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Augsburg

Optimized Performance of Nanoparticle Composites for Solid Oxide Fuel Cells by a new Generation of Powder Processor

Abstract

One fundamental of our economics is the availability of power. Nowadays the gross of power is produced by fossil fuels.

Fuel cells seem to be an alternative power generation form except for solar cells and wind power. Comparing to the conventional power generation the main advantage of fuel cells is the direct conversion into energy by chemical reaction (oxidation) in a galvanic cell. At the moment the efficiency of fuel cells is limited to 40...60 %. But there is a high potential to optimize their performance. The performance is connected closely with the morphology of the powdery components and composites. Morphology includes the grain size, distribution, dispersion, connection and porous structure of the composites.

Topic of this article will be the connection between the requirements from the scope of material science

on the one hand and the methods of resolution provided by process engineering on the other hand. At first, the structure and function of a Solid Oxide Fuel Cell will be described. Concerning this matter the requirements on suitable components and composites will be derived and procedural methods of resolution will be presented. At last, the advantages of nanoparticle based SOFC components will be discussed.

Introduction

One fundamental of our economics is the availability of power. Nowadays the gross of power is produced by fossil fuels. Following the actual forecasts the reserves of fossil fuels will be limited to the next 50 or 100 years. An additional aspect is the fact that the combustion of fossil fuels generates the climate affecting greenhouse gas CO₂. During the last years the activities increased to

develop alternative, regenerative and also climate neutral forms of power generation that will be accepted by the society, too.

Fuel cells represent one possibility for power generation. They are defined as a galvanic cell in which chemical reaction energy generated by oxidation of a continuously fed fuel is converted to electrical energy by an oxidant. In contrast to conventional power generation the energy source is converted directly into electrical energy. Hydrogen H₂ and methane CH₄ are used as energy sources. Those are converted directly into electrical energy in the galvanic cell by chemical reaction in presence of oxygen. This way of energy storage offers an obvious favorable power loading in comparison to conventional accumulators. Therefore, fuel cells become interesting for mobile applications.

In principle fuel cells consist of two electrodes that are separated spatially by a membrane or electrolyte. The anode is bubbled by fuel which delivers electrons. That means it is oxidised. The generated anions are transported by the electrolyte to the cathode. There the oxidant accepts electrons by an external electric circuit. That means it is reduced.

The various types of fuel cells differ in the used electrolytes, the mobile ions as well as the anode gas as shown in Tab. 1. In general, oxygen is used as cathode gas, in most cases atmospheric oxygen. Anode gases are basically hydrogen, methane and methanol. Either anions or cations (hydroxyl-, carbonate- or oxide-ions) are used as mobile ion. The obtainable power output depends on the operating temperature. At operating temperatures below 200°C the maximum power output is roundabout 500 kW. As the operating temperature increases power outputs of 10 000 up to 100 000 kW are possible. The degree of efficiency of the cells shows clear-

Tab. 1
Overview of different types of fuel cells und their degree of efficiency according to [1] and [2].

¹⁾ means single fuel cells
²⁾ system.

