O \leftrightarrow 2(OH)_O^{\bullet} \quad V_O^{\bullet\bullet} + H_2O\,(OH)_O^{\bullet} + H_i^{\bullet}.$$

Due to the presence of these proton defects, the proton migrates by a series of jumps to the next O_O^X involving neighbour proton defects, as illustrated in Fig. 4 from Iwahara [7] and Kreuer [8].

A main consequence for proton conducting SOFC is the need of a sufficiently wet atmosphere to allow the formation of proton defects in the electrolyte. As illustrated in Fig. 5, oxygen (or air) and hydrogen are classically introduced at the cathode and anode, respectively. At the cathode side, the oxygen reduction reaction produces water (Eq. 1) and guarantees the atmospheric humidity. At the anode side, assuming hydrogen adsorption on a metallic site for example, hydrogen oxidation produces protons able to migrate on proton defects (Eq. 2).

Oxygen reduction:

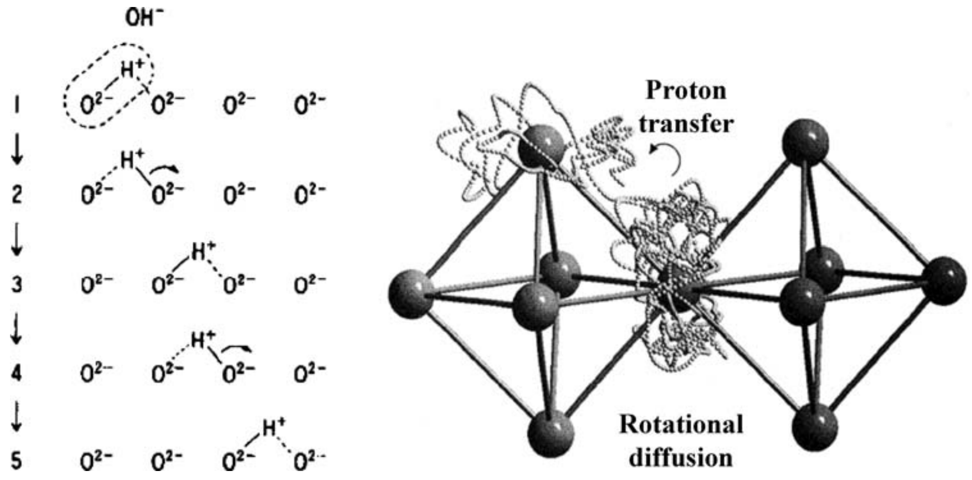
$$1/2O_2 + 2e_M^- + 2OH_O^{\bullet} \rightarrow H_2O + 2O_O^X \qquad (1)$$

Hydrogen oxidation on a metallic site:

$$2s_M - H + 2O_O^X \rightarrow 2OH_O^{\bullet} + 2e_M^- \qquad (2)$$

Some early publications mention stable operation at 800 °C using $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ as electrolyte with porous Pt electrodes [9]. However, recent work from Dahl and Norby [10] highlights the major impact of water vapour

Fig. 4 Mechanism of proton conduction by series of jumps to the next as proposed by Iwahara [7] and detailed further by Kreuer [8]



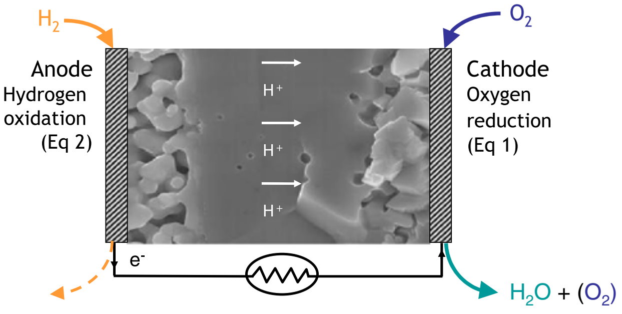


Fig. 5 Schematic of gas production and evolution in a proton conducting SOFC

partial pressure in hydrogen between 500 and 1,000 °C on the total and partial conductivities of the same electrolyte. At low temperature proton conductivity is found to dominate for almost all p_{H_2O} whereas oxygen ion conductivity is almost negligible except in very dry atmospheres ($p_{H_2O} < 10^{-4}$). In contrast, at high temperature, all types of conductivity become significant, oxygen ion conductivity having a large influence at almost all p_{H_2O} and proton conductivity contribution being almost negligible except at high p_{H_2O}. Thus, at the anode side of a PCFC, the lower the temperature the lower the influence of water partial pressure on proton conductivity; but in contrast, the higher the temperature the higher the need of a high water partial pressure to ensure predominant proton conductivity.

