ABSTRACT: Microparticle porosity is normally determined in bulk manner providing an ensemble average that hinders establishing the individual role of each microparticle. On the other hand, single particle characterization implies expensive technology. We propose to use ion concentration polarization to measure differences in mesoporosity at the single particle level. Ion concentration polarization occurs at the interface between an electrolyte and a porous particle when an electric field is applied. The extent of ion concentration polarization depends, among others, on the mesopore size and density. By using a fluorescence marker, we could measure differences in concentration polarization between particles with 3 and 13 nm average mesopore diameters. A qualitative model was developed in order to understand and interpret the phenomena. We believe that this inexpensive method could be used to measure differences in mesoporous particle materials such as catalysts.

INTRODUCTION

Porous materials are key components in many fields that rely on their void volume, network distribution, and pore size and shape.\textsuperscript{1-3} They are particularly interesting in applications such as catalysis, supercapacitors, fuel cells, and batteries, due to their unique interaction with atoms, ions, and molecules at the nanometer and sub-nanometer scale. In chemistry, in particular heterogeneous catalysis, the porosity of solid materials is normally used to enhance the available area in contact with reagents and products, thus increasing the activity per unit volume.\textsuperscript{4} In practice a porous catalyst is used or a catalyst support with immobilized nanoparticles. However, small differences in the porosity of these materials can cause large variations in mass transport of reagents through the pores which can result in a reduction or even loss of catalyst activity.\textsuperscript{5-7} Normally, these catalysts or catalyst supports are fabricated in batch reactors in a noncontrolled but reproducible manner, resulting in large inter- and intraparticle heterogeneities.

Nanopores are generally subdivided into three groups depending on the pore dimensions: micro- (<2 nm), meso- (2–50 nm), and macropores (>50 nm). There are many techniques available to measure the pore size distribution of nanoporous materials, where the most popular ones are based on gas adsorption, fluid intrusion, microscopy, and spectroscopy.\textsuperscript{5,8-12} The Brunauer–Emmett–Teller (BET) method uses the adsorption of chemically inert gases on the porous material walls to determine the available surface area in the volume measured.\textsuperscript{13} The pore size distribution can also be derived from the pressure needed to drive the flow of fluids such as Hg into the porous media.\textsuperscript{14} Both methods are widely used, but the volumes of porous material needed are large, providing an ensemble-averaged porosity instead of the porosity of single microparticles. For the latter, among others, scanning electron microscopy (SEM) and X-ray diffraction are used to determine meso- and macroporosity at the single microparticle level. These methods, however, imply the use of expensive technology and can study only very small quantities.\textsuperscript{7,15,16} Therefore, new ways to measure the porosity of particles at the single particle level are needed in order to understand and increase the efficiency of porous systems. In this study, ion concentration polarization (ICP) is used to
measure the mesoporosity at the single particle level. ICP occurs at the interfaces of an ion-perselective material and free solution on application of an electric field.\textsuperscript{17–20} It results in the formation of ion accumulation and depletion zones at the opposite sides of the material due to the ion flux imbalance between free solution and inside the particle; see Figure 1a. Porous materials become ion-perselective when their pore dimensions are of the order of the electrical double layer thickness at the pore walls (typically nanometer scale).

![Figure 1. (a) Schematic of ICP at a cation-selective porous particle. The depletion and accumulation zones are indicated. (b) Schematic of the porous particle under an electric field. ICP occurs as a result of the ion flux imbalance at the particle/solution interfaces as shown by the flux vectors and the electrical transport numbers, $\tau$, in the particle and solution. At the anodic side, a depletion zone is formed close to the interface of the particle while an enrichment zone is formed at the cathodic side. For simplicity a solution is assumed with a 1:1 electrolyte.](image)

Here, we propose to use ICP in a microfluidic system to analyze the mesoporosity of two types of porous polystyrene particles with different mesoporosities. We first present an approximative theory describing ICP at the single particle level. Then, we show measurements and analysis of the ICP experimental fluorescent response of both types of particles at different electrolyte concentrations using a fluorescent dye marker with constant concentration.