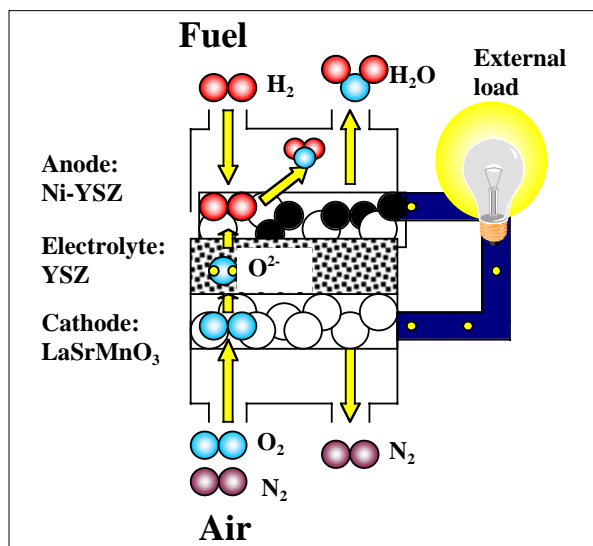
Notation	Electrolyte	Mobile ion	Anode gas	Cathode gas	Power P/kW	Temp. T/°C	Efficiency η
AFC Alkaline Fuel Cell	Caustic potash	OH ⁻	H ₂	O ₂	10 ...100	< 80	60...70% ¹⁾ 62% ²⁾
PEMFC Proton Exchange Membrane Fuel Cell	Polymer membrane	H ⁺	H ₂	O ₂ (air)	0.1...500	70-200	50...70% ¹⁾ 30...50% ²⁾
DMFC Direct Methanol Fuel Cell	Polymer membrane	H ⁺	CH ₃ OH	O ₂ (air)	0.001...100	90-120	20...30% ¹⁾
PAFC Phosphoric Acid Fuel Cell	Phosphoric acid	H ⁺	H ₂	O ₂ (air)	<10,000	200	55% ¹⁾ 40% ²⁾
MCFC Molten Carbonate Fuel Cell	Alkaline carbonate melt	CO ₃ ²⁻	CH ₄ , H ₂	O ₂ (air)	100,000	650	55% ¹⁾ 47% ²⁾
SOFC Solid Oxide Fuel Cell	Oxidic ceramics	O ²⁻	CH ₄ , H ₂	O ₂ (air)	<100,000	800-1000	60...65% ¹⁾ 55...60% ²⁾

Notation	Electrolyte	Anode material	Cathode material	Separator material
AFC Alkaline Fuel Cell	Caustic potash KOH	Au-Pt, Ni	Pt-Pd, Ni	Ni
PEMFC Proton Exchange Membrane Fuel Cell	Proton exchange membrane	Pt-catalysts, carbon, PTFE		Carbon, Ti, SUS
PAFC Phosphoric Acid Fuel Cell	conc. phosphoric acid H ₃ PO ₄	Pt-catalysts, carbon, PTFE		Carbon
MCFC Molten Carbonate Fuel Cell	Alkaline carbonate melt, e.g. (Li,K) ₂ CO ₃ , (Li,Na) ₂ CO ₃	NiO, NiO-MgO	Ni-Cr, Ni-Al	SUS, Ni alloy
SOFC Solid Oxide Fuel Cell	Oxidic ceramics, e.g. Y ₂ O ₃ -ZrO ₂	La(Sr)MnO ₃	Ni-YSZ	LaCrO ₃ , Ni alloy

Tab. 2
Basic materials for
Solid Oxide Fuel
Cells.

ly fluctuations in dependence of the cell type. For instance, the degree of efficiency of Direct Methanol Fuel Cell was determined to 20...30 %. This is much less than the typical level of the other fuel cells with 60...70%. The whole systems achieve only a degree of efficiency of 40...60% [1]. It's obvious to see in Tab. 2 that most types of fuel cells use the classic cathode materials like platinum, palladium and carbon except of Molten Carbonate Fuel Cells and Solid Oxide Fuel Cells. Those act as a catalyst. In MCFC nickel oxide is used generally as anode material; carbonate melt as electrolyte and nickel-chrome- and nickel-aluminium-compounds are used as cathode material. Oxide ceramics in combination with nickel are applied in SOFC as electrolyte and anode materials.

Fig. 1
Structure and
operation of a Solid
Oxide Fuel Cell
Tab. 3
In SOFC used
materials



Structure and Operation of Solid Oxide Fuel Cells

Fig. 1 shows the schematic structure of a Solid Oxide Fuel Cell. Nickel-Yttria-Stabilised Zirconia (YSZ) cermet is used as anode material. This anode and the LaSrMnO₃ cathode are separated by a ceramic electrolyte that bases also on YSZ. The internal ion transport is executed by oxide ions O²⁻. At temperatures above 700°C the ionic conductivity of this kind of oxide ceramic membrane will work [2]. The processes at the anode and the cathode can be described by the following electro-chemical reaction equation.