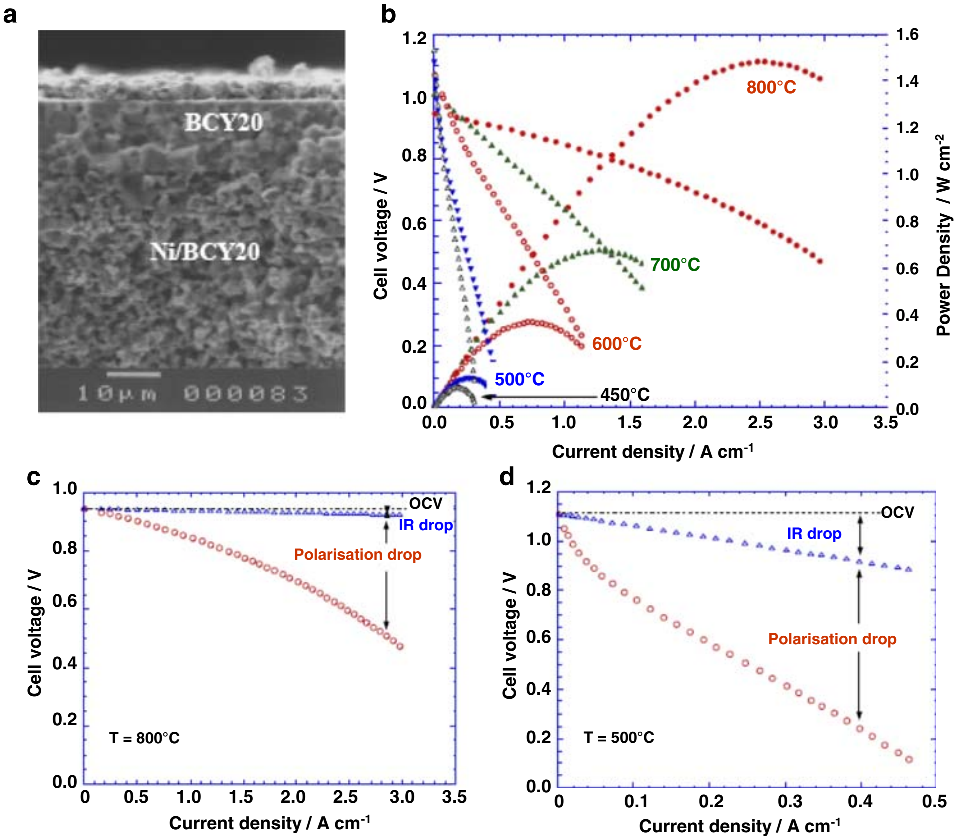
At the cathode side, the atmosphere is readily wet. But on this side also temperature has a major impact on proton conductivity. Indeed, some work from Iwahara [7, 9] in wet air, shows that the higher the temperature between 500 and 1,000 °C, the lower the proton concentration and the lower the proton transport number, this number becoming lower than the oxygen ion transport number above 800 °C.

As a first conclusion, a pure PCFC will require an operating temperature lower than 700 °C.