**THEORY**

Figure 1b shows the mechanism of ICP, occurring when a uniform electric field is applied across a porous ion-perselective particle. ICP occurs when a difference exists in the fraction of the current that is carried by the different ionic species in particle and bulk solution and involves gradients in the migration and diffusion fluxes. The ion-perselectivity of the particles is caused by the difference in ionic concentration composition in the mesopores and the bulk. Assuming negative surface charge on the pore walls, more cations are present in the solution in the pores due to electroneutrality, and therefore more current will be carried by the cations in the pores than by the anions when compared to the bulk solution. A depletion zone, where the concentrations of all ionic species will be lower than in the bulk, will then form at the anodic side of the particle (left side on Figure 1b). An accumulation zone, where the concentration of all ionic species will be higher than in the bulk, will form on the cathodic side (right side on Figure 1b). In the depletion and accumulation zones additional diffusion fluxes maintain a steady-state constant flux of cations and anions. In order to quantify the extent of ICP, we use a fluorescent reporter ion and measure the difference of its fluorescent intensity in the depletion and accumulation zones during 4 s over several alternating potential cycles assuming a linear relation between fluorescent intensity and concentration of the reporter. NaCl is used as bulk electrolyte salt (diffusion coefficients of $1.374 \times 10^{-5}$ and $1.957 \times 10^{-5}$ cm$^2$/s$^2$ for Na and Cl, respectively, and electrophoretic mobilities calculated with Einstein’s relation). We will first theoretically derive the concentration profile of our fluorescent reporter bodipy disulphonate (BDP$^{2-}$) in the solution as a function of time and distance from the particle surface ($C_{\text{BDP}}(x,t)$), in an approach similar to that of Bergveld et al.\textsuperscript{22}

Because our theoretical model is designed only to estimate a qualitative behavior of our system, a series of strong assumptions are made: (i) The model is one-dimensional, (ii) the convective flux (electroosmotic flow) can be neglected, (iii) the particle pores are assumed to be perfectly cylindrical running the whole length of the particle, (iv) the particle is assumed to be rectangular with a length equal to the diameter of the real particle, (v) the particle is assumed to be a square part of a continuous membrane, with uniform noncylindrical mesopores passing through it, (vi) the concentration distribution at the enrichment and depletion zone does not affect the local electric field, and (vii) the diffusive flux inside the particle is neglected.

**Nernst–Planck.** To calculate the concentrations of BDP$^{2-}$ ($C_{\text{BDP}}(x,t)$), we will use the one-dimensional Nernst–Planck flux equations. The current density ($j$ [A/m$^2$]), the local conductivity ($\kappa$ [S/m]), and the local electric field ($E$ [V/m]) are related by

$$\kappa(x, t) E(x, t) = j$$

We will first consider the transport of BDP$^{2-}$ in the electrolyte bordering the particle. Ignoring the convective flux contribution to the Nernst–Planck equation (hereby included electroosmotic flow), we can write the flux, $J_e$, of BDP$^{2-}$ in the electrolyte as composed of a migration and a diffusion term,

$$J_{\text{BDP}}^e(x, t) = -\frac{\tau_{\text{BDP}}^e}{F} D \frac{\partial C_{\text{BDP}}^e(x, t)}{\partial x}$$

where $\tau_{\text{BDP}}^e$ is the dimensionless transport number of BDP$^{2-}$ in the electrolyte, $F$ the faraday constant, and $D$ the diffusion coefficient of BDP$^{2-}$. By applying the continuity equation

$$\frac{\partial C_{\text{BDP}}^e(x, t)}{\partial t} = - J_{\text{BDP}}^e(x, t)$$

and realizing that the migration term in the electrolyte is constant in $x$, we arrive at

DOI: 10.1021/acs.langmuir.9b00802
Langmuir 2019, 35, 9704–9712
We thus will derive the transport numbers of BDP\textsuperscript{2−} in the particle. Assuming no concentration gradient inside the particle, therefore only a migration contribution, the BDP\textsuperscript{2−} flux in the particle, equals

$$\mathbf{J}_\text{BDP}(0, t) = -\frac{e^{\text{BDP}}}{F} \tilde{r}$$

We solve eq 4 using the following boundary conditions at $x = \infty$, at any time $t$:

$$C^e_{\text{BDP}}(\infty, t) = C^B_{\text{BDP}}$$

at $t = 0$, at any $x$:

$$C^e_{\text{BDP}}(x, 0) = C^B_{\text{BDP}}$$

at $x = 0$, at $t \neq 0$:

$$\frac{\partial C^e_{\text{BDP}}(0, t)}{\partial x} = -j(\tilde{r}^B_{\text{BDP}} - \tilde{r}^e_{\text{BDP}}) \frac{FD}{\rho}$$

