JOURNAL OF APPLIED ELECTROCHEMISTRY **19** (1989) 605–610

Ceramic diaphragms for advanced alkaline water electrolysis*

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Received August 1988; revised 7 November 1988

Chemically stable and physically strong, but relatively expensive diaphragms with low electrical surface-specific resistance have been developed for alkaline water electrolysis intended to work at temperatures around and above 120° C at increased current densities and yet reduced cell voltage. These diaphragms are made of a porous cermet produced from ceramic particles (group 2A titanates) and NiO by reductive sintering. Two versions of such cermets have been investigated: a nickel net-supported diaphragm and a diaphragm which is supported by two porous metal electrodes.

1. Introduction

During the last decade national and international R and D programmes in Canada, Japan, Brasil and the European Communities [1] have been in progress in order to improve water electrolysis technologies with the aim of minimizing costs for electrolytically generated hydrogen by reducing, particularly, the cell voltage. Apart from a sizeable reduction of overvoltage of the H_2 cathode and the O_2 anode it is, first of all, most important to reduce the internal electrical resistance of the cell in order to obtain low cell voltages at high current densities. Cells of the older, established, alkaline electrolysis technology have specific cell resistances (k values) of the order of $10^{-4}\,\Omega\,m^2$ which permit current densities of not much more than $3\,kA\,m^{-2}$. An advanced electrolyzer should exhibit k values not exceeding $2 \times 10^{-5}\,\Omega\,m^2$.

This means that one has to dispense completely with asbetos as a diaphragm material. Such asbestos diaphragms have to be several mm thick, are not stable at temperatures above 100° C and, furthermore, are not attractive because of the carcinogeneity of the material.

The general experience in the field of diaphragm development shows that mainly 'composite' materials may meet the very stringent demands (porosity, mechanical strength, chemical stability, hydrophilicity) necessary for any material to meet the requirements of a diaphragm/membrane in large-scale alkaline water electrolyzers under conditions of enhanced temperature.

Apart from polymer-reinforced asbestos diaphragms, which are expected to offer only a limited solution for the diaphragm problem for a limited time, spinnable fibers and castable hydrophilized organic and inorganic polymers, for instance of polyphenyl sulfide for cloths or polyphenyl sulfon for film cast diaphragms [2–4], and nickel net-supported oxide ceramic diaphragms [5, 6] have been developed which meet the outlined requirements to a large extent.

2. Metal net-supported diaphragms

In 1983 the authors of this article applied for a patent [7] protecting the idea of metal net-supported porous oxide ceramic diaphragms for electrolyzers and filters (see Fig. 1a). The supporting metal net has the purpose of lending flexibility and tensile strength to the usually brittle oxide ceramic material.

2.1. *Materials for the metal net*

Only few metals are corrosion resistant in caustic potash at enhanced temperature in oxygen atmospheres. Titanium, zirconium and low carbon/low sulphur, nickel are three of the most corrosion-resistant materials due to passivation. These three metals were subjected to accelerated corrosion tests in 50 wt % KOH at 220° C. Titanium and zirconium were dissolved completely after approximately 100 h and only bulk low-C, low-S nickel was stable against caustic corrosion even in the presence of oxygen. In the presence of hydrogen, i.e. at the cathode, nickel is immune. Therefore nickel seems to be the only reasonable choice for advanced alkaline electrolysis.

2.2. *Oxide ceramics for supported diaphragms*

In simultaneous contact with caustic potash and oxygen at the anode and caustic potash and hydrogen at the cathode only a limited number of inorganic oxides are expected to be stable: zirconia, some zirconates and titanates (especially K-hexatitanate and alkaline-earth titanates) are possible candidate materials. Stability in hydrogen and oxygen evolution conditions will be established for any oxide of stoichiometry Me_nO_m if its free energy of formation

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* Paper presented at the meeting on Materials Problems and Material Sciences in Electrochemical Engineering Practice organised by the Working Party on Electrochemical Engineering of the European Federation of Chemical Engineers held at Maastricht, The Netherlands, September 17th and 18th 1987.

