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A novel route to produce porous ceramics

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Abstract

The possibility to consolidate alumina powder stabilized Pickering emulsions of paraffin oil in ethanol by means of electrophoretic deposition (EPD) into freestanding porous objects is reported. The pore forming paraffin is extracted from the consolidated powder compact by means of evaporation prior to sintering. The sintered ceramics contain spherical pores with a diameter that can be tuned from 200 μm to 20 μm. Both open and closed porosities can be obtained by altering the emulsion composition. Since no pore forming fugitive solid organic binder is used, the delicate and time-consuming debinding step during processing is eliminated.

Keywords: Porosity; Al_2O_3; Biomedical applications; Fuel cells; Refractories

1. Introduction

When two immiscible liquids are brought together, an interphase area will be formed. By stirring the liquids, droplets are created increasing the interphase surface area. This is however an energetically unfavourable situation and the two phases will separate again when mixing is stopped. The droplets however can be stabilized in the continuous phase using stabilizers. The most common stabilizers are low molar mass surfactants and surface-active polymers. When these substances are added, an equilibrium between adsorption at the interphase and desorption into the continuous phase will be established, stabilizing the droplets.

Solid particles can also be used to stabilize the emulsion droplets, as reported by Pickering in 1907.[1–3] In these so-called Pickering emulsions, particles locate themselves on the liquid–liquid interphase, driven by thermodynamics forces. If enough particles are present, a hexagonal close packing (HCP) of solid particles can be achieved at the interphase. In this way, emulsion droplets can be stabilized with all solid particles located at the interphase as graphically presented in Fig. 1. The amount and the size of the emulsion droplets can be controlled by the amount of solid material added. Upon consolidation of the emulsion and extraction of the internal liquid, hollow spheres with tailored diameter can be formed in a solid particle powder compact.

In this work, the possibility to consolidate the particle stabilized emulsions by means of electrophoretic deposition (EPD) is investigated.[4] Hamaker and Verwey described the electrophoretic deposition process as early as 1940.[5] However, it was not until the beginning of the 1990s that EPD was suggested as a commercial viable method for the production of ceramic objects and coatings. Electrophoretic deposition itself is fundamentally a two-step process.[6] In the first step, charged particles in an electrical field move towards an electrode (electrophoresis). In the second step, the particles collect at the electrode and form a coating or solid object on this electrode. Porous ceramics can be obtained with EPD by co-deposition of organic materials, such as starch, carbon black, polystyrene and polyethylene,[7] that are removed in an often very delicate and time-consuming debinding step before the actual sintering.

2. Experimental procedure

In most cases, solid particle stabilized emulsions are studied for water and oil systems. Water is however not desirable for EPD experiments since the electrolysis of this solvent limits the maximum voltage that can be used to 3–4 V. For this reason, electrophoretic deposition is commonly carried out in organic media such as ethanol. In order to form emulsions, a second liquid has to be added. A small test series with common non-polar solvents revealed that liquid paraffin, which is a mixture of several long chain alkanes, is sufficiently insoluble in ethanol.

In this work, Pickering emulsions were made with γ-Al_2O_3 nanopowder (Baikowski grade CR125) with an average

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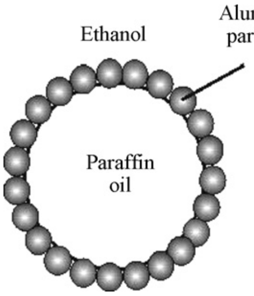


Fig. 1. Schematic representation of a solid particle stabilized emulsion droplet.

particle size of 60 nm using technical ethanol (Marchem) and liquid paraffin (Nujol mull grade for IR-spectroscopy, Acros). The γ-Al_2O_3 particle size distribution was measured using an acoustic particle sizer (Matec APS 100) (Fig. 2). A 0.1 N HNO_3 solution prepared from concentrated HNO_3 (68%, Fluka) is used for the charging of the alumina particles.

The alumina is suspended in ethanol with the charging agent by magnetically stirring for one hour. Subsequently, the suspension is placed in an ultrasonic bath (Branson 2510) for 15 min. For each emulsion system two of these suspensions are prepared (Table 1). One is used to stabilize the emulsion, the other is used for adding additional alumina which will form the interpore structure.

