GERMANY

Porous Zirconia Diaphragms for Electrochemical Sensors

Porous yttria-stabilized zirconia (Y-FSZ) diaphragms can serve as diffusion-restricting and protective components in electrochemical sensors, forming a controlled interface between the internal reference electrolyte and the sample. The electrolyte-filled pore network provides the ionic conduction pathway, while the diaphragm's low permeability and restricted mass transport reduce contamination by the sample and help limit loss of electrolyte. Thus, the diaphragm regulates the electrolyte exchange at the reference point, influencing the measurement behavior.

Fig. 1
Measuring tip of an electrochemical sensor with a porous zirconia diaphragm
Image source: Rauschert

Functional role of a porous diaphragm

From a design perspective, the diaphragm microstructure is a key functional parameter of the reference junction in industrial pH electrodes. Porosity, pore-size distribution, pore connectivity, tortuosity, and diaphragm thickness determine the junction resistance and the effective ionic transport through the electrolyte-filled pore network. Together, these parameters set the trade-off between dynamic response and long-term stability. Higher porosity generally lowers junction resistance and improves response time, but may reduce mechanical robustness, complicate reliable sealing, and increase the risk of electrolyte leakage or loss. Conversely, a less porous diaphragm improves mechanical robustness and electrolyte retention, but increases junction resistance. A ceramic diaphragm inserted into the glass shaft can be seen in Fig. 1.

In industrial pH electrodes, the diaphragm must provide ionic contact between the internal electrolyte and the sample while keeping mixing as low and as reproducible as possible. In practice, several diaphragm concepts are used. Platinum diaphragms use defined channels between twisted platinum wires, giving a more constant and higher outflow with lower resistance, but they are mechanically more sensitive and less suitable in strongly oxidizing/reducing media due to possible interference potentials. Ground-joint (gap) diaphragms use a fine glass slit, combining very low resistance with high outflow and easy cleaning. Polymer/gel reference systems can replace a classical diaphragm with a hole- or ring-gap interface, which is comparatively fouling-insensitive and low-maintenance, but the very small or absent outflow can increase diffusion-potential-related errors in strongly acidic/alkaline or low-ionic-strength samples [1].

Porous diaphragms can be used in many industrial applications. The ceramic skeleton provides mechanical robustness, corrosion resistance and chemical inertness, while the diffusion-restricting pore network limits electrolyte loss and reduces sample back-diffusion and contamination of the reference system. At the same time, parameters can be engineered systematically via porosity, pore-size distribution and connectivity (tortuosity), and diaphragm thickness to meet application-specific targets without sacrificing long-term stability. Another advantage is the thermal expansion of Y-FSZ membranes, which is compatible with glass and therefore does not cause any stress due to extreme temperature changes when inserted into the glass shaft.

Manufacturing and microstructure control

A porous diaphragm is defined by its pore network after firing. Most variability originates from feedstock preparation, debinding, and the sintering window [2]. Fig. 2 summarises a typical manufacturing flow with control points.

Tim Schumann
Rauschert Heinersdorf-Pressig GmbH,
96332 Pressig, Germany,

t.schumann@prg.rauschert.de
www.rauschert-tec.com/

Keywords
zirconia-based ceramics, ceramic diaphragms, porous ceramics, industrial manufacturing, functional ceramic components

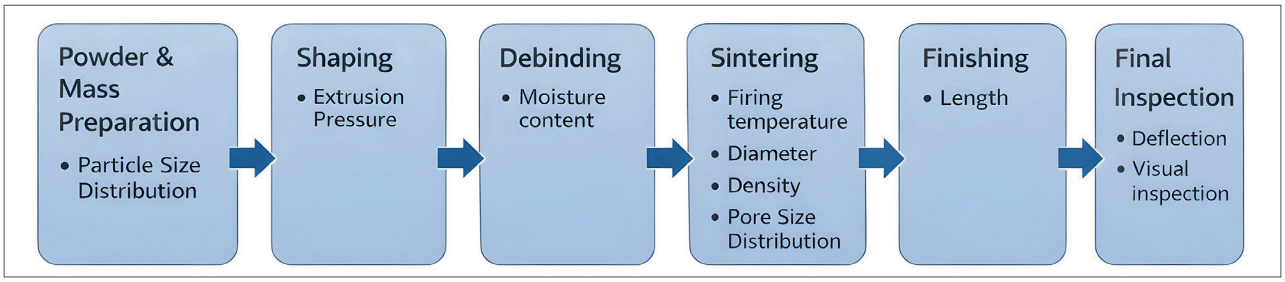

Fig. 2
Manufacturing steps for porous Y-FSZ zirconia diaphragms at Rauschert, including recommended quality control points *Image source: Rauschert*