Here $x = 0$ is the location of the particle/solution interface at the cathodic side of the particle and $x = \infty$ is a sufficient distance away from this point where there is no effect of the particle and hence the BDP\textsuperscript{2−} concentration retains its initial bulk value ($C^B_{\text{BDP}}$). Equation 8 simply expresses the conservation of mass for the fluxes crossing the plane at $x = 0$. The result is

$$C^e_{\text{BDP}}(x, t) = e^{\text{BDP}} \frac{K^{\text{BDP}} - \tilde{r}^e_{\text{BDP}}}{FD} \left[ 2\left(\frac{D^1}{\pi}\right)^{1/2} \exp\left(-\frac{x^2}{4D^t}\right) - x\text{erfc}\left(\frac{x}{2(D^t)^{1/2}}\right) \right]$$

where erfc is the complementary error function. In eq 9 the variables, current density ($j$) and transport numbers ($\tilde{r}^B_{\text{BDP}}$, $\tilde{r}^e_{\text{BDP}}$), depend on the electrolyte bulk salt concentration and the particle pore size, and we will investigate them separately in the following subsections.

**Transport Numbers, \(\tilde{r}\).** The difference of BDP\textsuperscript{2−} transport numbers between electrolyte and particle ($\tilde{r}^B_{\text{BDP}} - \tilde{r}^e_{\text{BDP}}$) indicates the ion-permselectivity of the particle toward BDP\textsuperscript{2−}. We thus will derive the transport numbers of BDP\textsuperscript{2−} in the electrolyte and in the particle. The ion transport number of a species $i$ is defined as the fraction of the total electric current density ($j$) carried by this species. In the electrolyte the transport number for BDP\textsuperscript{2−} equals

$$\tilde{r}^e_{\text{BDP}} = \frac{2c^{\text{BDP}}D^{\text{BDP}}}{\sum_j \overline{z_jc_jD_j}}$$

In the particle we use the same equation but now with the area-averaged concentration of BDP\textsuperscript{2−} in the mesopore

$$\tilde{r}^p_{\text{BDP}} = \frac{2c^{\text{BDP}}D^{\text{BDP}}}{\sum_j \overline{z_jc_jD_j}}$$

In order to calculate the concentration in the pore, we must account for the concentration distribution of the species in the electric double layer. We will follow the approach of Rice and Whitehead,\textsuperscript{24} who solved the Poisson–Boltzmann equations for a circular mesopore. Starting from the 1D Poisson equation for radial coordinates,

$$\frac{\partial^2 \psi}{\partial r^2} = -\frac{4\pi}{\varepsilon_0} \rho(r)$$

where $\psi$ (V) is the local electric potential, $r$ (m) is the distance from the pore center, $\varepsilon_0$ and $\varepsilon_i$ are the vacuum and medium permittivities, and $\rho$ (C/m\textsuperscript{3}) is the local electric space charge density, which is defined as

$$\rho(r) = \sum \varepsilon_i z_i c_i(r)$$

The concentration of the ions follows the Boltzmann distribution:

$$c_i(r) = c_i^0 \exp\left(-\frac{\varepsilon_i z_i \psi(r)}{k_B T}\right)$$

where $c_i^0$ (mol/m\textsuperscript{3}) is the pore electrolyte concentration of species $i$, $c$ (C) the electron charge, $k_B$ the Boltzmann constant, and $T$ (K) the absolute temperature. It is worth mentioning that for $c_i^0$ the bulk concentration of the species is used which does not hold for overlapping double layers. Hence, at low concentrations the results should be taken tentatively.