Anode (oxidation):



Cathode (reduction):



Cell:



$$\Delta_r H = -237 \text{ kJ/mol}$$

Components	Materials
Electrolyte	Stabilised Zirconia ZrO ₂ : Y ₂ O ₃ Stabilised ZrO ₂ (YSZ)
	Sc ₂ O ₃ Stabilised ZrO ₂ (ScSZ)
	Doped Ceria CeO ₂ : Sm ₂ O ₃ Doped CeO ₂ (SDC)
Anode	Perovskite oxide: BaCeO ₃ , SrZrO ₃ , (La,Sr) (Ga,Mg)O ₃
	Ni/YSZ-cermet, Ru/YSZ-cermet, Ni/SDC-cermet
Cathode	LaMnO ₃ : (La,Sr) MnO ₃ , (La,Ca) MnO ₃
	LaCoO ₃ : (La,Sr) CoO ₃ , (La,Ca) CoO ₃
	SmCoO ₃ : (Sm,Sr) CoO ₃
Separator	LaCrO ₃ : (La,Sr) CrO ₃ , (La,Ca) CrO ₃
	Alloys : Ni/Cr, ferrites

Requirements on Fuel Cell Components

In SOFC used materials have to perform two fundamental functions. On the one hand they have to feature a high stability against predominating operating conditions (high temperatures, 700...1000°C). On the other hand the aspired chemical and physical properties (ionic conductivity, low resistance, thermal expansion, mechanical strength, low reactivity, anode gas barrier) are immense important. Therefore, especially the choice of suitable, functionally optimized materials gets a very high priority.

In Tab 3 the basic materials ordered regarding to components in the SOFC are given, which are usually used in fuel cell stacks by *Hosokawa Micron Corporation*, Japan. It's obvious to see that stabilized Zirconia and doped Ceria are used as electrolytes in general. Those feature sufficient ion conductivity, but a relative high electrical resistance. Thus, the thickness of the electrolyte has to be chosen as small as possible to reduce the total resistance. In the manufactured fuel cell stacks a layer thickness in the range of 10...15 µm could be prepared. Furthermore, the electrolyte has to prevent diffusion of anode gases to the cathode. Concerning to these elementary functions of the electrolyte all properties of the further components e.g. thermal expansion have to attune to this.

Requirements on the Preparation Process of Anode Material

The performance of fuel cell stacks is determined by the morphology and the composition of the used starting material (particle size, particle size distribution, particle form, homogeneous dispersion of the compo-

nents, structure of the composite) and the morphology of the cell structure (grain size, grain size distribution, bonding, pore structure).

The schematic structure of the anode material after sintering and the formed pore structure are shown in Fig. 2. Nickel functions as conductor for the emitted electrons. The transport of the oxide ions from the electrolyte to the anode is taken over by Yttria Stabilized Zirconia. Hydrogen is transported by diffusion processes through the porous system to the 3-phase interface (Ni-YSZ-H₂) and also the transport of the generated steam. This short description of the complex transport processes depicts the enormous meaning of the morphology of the anode material. Relevant for the final pore structure and the distribution of the components of the anode material is the processing that is foregone the sintering process. In this process step not only the components have to be mixed as homogeneous as possible. At the same time structures that are fixed by Mechano Chemical Bonding (MCB) can be generated on the level of composites in the submicron range which are basis for optimized performance of fuel cell stacks.

Since powders in the nano-scale that can be generated by e.g. plasma reactor (licenser: NanoProducts Corp., USA; distribution of generated nano particles in Asia) performed by Hokawa Micron Corporation, are used as raw materials, special technologies are required to mix nanopowders homogeneously and dispersively as well as to generate nanopowder based composites.

Fig. 3a shows the system Nobilta™ made by Hosokawa Micron Corporation. In this mixing system macro- and micro-mixing, surface modification, generation of composites by mechanical prefaced particle fusion (MechanoFusion, Mechano Chemical Bonding) and particle shape change (sphericalisation) can be performed.