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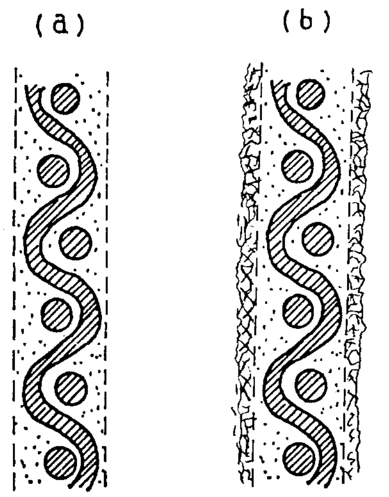

Fig. 1. (a) Scheme of a metal net-supported cermet diaphragm. (b) Scheme of a sandwiched electrode–diaphragm–electrode unit.

per atom of oxygen is more negative than the free energy of formation of water.

$$\frac{1}{m}\,\Delta G^0(\mathrm{Me}_n\mathrm{O}_m) < \Delta G^0(\mathrm{H_2O}) \qquad (1)$$

Correspondingly, the oxide of any metal which is more noble than hydrogen will not be an appropriate material. Further, the solubility of the oxide in hot caustic potash should be as low as possible and should not be greater than several $10^{-5}\,\mathrm{mol\,l^{-1}}$. Apart from these thermodynamic conditions the oxides intended to be processed in a sintering procedure must fulfil an additional condition: their melting point must be so low that they are sintered easily at temperatures below the melting point of the metal support.

Since nickel is the only acceptable choice for the supporting metallic screen and its melting point is 1453° C and since the absolute sinter temperature of any substance is established to be roughly two-thirds of its absolute melting point [8], the chosen oxides must have a melting point below 2300° C. According to these demands, only alkaline-earth zirconates and, in particular, alkaline-earth titanates which exhibit lower melting points than the zirconates, are suitable and are predicted to be processed and sintered more easily (Table 1). Potassium hexatitanate cannot be used because it shows complicated phase transformations on heating and cooling and therefore does not form a mechanically strongly coherent sintered structure.

Table 1. Melting point (T_m) *and sintering temperature* (T_s) *for different oxide ceramics [14]*

Material	T_m (° C)	T_s (° C)
Ni	1455	870
$NiTiO_3$	1900	1150
ZrO_2	2715	1720
TiO_2	1640	1000
$BaZrO_3$	2500	1600
$BaTiO_3$	1975	1230
$CaZrO_3$	2550	1600
$CaTiO_3$	1630	1000

At KfA Jülich [9] a nickel net-supported nickel oxide diaphragm was developed, which is prepared from carbonyl-nickel rolled into supporting nickel nets. Oxidation of this carbonyl nickel by air at 1000° C leads to formation of firmly adhering and electrically insulating nickel oxide. Although, due to very slow reaction between the NiO matrix and hydrogen, the nickel oxide is said to be reliably stable over the lifetime of the electrolyzer, its long-term stability cannot be really guaranteed because it does not meet the requirement of thermodynamic stability given by Equation 1.

This was the reason for the authors to develop diaphragms, based on alkaline-earth titanates as ceramic material, since these titanates possess the necessary thermodynamic stability and low solubility and can be processed at sintering temperatures below 1300° C.

3. Structural properties postulated for diaphragms of water electrolyzers

The purpose of the diaphragm in an electrolysis cell which produces gases at either electrodes in a zero gap arrangement is threefold: (1) the diaphragm has to allow a high ionic flux at low electrical resistance and at the same time it has to prevent unhindered intermixing of catholyte and anolyte, in order to obtain high gas purities; (2) the diaphragm, therefore, must be thick and sufficiently dense to form an efficient diffusion and convection barrier for the dissolved gases to prevent contamination of the evolved gases by molecular diffusion and convective mixing; (3) most important is that clogging of the diaphragm pores by gas bubbles, which may either intrude into the pore mouths or which may precipitate within the pores from supersaturated electrolyte solutions, must be excluded completely; otherwise the electrical resistance of the diaphragm increases in an uncontrolled manner with time.

Dealing with points (1) and (2) one has to take into account that anolyte and catholyte are saturated with oxygen and hydrogen, respectively. Therefore, the diaphragm must offer a sufficiently high hydrodynamic resistance to retard intermixing of oxygen-saturated anolyte with hydrogen-saturated catholyte and vice versa, caused by occasional pressure differences between cathode and anode chambers, and must prevent the breakthrough of the gaseous products.