The actual emulsion is prepared by adding liquid paraffin to ethanol (Table 1) and vigorously stirring using a mechanical stirrer (IKA, RW20n) equipped with a standard 4-blade impeller. This emulsion is stabilized by adding one of the previously prepared suspensions (stabilizing suspension) (Table 1) and mixed for an additional 5 min. The obtained Pickering emulsion is kept in motion by gently stirring it on a magnetic plate. Another volume of alumina suspension (bulk suspension) (Table 1) is added to the stabilized emulsion before starting the EPD experiment.

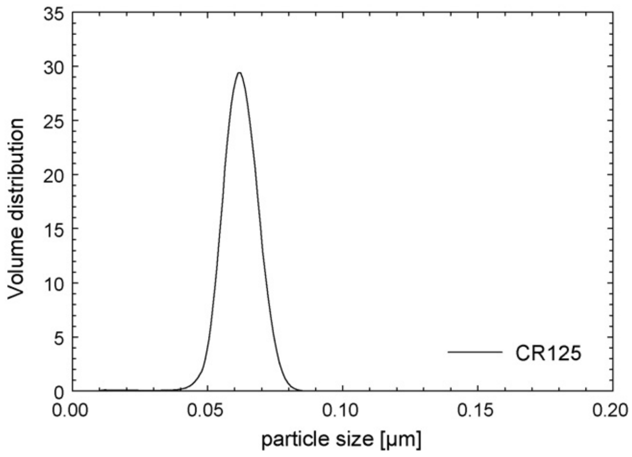


Fig. 2. CR125 particle size distribution.

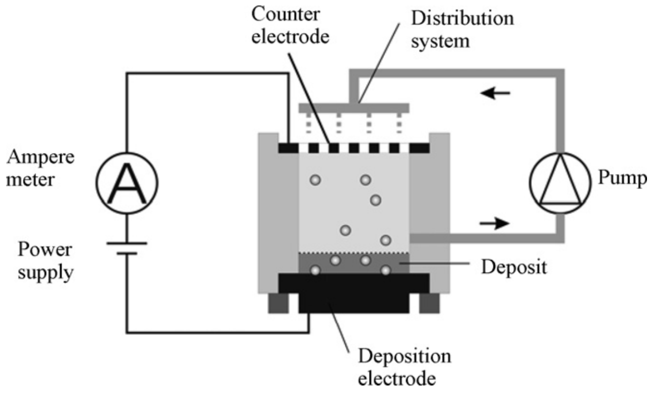


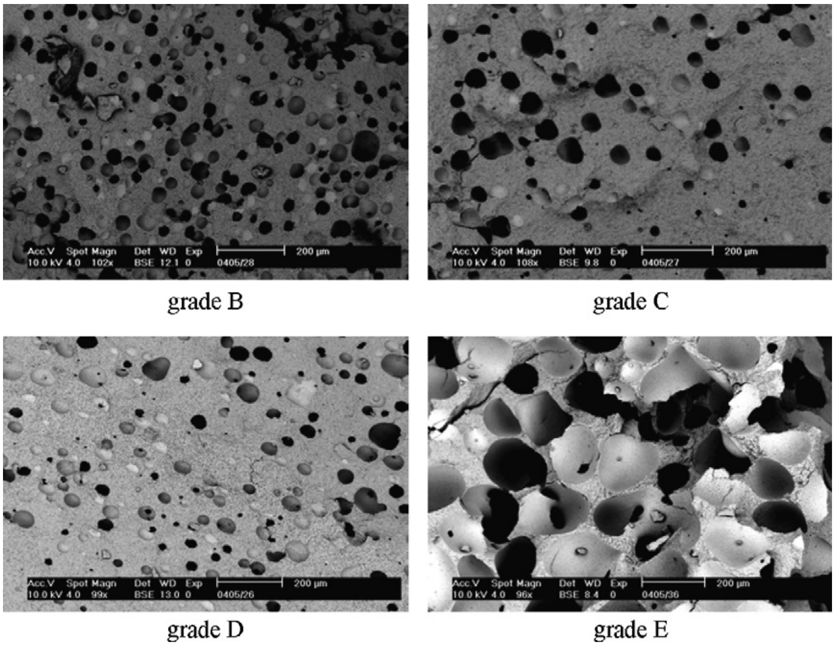
Fig. 3. Schematic of the EPD set-up.