Basic principle of the different kinds of processing is the movement of the

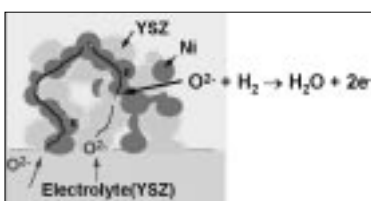


Fig. 2 Pore structure of the anode material

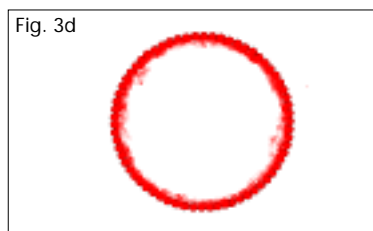
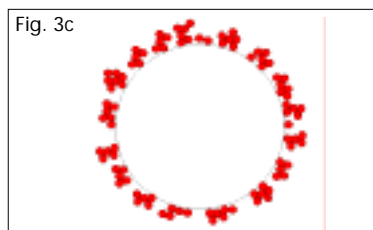
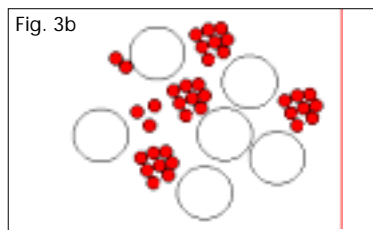
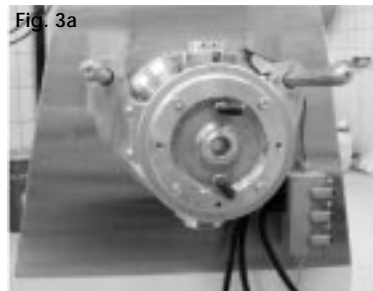


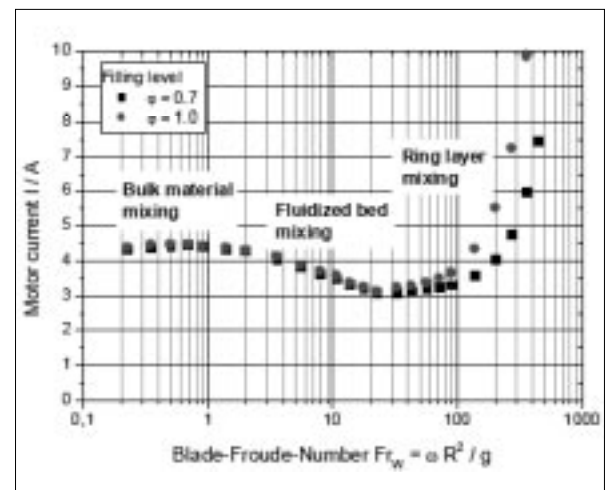
Fig. 3
a) System NOBILTA NOB-130
b) Macro-mixing
c) Precision or micro-mixing
d) Mechano Chemical Bonding

bulk material corresponding to the rotation speed. The three states of bulk material movement behaviour depending on the rotor speed are shown in Fig. 4. Fr_w represents the Blade-Froude-Number which is defined as the ratio of centrifugal acceleration $\omega^2 R$ to gravitation acceleration g .

Starting with low circumferential speed (Froude Number $Fr_w \leq 1-2$) a so called bulk material mixing is observed. This state is characterized by nearly constant current. Rising circumferential speed effects decreasing current. This result can be interpreted by the modeling that more and more particles leave the cohesive bulk good with increasing circumferential speed. The resistance performed by the bulk material also decreases because the bulk consists of fewer particles. The particles are fluidized increasingly. This state of particle movement is generally called mixing in a mechanically generated fluidized bed. Further rising of the circumferential speed causes centrifugation and compaction of the whole bulk material at the inner walls of the casing. A rotating ring layer is generated. In this state the motor current increases very strongly what is typical for high intensive mixing. Generally, it's obvious to see that the motor current depends on the filling level φ . In the state of the ring layer mixing the exponential rising current, that's characteristic for the higher resistance of the compressed bulk material, is caused by the thickness of the compressed bulk material.