4 First PCFC cell results

Most work performed on PCFC has been carried out using Pt electrodes surrounding a proton conducting electrolyte based on doped cerates ($ACeO_3$) or zirconates ($AZrO_3$). Recent work from Balachandran et al. [11] presents the performance obtained between 500 and 800 °C in dry hydrogen and wet air with a 10 μm dense $BaCe_{0.8}Y_{0.2}O_{3-\delta}$ electrolyte (BCY20) deposited on a Ni-BCY20 cermet anode substrate with Pt paste as cathode (Fig. 6a). On both electrode sides, current collection is obtained, respectively, with a Ni and a Pt mesh. The cell diameter is 2.5 cm. Polarisation curves are presented on Fig. 6b. Maximum power densities are found to increase significantly from 150 W cm^{-2} at 500 °C to 1.5 W cm^{-2} at 800 °C. At the highest temperatures, the experimental open circuit voltage is lower than the calculated Nernst potential. This is attributed to a possible contribution at these temperatures of electronic conductivity in the electrolyte, as proposed in [10]. With decreasing temperature, the open circuit voltage reaches the calculated Nernst potential value, assessing the electrolyte integrity. However, simultaneously the cell becomes more resistive. Decomposition between the respective contributions of the electrolyte and the electrodes in this voltage loss is proposed in Fig. 6c at 800 °C and 6 days at 500 °C on the basis of polarisation and impedance measurements. The electrolyte contribution (namely the ohmic drop, iR) is found to increase with decreasing temperature, from an almost negligible value at 800 °C to a more significant value at 500 °C. It is, however, electrode polarisation that generates the major component of the voltage drop. At 500 °C the shape of the overvoltage curves indicates a large activation polarisation with additional ohmic drop, whereas at 800 °C, electrode polarisation although limited, constitutes the major loss, reinforced at high current densities by concentration polarisations.

Fig. 6 Complete cell results—air | Pt | BCY20 | Ni-BCY20 | H_2—from [11]. **a** SEM micrograph of a fracture surface of the cell after testing. **b** Polarisation curves in dry H_2 and wet (2.6% vol H_2O) air from 450 °C to 800 °C. **c** Decomposition of voltage drop between electrolyte and electrodes at 800 °C. **d** Decomposition of voltage drop between electrolyte and electrodes at 500 °C



Similar tendencies are also reported by Ranran et al. [12] on a complete ceramic PCFC. In this work, a button cell (diameter 1.3 cm) was made of a 50 and 75 µm dense $BaCe_{0.8}Sm_{0.2}O_{2.90}$ (BCSO) electrolyte, deposited on a Ni-BCSO cermet anode substrate with $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) as cathode material. Tests were performed at 600 °C and 700 °C with wet H_2 and wet O_2 (Fig. 7).

In these two recently published cases the authors find promising power densities. They have separated the electrolyte and the electrode contributions in the area specific resistance (ASR) of the complete cell by impedance spectroscopy. At 600 °C and below electrodes and interfaces are shown to have the major contribution, whereas above 700 °C, the electrolyte is found to generate 70% of the cell resistance.

As a partial conclusion it appears that some promising results are reported in the literature with PCFC compared to classical anion conducting SOFC (Table 2), but that significant improvements are still required, specifically to optimise electrodes and interfaces before reaching or even exceeding current nominal performances.

Owing to the high power density obtained by Balchandran at 800 °C the question whether it is a problem to have mixed hydrogen and oxygen ion conductivity or not should also be more carefully considered.