The electrophoretic deposition experiments are carried out in an experimental set-up as depicted in Fig. 3. This set-up is comprised of a flow-through horizontal deposition cell and an emulsion circulation system driven by a peristaltic pump. The total volume of emulsion used in this system is 150 ml. The distance between the two circular electrodes is 35 mm and their diameter is 37.5 mm. The deposition was performed at a constant voltage of 300 V for 900 s using a DC power supply (F.U.G., MCN 1400-50). The deposition process was monitored by recording the cell current (Onron, K3NX).

The resulting deposits were subsequently dried for 2 h in a vacuum chamber and sintered in air for 20 min at 1550 °C with an initial heating rate of 20 °C/min up to 1100 °C, a final heating rate of 10 °C/min and a cooling rate of 25 °C/min. The remaining pores in the deposits after sintering are investigated by means of scanning electron microscopy (SEM, FEI, XL30-FEG). The density of the sintered pieces is measured by the Archimedes method in ethanol. A lacquer with known density was used to seal the pores before submerging the pieces. Mercury porosimetry (Micrometrics, Autopore IV 9500) is used to check the open or closed porous character of the sintered samples. In the case of open porous structures, the window size distribution in-between the pores is quantified.

Table 1
Composition of the investigated mixtures and density of the resulting sintered porous ceramics

Mixture	Emulsion		Stabilizing suspension			Bulk suspension			Density [%]
	V_{Ethanol} [ml]	V_{Paraffin} [ml]	V_{Ethanol} [ml]	V_{acid} [ml]	$m_{\mathrm{Al_2O_3}}$ [g]	V_{Ethanol} [ml]	V_{acid} [ml]	$m_{\mathrm{Al_2O_3}}$ [g]	
A	0	0	0	0	0	150	4.5	30	87.8
B	25	25	50	3.0	20	50	1.5	10	49.8
C	25	25	50	1.5	10	50	3.0	20	57.0
D	25	25	50	1.5	10	50	1.5	10	67.0
E	25	75	50	2.25	15	25	0.75	5	33.8



grade B grade C

grade D grade E

Fig. 4. SEM micrographs of fracture surfaces of material grades B, C, D and E as summarized in Table 1.

3. Results and discussion

The microstructure of the obtained materials largely depends on the composition of the emulsion used in the electrophoretic deposition experiments. The three most important factors are the amount of emulsified liquid, the amount of particles used for stabilizing the emulsion and the amount of bulk powder used for creating the matrix in-between the pores.

The ratio of the volume of emulsified liquid and the quantity of powder used to stabilize the droplets determines the size of the pores. When more liquid has to be stabilized with the same amount of powder, larger droplets are obtained. Some examples are given in Fig. 4. Material grades B and D have approximately the same pore size, the pore size of grade C is slightly larger and grade E shows the largest pores.

The overall porosity depends on the ratio of emulsified liquid and the bulk powder. This is confirmed both by density measurements (Table 1) and microscopic evaluation (Fig. 4). In theory, a porosity of 74% can be reached when monodisperse droplets forms the closest packed configuration with the voids between the drops completely filled with powder. In this ideal case, and when the pores between the particles themselves are neglected compared to the pores caused by the droplets, at least 26 vol% of bulk powder needs to be added to fill the voids between the droplets. If less bulk powder is used and the spheres are completely rigid, residual porosity would remain between the spherical pores and higher porosities can be reached.

After electrophoretic deposition in theory only green structures without large windows between the macropores are obtained since it is assumes that all droplets are completely covered with solid material. However, after sintering the samples with high porosity show an open porous structure. Thus during sintering, the structure is transformed from closed porosity to open porosity. When the porosity is high the pores are in close contact in the green structure, separated by thin walls. These walls are subjected to thermal stresses during sintering, causing cracking and or collapsing of the interpore walls. An example of such a collapsed wall is given in Fig. 5(b). From this observation it is safe to conclude that products with a relative density below 40% still have some open porosity. The most extreme case for this is grade E, shown in Fig. 4. Materials with a density above 60% probably mostly contain closed pores.

One sample (grade A in Table 1) that was made without paraffin, was prepared as a reference. The density of this material after

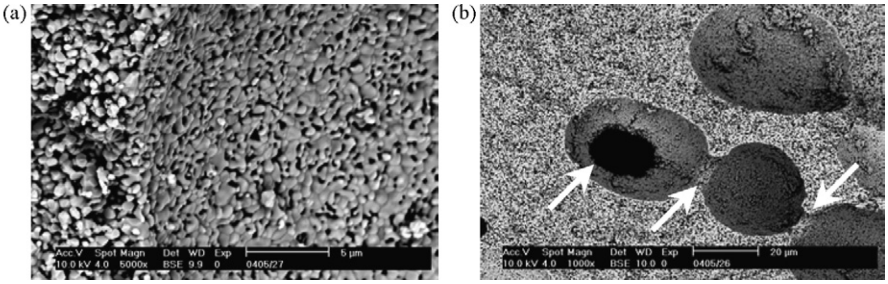


Fig. 5. Detail of pore edge as seen in grade C (a) and collapsed pore walls, indicated by arrows, as seen in grade D (b).