Tab. 1
Representative specification window of porous Y-FSZ zirconia diaphragms manufactured at Rauschert

Parameter	Specification
Colour	White
Shaping Process	Extrusion
Main Element Concentration	>99,7 % (including Y_2O_3)
Density	4,0 ± 0,25 g/cm^3
Open porosity	25–35 %
Dominant macropore diameter	200–800 nm
Water Absorption	7,0–10,0 %
Length	≤100 mm
Diameter	0,65–1,50 mm
Coefficient of thermal expansion (CTE) 30-1000°C	11,0 × 10^{-6} K^{-1}
Chemical Resistance	pH 0–14

The final pore size distribution is commonly engineered by raw material particle size distribution (PSD) and firing temperature, influencing porosity and sintering kinetics. If necessary, pore forming additives can be used to adjust the final pore structure but this is rather atypical.
Depending on component geometry (disc, cap, tube), shaping routes include pressing or extrusion. Regardless of the route, consistent green density (density of unfired ceramic) is essential to avoid local permeability gradients and warpage after firing.
Debinding is one of the highest-risk steps, particularly for thin and porous components, due to the potential for internal pressure buildup. Rapid decomposition of organics can create internal pressure and lead to radial cracking (Fig. 3) [3]. Heating ramps with intermediate holds are designed to keep gas evolution below the mechanical fracture stress of the green body (unfired ceramic component). Intermediate holds during heating allow gradual binder removal, preventing rapid gas evolution that could exceed the fracture strength of the green body.
An optimised debinding process, adjusted to the decomposition profile of used binders, reduces the risk of cracks in the green body (Fig. 4), though other factors such as material inhomogeneity or external stresses may still contribute to defects. The sintering profile must form a mechanically stable zirconia skeleton while keeping the pore network open and connected. Excessive temperature or dwell time can cause pore closing, decreasing permeability through the pore network, which in turn increases diffusion resistance and batch-to-batch variation.
At Rauschert, porous Y-FSZ zirconia diaphragms are manufactured by extrusion in serial production. The produced diaphragms can reach an open porosity of 25–35 % and modal pore diameter between 200 and 800 nm. Typical component dimen-

Fig. 3
Y-FSZ rod with cracks due to an incorrect debinding process
Image source: Rauschert

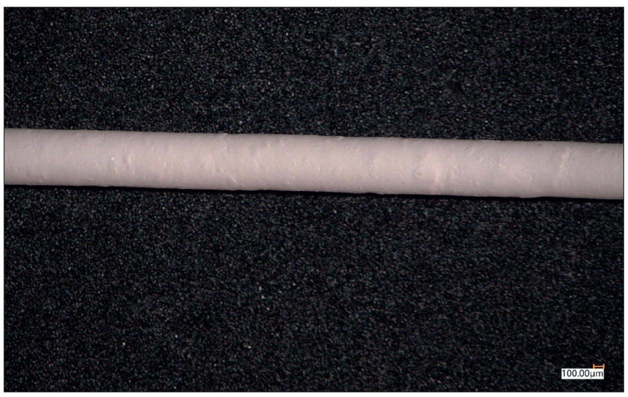

Fig. 4
Y-FSZ rod without cracks due to an optimised debinding process
Image source: Rauschert

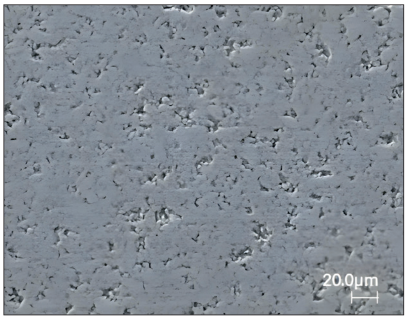

Fig. 5
Microstructure of a porous Y-FSZ diaphragm
Image source: Rauschert

sions cover an outer diameter range of 0,65–1,50 mm with lengths up to 100 mm. A density range of 3,75–4,25 g/cm³ was chosen based on empirical testing which showed that lower densities compromised handling strength, while higher densities reduced diffusion rates below sensor requirements. Tab. 1 shows the specification window for Y-FSZ diaphragms from Rauschert.