5 PCFC electrode development status

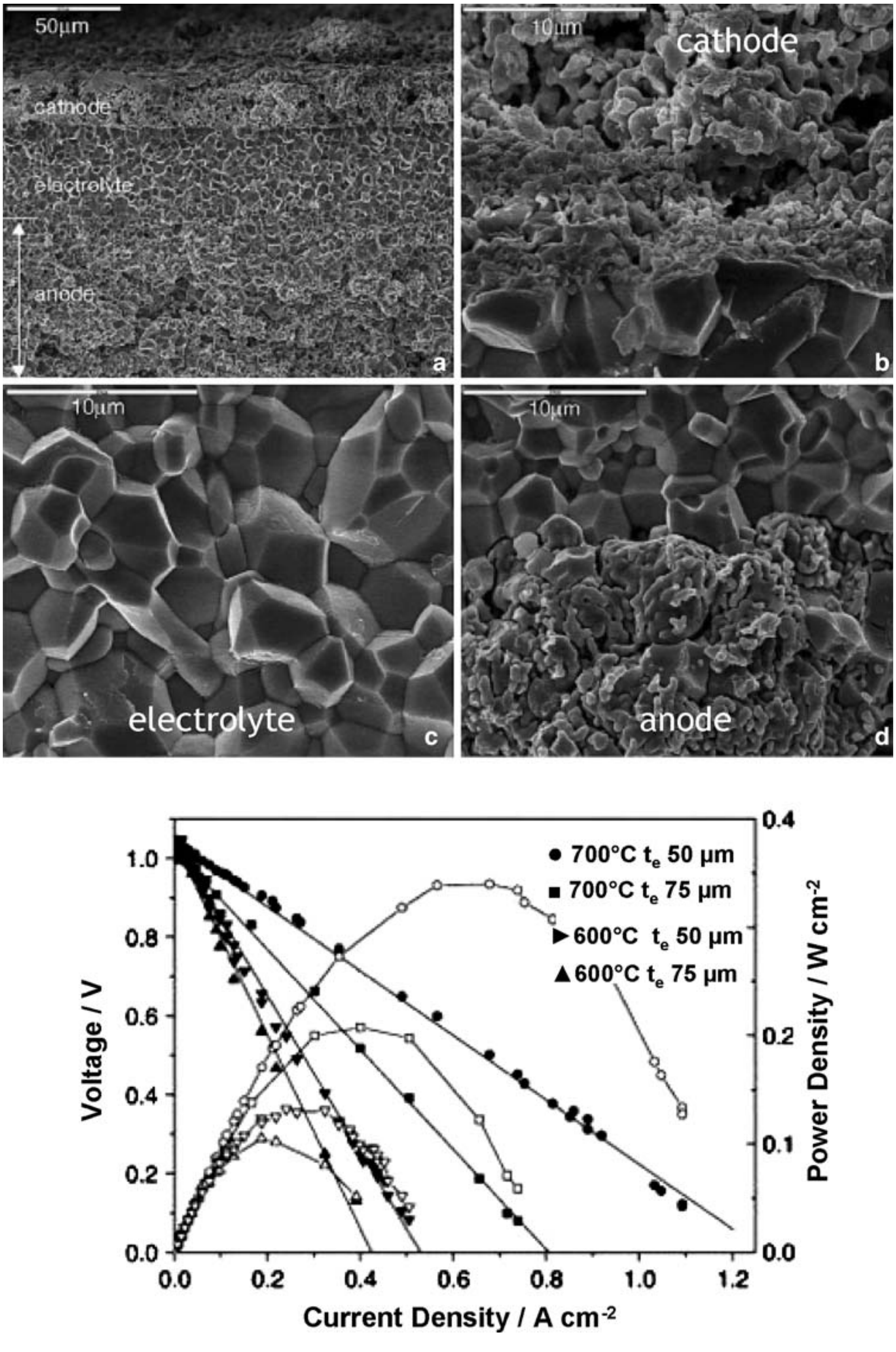
Depending whether the SOFC is anion or proton conducting or both, the electrode reactions vary as illustrated in Fig. 8 reproduced from [13] and [14].

The nature of the metal used in the anode cermet has a significant influence via electrode reaction kinetics. Rate determining steps such as H_2 dissociation chemical reaction or adsorbed hydrogen diffusion are found to vary with the metal and with pH_2. As in classical SOFC, in PCFC, a Ni anode is found to be the most efficient metallic anode even though it is sensitive to pH_2 decrease [13].

The composition of the proton conducting oxide surrounding Ni in anode cermets is found to significantly influence the electrochemical response of symmetric cells and this is attributed to electrode reactions that would be modified [13–15]. Moreover, in all reported cases, ohmic resistances are found to remain rather high [15]. At this stage, understanding of electrode mechanisms is a necessary step to further optimise cermet microstructure.

After testing, cerate based Ni-Cermet, show traces of CeO_2. Indeed, in reducing environment, this phase is formed because it is more tolerant to the reduction of Ce(IV) to Ce(III). When cerate is doped with strontium, traces of $SrCO_3$ are also found. These can be attributed to

Fig. 7 Complete cell results—air | BSCF | BCS0 | Ni-BCS0 | H_2 from [12]. **a** Fuel cell microstructure. **b** Performance curves



an excess of strontium oxide resulting from perovskite degradation that has reacted with atmospheric CO_2. As a consequence, $SrCeO_3$ stability in reducing atmosphere, as well as regarding CO_2, constitutes an issue for long term operation.