If a contamination of less than 1% of the gases is allowed, then Equations 2a and 2b determine the permissible relative magnitude of hydrogen and oxygen cross-flow flux densities ($\dot{n}$ gas) and production densities:

$$\dot{n}(\mathrm{O_2})\ \text{(cross-flow)} < \dot{n}(\mathrm{H_2}) \times 10^{-2}\ \text{(production)} \qquad (2a)$$

$$\dot{n}(\mathrm{H_2})\ \text{(cross-flow)} < \dot{n}(\mathrm{O_2}) \times 10^{-2}\ \text{(production)} \qquad (2b)$$

Cross-flow fluxes of the gases are determined by volumetric flow rate of the electrolyte and the saturation concentration of the respective gas (Equation 3a). The volumetric flux density $\dot{v}$ ($\mathrm{cm^3\,cm^{-2}\,s^{-1}}$) of the electrolyte across the membrane depends on the applied pressure difference, Δp, the viscosity, η, of the electrolyte and the surface-specific hydrodynamic permeability K:

$$\dot{n}(\mathrm{gas})_{(\text{cross-flow})} = \dot{v}c_s(\mathrm{gas}) \quad (3a)$$

$$\dot{v}c_s(\mathrm{O_2}) = K\Delta p c_s(\mathrm{O_2})\eta^{-1} \leqslant 0.50 \times 10^{-2}\,(j/F) \quad (3b)$$

$$\dot{v}c_s(\mathrm{H_2}) = K\Delta p c_s(\mathrm{H_2})\eta^{-1} \leqslant 0.25 \times 10^{-2}\,(j/F) \quad (3c)$$

The saturation concentration $c_s(\mathrm{H_2})$ of hydrogen in concentrated caustic potash in the temperature range of special interest for alkaline water electrolysis does not exceed (according to Vogel *et al.* [10]) some $10^{-3}\,\mathrm{mol\,l^{-1}}$ under 30–60 bar hydrogen pressure. For oxygen, these data are less well known but can be estimated [11] to be comparable with those of hydrogen [12].

For a given electrolyte with given viscosity, η (e.g. approx. 1 centipoise for 30 wt% KOH at 90° C [10]) the quantity $K\eta^{-1}$ can be substituted by K_{eff}, the effective hydrodynamic permittivity ($\mathrm{cm^3\,cm^{-2}\,bar^{-1}\,s^{-1}}$).

Accounting for the relation $\dot{n}(\mathrm{H_2}) = 2\dot{n}(\mathrm{O_2})$ in the electrolyzer and for the fact that, because of this ratio, a small overpressure of the cathode over the anode chamber always exists, one can relate electrolyte mixing only to Equation 3c. Considering a driving pressure difference of some 10^{-3} bar (which are certainly the highest possible hydrostatic pressure fluctuations in the electrolyzer) one can calculate (using Equation 3c) a maximum effective hydrodynamic permeability of the diaphragm of

$$K < 1.6\,\mathrm{cm\,bar^{-1}\,s^{-1}} \quad (4)$$

Although, according to this estimation, a relatively high surface-specific hydrodynamic resistance of the diaphragm is necessary, it nevertheless must offer only a low electrical surface-specific resistance if immersed in the electrolyte. The surface-specific electrical resistance should not exceed $0.2\,\Omega\,\mathrm{cm^2}$ ($2 \times 10^{-5}\,\Omega\,\mathrm{m^2}$) and is preferably around $0.1\,\Omega\,\mathrm{cm^2}$ in order to avoid too high ohmic voltage drops across the diaphragm.

Referring to point (3), diaphragm clogging by bubble formation in fully wetted small cavities, pores, etc. of radius r may only be observed if a certain degree of supersaturation ($p - p_{\mathrm{sat}}$) is established:

$$p - p_{\mathrm{sat}} > \frac{2\sigma}{r} \quad (5)$$

where σ is the surface tension at the gas–electrolyte interface.

The supersaturation of the gas in the electrolyte which diffuses or drifts into the diaphragm pores will be significantly reduced. Therefore, at a working pressure of 30–60 bar, supersaturation pressures of hydrogen and oxygen of no more than a few tenths of a bar will exist at the diaphragm surface. According to Equation 5 for $\sigma = 60\,\mathrm{J\,cm^{-2}}$, pore diameters smaller than $5\,\mu\mathrm{m}$ will reliably prevent gas clogging of the diaphragm.

This discussion shows that, since the surface-related electrical resistance should be as low as possible, the diaphragm should be thin and it should be highly porous but with a small pore size. One should therefore aim at pore diameters below $5\,\mu\mathrm{m}$ and at porosities approaching 50%.