The Nobilta is an intensive mixing system that is distinguished by high energy input into the bulk material. The energy input takes place by pressure, impact, shear stress and friction. Friction occurs between the

Fig. 4 Different states of bulk material movement in dependence to the rotor speed and filling level



bulk material and the inner drum wall (external friction) as well as within the ring layer (inner friction) that is compressed by the working centrifugal force. The bulk material is mixed distributively (macro-mixing) as well as dispersively (micro-mixing). In dependence of the energy input, the fineness of the involved components (nano-scale) and their melting points (mechanic, initialized sintering processes (MechanoFusion, Mechano Chemical Bonding) are possible, too. In this way particles of the different materials are fused with each other and composites of the participating components are generated. The rounding of particles is also feasible. The selective breakage of edges can be initiated by moderate energy input into the bulk material to avoid the total destruction of the single particle.

Advantages of SOFC Components Based on Nanoparticles

One advantage of fuel cells in comparison to conventional thermal engines is that they aren't limited to the Carnot Cycle. The real loss in the degree of efficiency can be attributed basically to inner resistances. Therefore, the activities in optimizing fuel cells concern especially on the reduction of Ohmic loss in the electrolyte, at the electrodes and in the separator as well as the polarization losses of the electrodes. The electrolyte can be optimized respectively to the oxide ion conductivity, the electrodes regarding to the electric conductivity and catalytic activity and the separator concerning to the electric conductivity, too. Especially processes that improve the cell performance by irreversible homogeneous distribution of the components (composite production) become more and more interesting. The performance of manufactured anode material by MechanoFusion and by the conventional method in

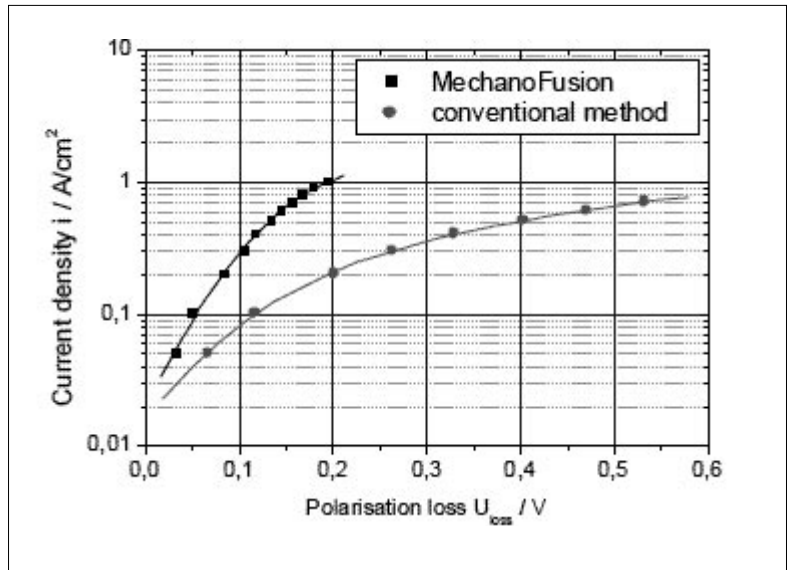


Fig. 5 Comparison of the performance of the anode material Ni-YSZ manufactured by MechanoFusion and by the conventional method according to [4]

