Innovative ceramic diaphragms – flexibly adjustable for every application

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Porous ceramic diaphragms, as inconspicuous as they may look and as difficult to detect as they often are, are elementary components of many sensors in laboratories and in the process industry. As current keys, they close the circuit in pH combination electrodes and sensors for determining the redox potential.

By setting different porosity levels and pore size distributions, the diaphragms can be tailored to the requirements of the respective application. If these are melted into glass, the coefficient of thermal expansion is also adapted to that of the glass. Ceramic diaphragms compete with ground-joint diaphragms, porous ceramic sponges and porous plastics.

Production of porous ceramics

For the production of porous ceramics, different process routes can be used depending on the requirement profile and material:

- Use of placeholders
- Use of default grit sizes
- Adapted sintering process
- Moulding of carrier structures
- Conversion procedure

For the manufacture of porous diaphragms, only the first three processes mentioned above can be considered individually or in combination. Further details can be found in the literature [Wer14].

Requirements for porous ceramic diaphragms

Since in many cases, the porous diaphragms have to be fused into glass, the coefficient of thermal expansion (CTE) of the materials must match that of the glass used; typical values are in the range of 10-11 x 10^{-6} K^{-1}, and often an attempt is made to select a slightly higher CTE of the glass than that of the ceramic, so that the diaphragm is slightly subjected to compressive stress, thus reliably ruling out the possibility of leakage at the ceramic-glass interface. On the other hand, the difference in the CTE must not be too large, otherwise cracks in the glass may occur.

Furthermore, no substances may outgas from the ceramic when the diaphragm is melted down that would lead to bubbles at the ceramic-glass interface; these could also cause uncontrollable leaks. Due to the preceding sinter firing > 1000 °C all possible interfering substances are already burnt out.

In addition, the diaphragms must establish a reliable electrical contact between the reference electrode and the medium to be measured – for this purpose, the largest possible pores and the highest possible porosity values are desirable. On the other hand, the electrolyte of the reference electrode should neither leak out too quickly nor should components of the medium to be analysed diffuse through the diaphragm into the reference electrode, thereby "poisoning" it. This requirement is best met by small pore sizes and the lowest possible porosity values. This contradiction has to be solved, hence products are tailor-made for customer requirements.

Last but not least, the diaphragms must have sufficient mechanical and chemical stability. Materials from the group of zirconium oxides are used where there are high demands on chemical resistance. If no aggressive environmental conditions prevail, steatite-based materials are certainly an economical alternative (see below).

Materials for porous ceramic diaphragms

At present , porous materials based on steatite (Rapor P0.3) or fully stabilized zirconium oxide are typically used.

If the diaphragm is not fused into glass but is inserted into the sensor in some other way, porous aluminum oxide can also be used, which is so low in CTE that it cannot be fused into the glasses normally used.

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Steatite-based materials are used when the demands on chemical resistance are not very high. These materials have the advantage that their coefficient of thermal expansion (CTE) can be adjusted within certain limits. However, it should be noted at this point that the adjustment of the CTE also has an influence on the open porosity and pore size distribution. The CTE can be specifically adjusted in ranges between 9.5 x 10^{-6} K^{-1} and 11.5 x 10^{-6} K^{-1}. The open porosity then varies between 24% and 29% by weight. Experience has shown that these fluctuations are perfectly tolerable in the most common applications (see Figure 1).

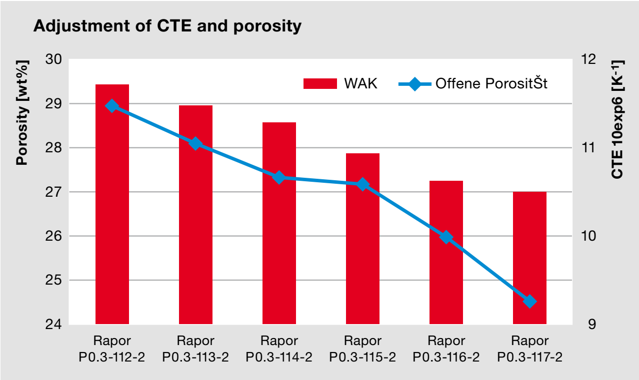

Figure 1: Variation of the coefficient of thermal expansion for Rapor P0.3

Diaphragms based on fully stabilized zirconium oxide materials can be varied in pore pattern within even wider limits than steatite-based materials. Total porosities between 25 wt% and 45 wt% can be set, the pore size distributions can be adjusted to be narrow or wide and can cover different pore size ranges (see Figure 2).

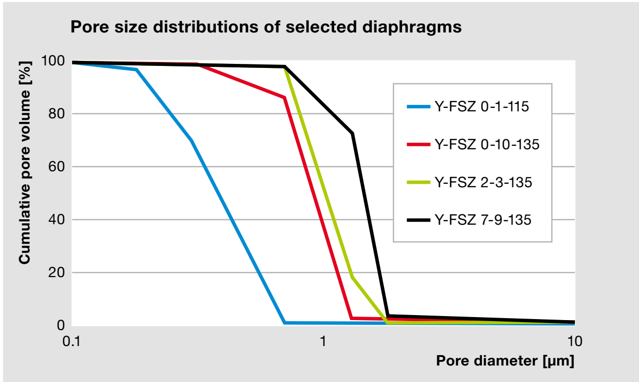

Figure 2: Pore size distributions of selected diaphragms based on Zirconia oxide

Due to their great versatility, a suitable diaphragm material has been found for every application so far, meeting all customer requirements.

Summary

Although small and inconspicuous, porous diaphragms contain a lot of potential and know-how that ensures safe and reproducible operation of many sensors for pH and redox potential. Rauschert has a wide selection of materials at its disposal as well as many possibilities to adapt their properties to customer requirements. In this way (almost) all customer projects can be implemented in series.

Werr, U. (September 2014).
Porous Ceramics Manufacture-Properties-Applications.

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