4. Diaphragm preparation

4.1. *Ceramic granulometry*

Production of porous matrices allows predetermination of the void and mean pore diameters of the pores by choosing the appropriate granulometry of the particulate material which is used to produce the green, unsintered specimens provided excessive shrinking is avoided during sintering.

In order to arrive at a predeterminable granulometry the ceramic raw material ($\mathrm{CaTiO_3}$, $\mathrm{BaTiO_3}$ and, for cermets, additionally NiO) has initially to be sintered to a dense body. Successive grinding and sieving allows adjustment of any desired grain size

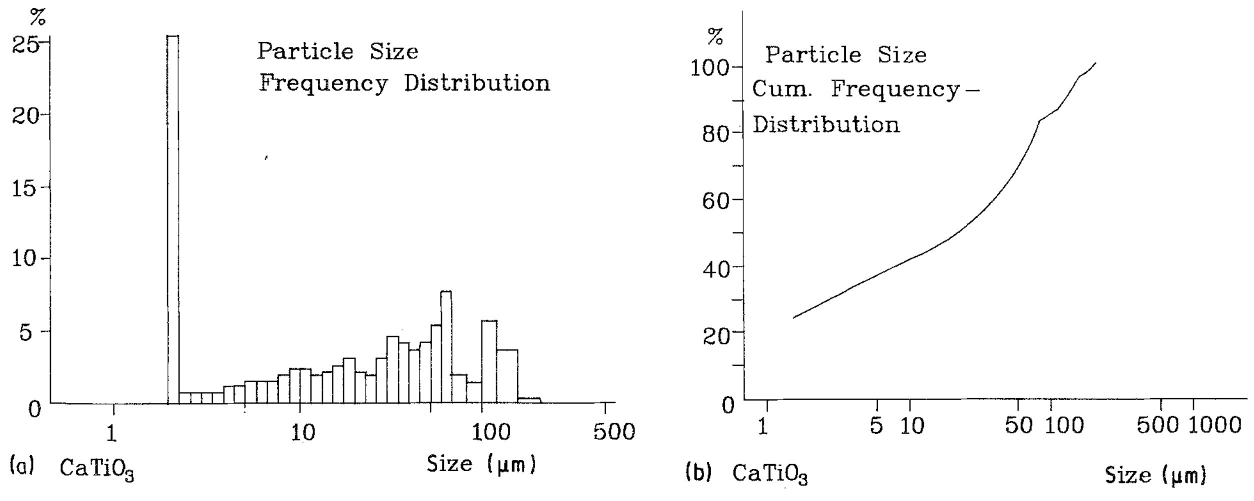

Fig. 2. (a) Differential granulometry of presintered and milled $\mathrm{CaTiO_3}$. (b) Cumulative granulogram of presintered and milled $\mathrm{CaTiO_3}$.

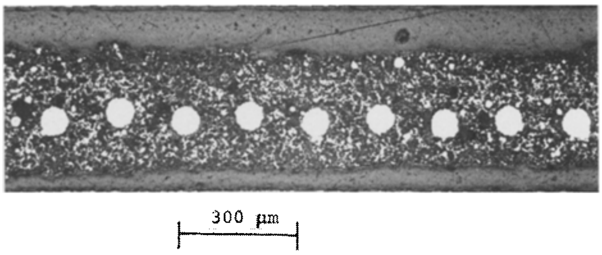

Fig. 3. Cross section of a cermet diaphragm.

distribution in the ceramic powder by mixing of different sieve fractions.

Due to presintering any single grain of this powder is a dense particle so that undesired excessive shrinking during the sintering procedure can be safely avoided. Figure 2a depicts the differential and Fig. 2b the cumulative granulogram of a presintered, milled $CaTiO_3$ powder, passed through a 50-µm sieve. The powder possesses 50% (numerical) particles of only 2 µm size, 30% of 50 µm and 10% of aggregates which measure between 100 and 150 µm. This means that more than 95 vol % of the ceramic powder possesses an average size of 50 µm. Assuming the particles are, on average, of spherical shape and are arranged in close packing, the mean diameter of the pores of this packing would be expected to be 20 µm. This is approximately the maximal pore size not regarding that part of the particles for which it is smaller than 50 µm and partially fills the pores, narrowing the pores and preventing additionally pore clogging by bubble precipitation. Powders for cermets, which are described below, are prepared from $CaTiO_3(BaTiO_3)$/NiO mixtures according to the same procedure and with identical granulometry as outlined for pure $CaTiO_3/BaTiO_3$ powders.