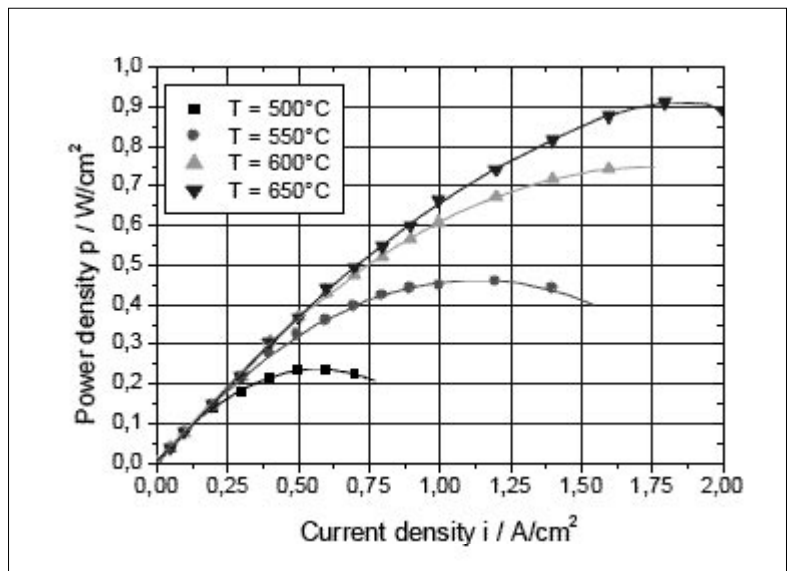


Fig. 6 Performance of the MCB performed anode material Ni-SDC according to [4] and [5]

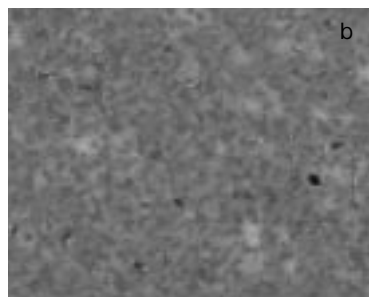
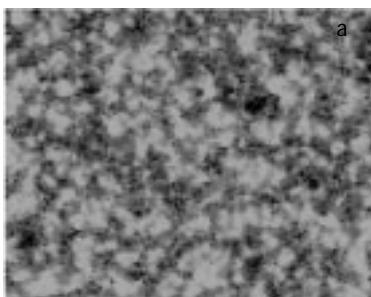
a ball mill with ethanol is compared in Fig. 5. It is obvious to see that the Ni-YSZ composite produced by MechanoFusion shows a polarisation loss of 0,2 V for a current density of 1 A/cm². In contrast the current densi-

ty for material produced according to the conventional method becomes clearly less than 1 A/cm² for a polarisation loss of 0,5 V. You can reason by this fact that the Ni-YSZ cermet produced by MechanoFusion shows very good electron conductivity via the nickel particles.

Fig. 6 shows the reachable power density p against the current density i for Ni-SDC anode material. The operating temperature changed in steps of 500°C, 550°C, 600°C and 650°C, is used as parameter in this diagram.

The diagram illustrates the clear influence of the operating temperature on the power density. Increas-

Fig. 7 Structure of the anode material made of Ni-SDC and EDX element mapping of nickel and oxygen [6]. a) Element mapping for nickel b) Element mapping for oxide ions.



ing operating temperature effects that the reachable power density raises and its maximum moves to higher current densities. It is also remarkable that the power density decreases with arising current density after passing the maximum. A comparison of the reached maximum power density of $p = 0,750 \text{ W/cm}^2$ to values from literature with $0,648 \text{ W/cm}^2$ [7] and $0,491$

W/cm^2 [8] indicates a very good performance of the anode material.

In Fig. 7a cross section of the Ni-SDC cermet anode is presented by EDX mapping pictures concerning to nickel (Fig. 7a) and oxygen respectively oxide ions (Fig. 7b). The bright areas symbolize the corresponding element. The distribution of the oxide ions represents also the distribution of the YSZ because the oxide ions are transported by the Yttria Stabilized Zirconia (YSZ). It can be derived by the pictures, too, that a high disperse distribution with large contact areas of both anode materials is available.

Conclusion

Fuel cells present an alternative to conventional fossil energy sources to provide sufficient energy for our economics in the near future. Solid Oxide Fuel Cells (SOFC) feature options like high degree of efficiency and relative high power density. Therefore, they play a major role under the available types of fuel cells.

First the structure and operating of the SOFCs discussed in this article. Then the demand on the fuel cell components were compiled and disputed. On this base the requirements on the preparation process are derived and the system Nobilta by Hosokawa Micron Corporation, is presented. In the system NOBILTA high effective processes like intensive or precision mixing, fusion of particles (sintering) and rounding can be realized. At last a comparison of the anode material performance is carried out. The anode material is performed by the system NOBILTA as well as the conventional method. It is obvious to see that the preparation by Nobilta gives an anode composite with clearly improved performance. Component composites in the submicron range can be generated by precision mixing and following particle fusion which are basis for the better performance.

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