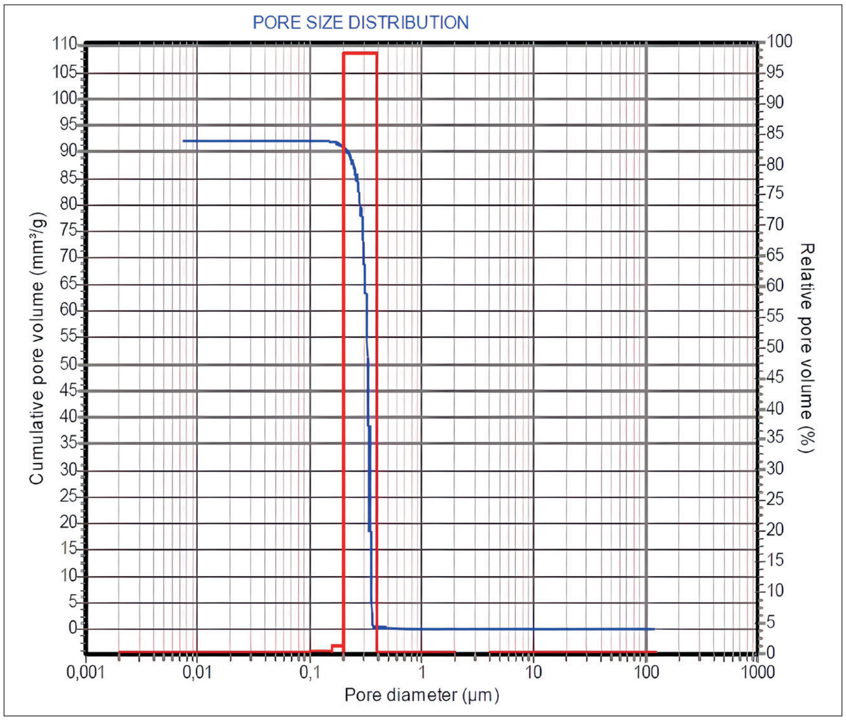

Fig. 6
Pore size distribution curve using mercury intrusion porosimetry for a Y-FSZ diaphragm produced by Rauschert, Image source: Rauschert

Properties that matter for sensor performance

In ceramic diaphragms the transport properties are the primary factors. They provide an ionic pathway and regulate electrolyte outflow. Open porosity, pore size distribution, and connectivity determine the ionic pathway as well as the electrolyte outflow and therefore the diffusion resistance.

Mechanical integrity (fracture resistance during handling and assembly) needs to be weighed against permeability. A diaphragm that is too porous will be robust but may slow response and increase susceptibility to clogging, as smaller pores are more easily blocked by particulates or contaminants. A diaphragm that is too porous can meet response-time targets, but it may be fragile and difficult to seal and increase the risk of inner buffer leakage. This trade-off should be addressed when setting Critical to Quality (CTQ) limits for porosity and pore size.

Typical failure modes:

Common field and manufacturing issues can often be traced back to a small set of root causes [5]:

- sensor-to-sensor scatter due to thickness or permeability variation
- slow drift caused by microstructure evolution or contamination
- leak paths driven by edge damage or unstable sealing interfaces.

Monitoring these root causes can reduce avoidable variation.

Characterization and quality control

In production, incoming powder PSD is commonly verified by laser diffraction. While Archimedes-based methods (density measurement by liquid displacement) provide porosity and bulk density, surface micrographs (Fig. 5) offer rapid assessment of local pore connectivity [4], and mercury intrusion porosimetry (MIP) delivers detailed pore size distribution. However, MIP may be affected by ink-bottle effects (narrow pre-necks that restrict mercury intrusion, underestimating pore size) and is destructive, so combining these methods ensures a more comprehensive quality control. MIP evaluation is standardised in ISO 15901-1 and provides a comparative pore size distribution for quality control (Fig. 6) [6]. Dimensional CTQs such as outer diameter are typically measured by caliper or micrometer, depending on tolerance. Deflection should also be checked because excessive deflection can increase leakage risk.

References

[1] Xylem Analytics Germany Sales GmbH & Co. KG: pH Handbook – Helpful guide for practical application and use. Weilheim 2024

[2] Rahaman, M.N.: Ceramic processing and sintering. Boca Raton 2003

[3] German, R.M.: Sintering theory and practice. New York 1996

[4] ASTM C373-18: Standard Test Methods for Determination of Water Absorption and Associated Properties by Vacuum Method for Pressed Ceramic Tiles and Glass Tiles and Boil Method for Extruded Ceramic Tiles and Non-tile Fired Ceramic Whiteware Products. 2018

[5] Chiang, Y.M.; Birnie, D.P.; Kingery, W.D.: Physical ceramics: principles for ceramic science and engineering. New York 1997

[6] DIN ISO 15901-1: Evaluation of pore size distribution and porosity of solid materials by mercury porosimetry and gas adsorption – Part 1: Mercury porosimetry. 2016