4.2. *Printing and sintering of nickel net-backed diaphragms*

A printing slurry is made up of the ceramic material, of water and of polyvinyl alcohol as organic binder and is sieve printed in several layers on either side of nickel nets of 0.3-mm wire diameter and 0.52-mm mesh width. These 'green' diaphragms were subjected to low-temperature (400° C) treatment in order to decompose the organic binder and to high-temperature (1200° C) sintering in a reducing atmosphere. The diaphragms obtained were, however, too brittle and lost their ceramic cover on bending or stretching. Admixture of nickel oxide from 5 to 30% allows preparation of diaphragms covered by a porous $CaTiO_3(BaTiO_3)$/nickel cermet, which adheres well to the supporting nickel net. The cermet is still sufficiently hard and has a porosity and pore size distribution which is comparable to that of the pure oxide ceramic material. Figure 3 shows a cut through one of these cermet diaphragms and Table 2 collects the relevant physical data of a number of samples of these diaphragms which were prepared in a size of 70 × 70 cm^2.

Table 2. Typical data of cermet $BaTiO_3$ diaphragms of 0.4 mm thickness

No.	*Gas breakthrough pressure* P (bar)	*Max. pore diameter* d (µm)	*Mean pore diameter* d (µm)	*Porosity* (%)
(1)	0.28	50	9	48
(2)	0.30	35	7	45
(3)	0.32	30	6	41
	R (Ω cm^2) in 30 wt % KOH, 25° C;		$K_{hydrd.}$ (cm centipoise bar^{-1} s^{-1})	
(1)	0.18		3	
(2)	0.20		3.2	
(3)	0.15		2.9	

Figures 4a and b give an impression of the pore size (volume distribution measured by Hg porosimetry). Interestingly enough, most of the mesopores have a diameter of approximately 3 µm. As demonstrated in Table 2, the nickel net-backed porous cermet diaphragms meet the conditions which are postulated for a diaphragm for advanced water electrolysis.

5. Long-term performance tests of nickel net-backed diaphragms

Nickel net-supported porous Ni/$BaTiO_3$ cermet

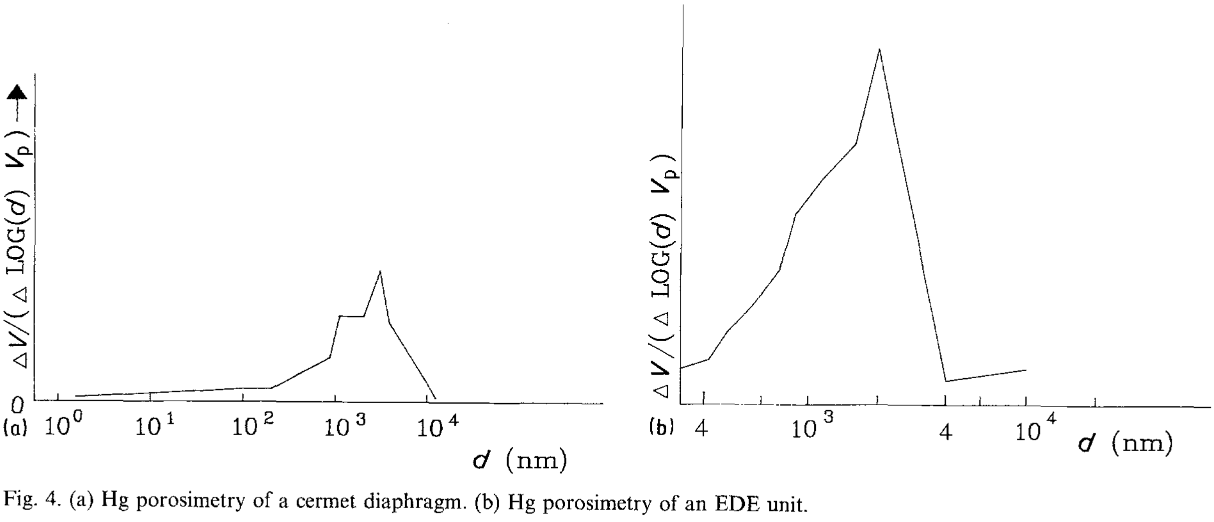

Fig. 4. (a) Hg porosimetry of a cermet diaphragm. (b) Hg porosimetry of an EDE unit.