In the air compartment, Pt paste and mesh are the cathodes most widely used. However, to extend the reaction area and resist highly corrosive atmospheres ($p_{O_2} + p_{H_2O}$) mixed proton electron conducting oxide material is preferable. Ongoing work on such materials is mostly dealing with phase stability. La*M*O_3 Perovskite (M = Co, Mn, Fe) are found to show promising stability with $BaZrO_3$ based electrolyte. Only a minor fraction of $La_2Zr_2O_7$ is detected after air annealing of powder mixtures [16]. In contrast, these La*M*O_3 Perovskite (M = Co, Mn, Fe) show high reactivity with $SrCeO_3$ based

Table 2 Comparison of SOFC performances from [5, 11, 12]

Cell tested	Maximum power density/mW cm^{-2}		
	600 °C	700 °C	800 °C
Air | Pt | BCY20 | Ni-BCY20 | H2 (small cell)	350	650	1,500
Air | BSCF | BCS0 | Ni-BCS0 | H2 (small cell)	130	350	
Air | LSCF(LSM) | 8YSZ | Ni-8YSZ | H2			(Nominal)
(Large single repeat unit)		350	700
(Classical single cell)		(Nominal)	>1,000

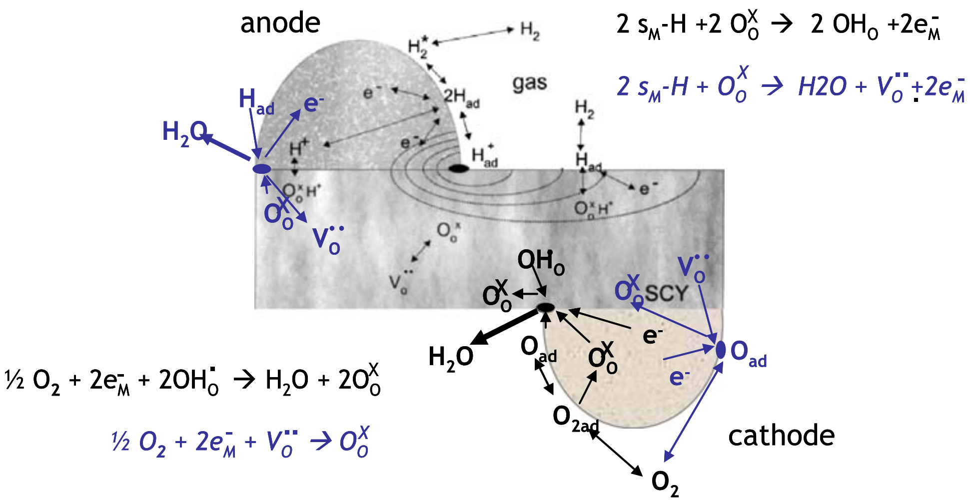


Fig. 8 Summary of electrode and interface reactions likely to occur in the case of a proton conducting SOFC and an anion conducting SOFC, after [13, 14]

electrolyte [17]. With this $SrCeO_3$ based electrolyte material, the $La_{2-x}Sr_xNiO_4$ family is found to offer the most promising stability [17]. Interesting results are also reported with a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) cathode on $BaCe_{0.8}Sm_{0.2}O_{2.90}$ electrolyte by [12], but no indications about stability and durability after 17 h are given in the paper.

At this stage, the development of efficient and stable cathode materials for proton conducting SOFC still constitutes an issue to be addressed.

6 Fuel flexibility with PCFC

It is commonly accepted that PCFC may also operate with methane or other hydrocarbon fuels. For this, various configurations have been proposed by Iwhara [18] (Fig. 9) and emphasised by Coors [19].

According to these authors, protons should be produced directly in the anode compartment before being absorbed in a proton defect of the electrolyte proton conducting ceramics. Without any water vapour introduction at the anode, it is expected by these authors that some steam permeation from the cathode to the anode will provide water and allow the methane reforming reaction to occur resulting in hydrogen production at the anode.

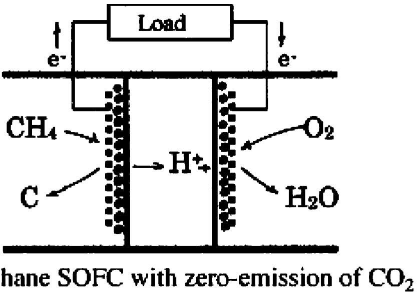


Fig. 9 Concepts of SOFC using proton conducting ceramics and operated directly with methane after [18]