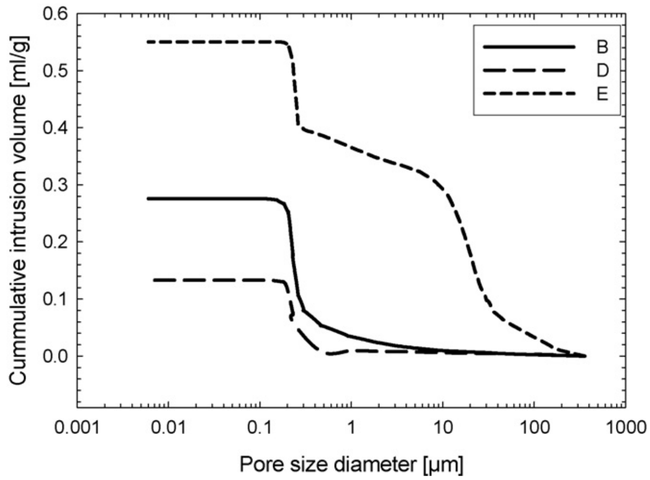


Fig. 6. Cummulative pore volume versus pore diameter for material grades B, D and E, measured with mercury porosimetry.

sintering is only 88% suggesting that a large amount of pores remains in-between the particles after the thermal cycle which is confirmed by the SEM micrograph (Fig. 5(a)) of the pore wall of material grade C. This is also confirmed by mercury porosimetry, as illustrated in Fig. 6. All measured samples indeed showed residual pores of approximately 230 nm that connect the individual macropores, even for the "closed" macroporous samples, causing them to fill with mercury. This is seen in the graph as a sudden stepwise increase of the cumulative pore volume. Grades B and E, which have higher porosity, contain windows with an average size of about 10–20 μm between the macropores. These windows are represented in Fig. 6 by the gradual increase in pore volume are higher pore size values. The degree of interconnectivity between the macropores by these windows, and the size of the windows increases proportionally with the overall porosity. The highly porous grade E is almost completely filled with mercury trough the windows, while grade B must rely on the interparticle pores to fill the majority of its macropores.

4. Conclusion

Experimental results showed that solid particle stabilized emulsions can be used to produce porous ceramics without the need for a debinding step. Moreover, the emulsion composition offers control over both the pore size and the overall porosity. Judicious selection of the amount of matrix material allows controlling the open or closed character of the pores. Changing the emulsion composition during the electrophoretic deposition offers the possibility of making materials with graded porosity, which are ideal for filter applications. Future work will show to what extent such graded materials can be produced.

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References

1. Pickering, S. U., Emulsions. *J. Chem. Soc. (London)*, 1907, **91**, 2001–2021.
2. Roy-Perreault, A., Kueper, B. H. and Rawson, J., Formation and stability of polychlorinated biphenyl Pickering emulsions. *J. Contam. Hydrol.*, 2005, **77**(1–2), 17–39.
3. Aveyard, R., Binks, B. P. and Clint, J. H., Emulsions stabilised solely by colloidal particles. *Adv. Colloid Interface Sci.*, 2003, **100–102**, 503–546.
4. Neirinck, B., *et al.*, A novel process for producing sintered porous materials from solid particle stabilized emulsions without debinding. UK patent GB 0512904.4, 2005.
5. Hamaker, H. and Verwey, E., Formation of a deposit by electrophoresis. *Trans. Farad. Soc.*, 1940, **36**, 180–185.
6. Van der Biest, O. and Vandeperre, L. J., Electrophoretic deposition of materials. *Annu. Rev. Mater. Sci.*, 1999, **29**, 327–352.
7. Hamagami, J. I., Ato, Y. and Kanamura, K., Fabrication of highly ordered macroporous apatite coating onto titanium by electrophoretic deposition method. *Solid State Ionics*, 2004, **172**(1–4), 331–334.