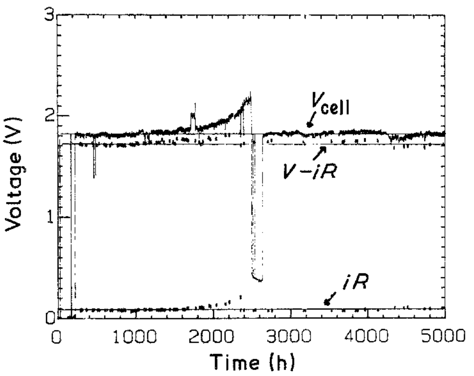

Fig. 5. *IR* drop across a cermet diaphragm during 5000 h of electrolysis operation measured at SODETEG, France (120° C, $1\,A\,cm^{-2}$).

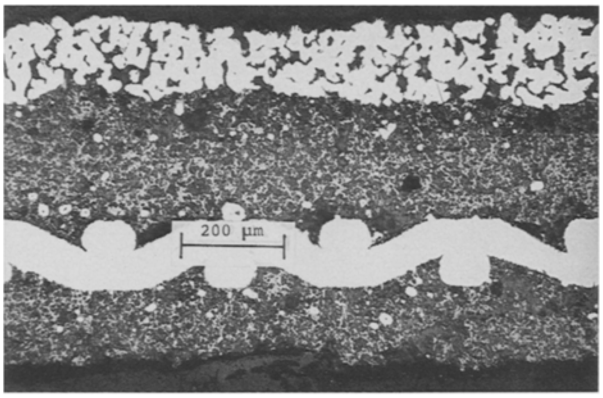

Fig. 6. Cross section of a half-sided EDE unit with a Ni net support.

diaphragms of up to $20 \times 50\,cm^2$ size were subjected to long-term performance tests in the laboratories of SODETEG (Buc/Paris) [6] and of Gaz de France [7]. Figure 5 shows the measurement of *IR* loss across such diaphragms over a period of more than 5000 h (SODETEG) [6]. The testing generally covered more than 10 000 h at 100° C, more than 5000 h at 120° C and 2500 h at 160° C. In all cases chemical and mechanical stability and gas separation properties of the diaphragms were as good as predicted, and no deterioration of the diaphragms could be detected.

6. Sintered cathode/anode sandwich structures and self-supporting electrode/diaphragm/electrode (EDE) units

The very nature of the diaphragm as a material prepared by sintering, particularly if modified by the application of cermets, suggests the preparation of electrode/diaphragm units by an analogous sintering technique. Using cermets not only increases the adherence of the porous matrix but also allows binding of the porous metal electrodes to the diaphragm surface. For this purpose prior to the sintering, and following the preparation of the 'green' diaphragm in a further printing process, metallic nickel powder or nickel oxide is painted or printed on either side of the diaphragm. Reductive sintering then results in the formation of the 'sandwich' (Fig. 1b) which may be readily incorporated into the electrolyzer cell. Whereas the electrical contact to the porous cathode may be established easily by mechanical pressure, the contact between the porous anode and the bipolar plate of the electrolyzer demands a welding technique in order to reduce the overall ohmic losses in current flow to less than 20 mV. Figure 6, which is a cut through a unit prepared by cosintering a Ni net-supported diaphragm with porous nickel layers, demonstrates the morphology of such electrode–diaphragm units.

Since the separate investigation of the porous nickel electrodes demonstrated that the tensile strength of each electrode comes close to that of the internal nickel net, it is possible to dispense with this net completely and to construct self-supporting electrode/diaphragm/electrode (EDE) units. For this purpose the 'green' cermet diaphragm is prepared by film casting and the 'green' electrodes are sieve printed as uniform layers reinforced by a perforated plate pattern which serves as current distributor, allowing simultaneously for spot welding, or laser welding, the anode to a current collecting bipolar (or monopolar) plate.

Figure 8 shows a cut through an EDE unit, demonstrating the relatively coarse electrode structure, which allows an easy release of evolved gases. This is achieved with a metal load of approximately $40\text{–}50\,mg\,cm^{-2}$ and with a mean grain size of $15\,\mu m$ and offers an effective specific electrode area which is approximately 20 times larger than the geometric one.