With such a hypothesis, the anode compartment is considered as a chemical reactor. Thermodynamic equilibrium constants of CH_4 and H_2O reactions are plotted according to the temperature in Fig. 10. Reactions producing H_2 from CH_4 are found to be favoured at high temperature, when the electrolyte exhibits both proton and oxygen anion conductivities. Between 500 and 600 °C, which is the temperature range of pure proton conductivity, owing to the low values of thermodynamic constants, only small quantities of H_2 are expected to be formed by steam reforming and this can only result in very limited current density. The most efficient reaction being CH_4 cracking, H_2 is expected to be formed preferentially with this reaction

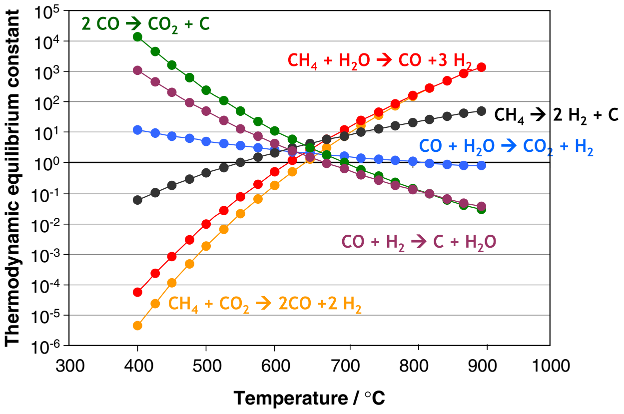


Fig. 10 Thermodynamic constants of CH_4 and H_2O reactions at 1 bar using GEMINI data [20]

and to be associated with carbon formation that will degrade the cell.

The experimentations reported by Coors [19] using an air | Pt | BCY10 | Pt | H_2 cell at 750 °C tends to confirm this analysis. Under wet hydrogen, initially $E_{i=0}$ is equal to the expected Nernst potential, whereas under wet CO, it does not exceed 600 mV indicating the low amount of H_2 formed at the anode. After 1 day, performance although very low, remains identical. After 12 days it is drastically decreased. This can be tentatively attributed to the formation of small quantities of CO_2 due to the Boudouard equilibrium ($2CO \rightarrow CO_2 + C$), that may react with the electrolyte. Intermediate behaviour is obtained under syngas composed of H_2 and CO with an initial $E_{i=0}$ close to 900 mV and a pronounced degradation visible even after 1 day. Under wet CH_4 without significant water vapour supply, cracking ($CH_4 \rightarrow C + 2\ H_2$) is expected to be the most efficient reaction. Owing to the value of $E_{i=0}$, varying from 400 mV to 700 mV after 12 days, it can be concluded that H_2 production remains rather low. Expected associated carbon deposition would initially not alter the cell performance as observed after 1 day, but can explain the drastic drop obtained after 12 days.

Without significant water vapour addition at the anode side, any steam permeation from the cathode to the anode will be insufficient to allow major CH_4 reforming and produce high current densities.

As a conclusion it seems that operating a proton conducting SOFC under dry hydrocarbon fuel will result in very poor performances due to a lack of hydrogen formed at the anode side and high degradation rates due to carbon formation.

It is also worth noting that in this work, under hydrogen, the cell performance is also observed to decrease significantly confirming the poor stability of cerates.

7 Conclusion

Proton conducting materials constitute promising candidates for efficient low temperature SOFC. Indeed, good performances are reported at 500–700 °C, temperatures at which proton conduction dominates, and also at 750 and 800 °C, temperatures at which proton and oxygen ion conduction are both contributing. This observation leads to the conclusion that for each system considered, the best operation temperature needs to be determined. In particular, operating fuel cells with both proton and oxygen anion conduction may be considered to improve the power output significantly.

Regarding operation conditions, wet hydrogen and wet oxygen (or air) supply appear to be preferable to dry gas supply regarding proton defect concentration and proton conductivity. Direct hydrocarbon fuel operation does not seem possible under 650 °C since the foreseen temperature range does not favour chemical H_2 production and since C and CO_2 production may constitute a degradation source for the electrolyte and the anode Cermet. At higher temperature, with water vapour supply at the anode side it may be possible, but experimental evidence is still required.

Major issues are still to be addressed; (i) the stability of proton conducting oxide materials, in particular regarding reducing environments and CO_2, to obtain acceptable durability and (ii) electrode stability and their interfaces with the electrolyte to further increase performance.

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