Figures 7a and b show the pore size/volume distribution which demonstrates that the pores are somewhat smaller with the EDE cermet than for the nickel

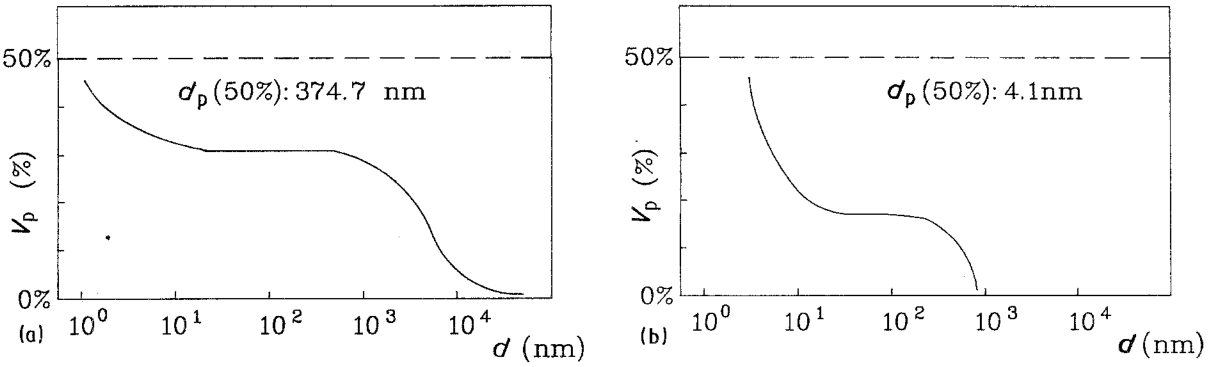

Fig. 7. (a) Pore size and volume distribution of a cermet diaphragm. (b) Pore size and volume distribution of an EDE unit.

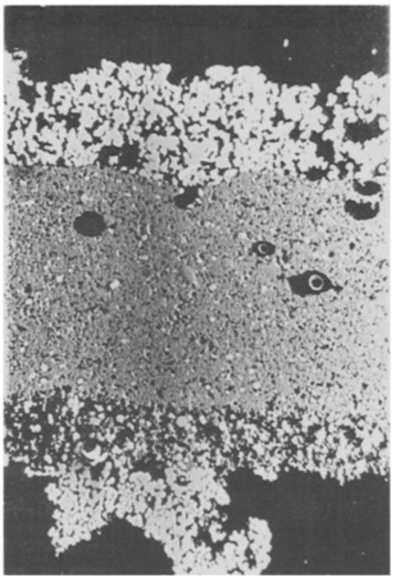

Fig. 8. Cross section of an EDE unit without a Ni net.

net-supported cermet diaphragm. The total porosity of the cermet alone amounts to 40%.

The surface-specific electrical resistance of the EDE unit, which possesses a total thickness of 700 μm, including both electrodes, amounts to 0.4 $\Omega \, cm^2$ if immersed in 30 wt % KOH at 30° C. The resistance of the intermediate cermet alone does not exceed 0.2 $\Omega \, cm^2$ at 90° C, as measured in an actively electrolyzing unit using the current interrupter technique.

7. Cost estimation

Cost estimation of the nickel net-based oxide ceramic structure predicts costs of US \$80–100 m^{-2} of the nickel net-supported $CaTiO_3$ diaphragm [15]. Production costs of the last development, the self-supporting EDE units, should not be higher, possibly even lower, because the Ni net is no longer necessary. This amounts to an investment contribution of US \$4 $\times 10^{-3}$ W^{-1} from the diagraphm alone or from the EDE unit.

Such costs are reasonably low compared to a total cost of US \$0.5 W^{-1} for large conventional electrolyzers. Although this type of diaphragm is obviously the most expensive material, as developed in the framework of the European R & D program [1] on advanced water electrolysis, it may well be that, due to its further development potential and chemical and mechanical stability, it will be used in high-current density, medium-temperature electrolyzers working at temperatures above 100 or even 120° C in the future. The application of sinter nickel electrodes adds little more to the total costs of the diaphragm than the price of the Ni or NiO powders applied. But dispensing with the Ni net and special galvanic baths or other costly procedures to achieve high catalytic activities of the electrodes, it reduces total costs, because catalytically active elements can be added easily within the EDE production process. The potential use of these self-supporting EDE units depends mainly on the engineering problems implied in incorporating these devices into large cells. Such problems should be solved in the near future.

Acknowledgements

This work was performed with financial support of the Commission of the European Communities and the Bundesminister für Forschung und Technologie (BMFT).

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