For $\psi \leq k_B T/\varepsilon_i$,

$$\frac{1}{r} \frac{\partial}{\partial r}\left( r \frac{\partial \psi}{\partial r} \right) = \frac{\psi(r)}{\lambda_D}$$

where $\lambda_D$ is the Debye length.\textsuperscript{35,26}

$$\lambda_D = \sqrt{\frac{\varepsilon_0 \varepsilon_i k_B T}{2 F^2 c_i}}$$

We use an approach similar to that of Taghioor et al.,\textsuperscript{27} for the determination of the surface charge density ($\sigma$ [C/m\textsuperscript{2}]). We then use the Grahame equation (eq 17) for the determination of surface potential ($\psi_0$ [V]) and eq 18 for the relation between the surface potential and $\zeta$ potential, the potential at the slipping plane.

$$\sigma = \sqrt{8c_i^0 N_A \varepsilon_i \varepsilon_0 k_B T \sinh\left(\frac{\varepsilon_i \psi_0}{2k_B T}\right)}$$

$$\psi_0 - \zeta = \frac{\sigma}{C_{\text{Stern}}}$$

where $N_A$ (mol\textsuperscript{-1}) is the Avogadro number and $C_{\text{Stern}}$ (F/m\textsuperscript{2}) is the specific Stern layer capacitance. Equation 15 is then analytically solved for the potential distribution in the diffuse double layer,\textsuperscript{26}

$$\psi(r) = \zeta - \frac{I_0\left(\frac{r}{\lambda_D}\right)}{\text{I}_0\left(\frac{\lambda_D}{2}\right)}$$

where $I_0$ is the zero-order modified Bessel function of the first kind.

From eqs 14 and 19 we can estimate the average BDP\textsuperscript{2−} concentration inside the mesopore. We subsequently calculate the BDP\textsuperscript{2−} transport number in the mesopore (eq 11) by integrating $C^{\text{BDP}}(r)$ over the pore cross-sectional area. Figure 2 shows the transport numbers of BDP\textsuperscript{2−} in the electrolyte and particle as a function of bulk electrolyte concentration using
the average mesopore size determined by BET measurements (Table 1). At low electrolyte concentrations, the concentration of BDP$^{2-}$ in the particle is extremely low compared to the total ion concentration (especially cation concentration) since the electric double layers overlap and BDP$^{2-}$ is almost completely excluded from both small and large mesopores. At high electrolyte concentrations, the electric double layer is extremely thin and the average species concentration is almost the same as the bulk concentration. The larger diameter pores approach this state at much lower electrolyte concentrations than the smaller pores.

**Current Density, $j$.** To determine the magnitude of this electric field, we need to consider our experimental system. In the CP model of sections 2.1 and 2.2, the porous particle was modeled as part of a continuous membrane. During the experiments, however, separate particles are placed at the bottom of a microfluidic channel and a constant potential is applied at the two reservoirs connected to this channel. The electric field across the particle will then depend on the conductance ratio between a particle and its surrounding electrolyte. Now when we vary the electrolyte concentration, the particle conductance scales differently from the electrolyte conductance, creating a dependency of the electric field across the particle on the electrolyte concentration. An equivalent 1D macroscopic electrical circuit is therefore needed to calculate the electric field as a function of concentration and is shown in Figure 4a. From the total system conductance, the separated conductance of the electrolyte and the particle, and the applied voltage, we can then calculate the potential drop over and hence the electric field across the particle.

We assume that a constant and uniform electric field ($E$) exists inside the particle; i.e., the concentration distribution of the ions in the electrolyte close to the particle surface does not affect the local electric field inside the particle. The current density ($j$) through the particle then equals

$$j = Ex$$  \hspace{1cm} (20)$$

where $\kappa$ is the area-averaged conductivity of the particle. The area-averaged conductivity of a single mesopore ($\kappa_i$) equals

$$\kappa_i = \frac{N_{\kappa}e}{r_0} \int_0^{r_0} \mu_i c_i(r) \, dr \hspace{1cm} (21)$$

where $c_i(r)$ was calculated as in the previous section. The electric conductance ($G_{i}$ [S]) of a single mesopore then is

$$G_i = \frac{A\kappa_i}{d} \hspace{1cm} (22)$$

where $d$ ($m$) is the diameter of the particle (mesopore length) and $A$ ($m^2$) is the cross-sectional area of the mesopore. Figure 3 shows the conductivity of a single mesopore of the two kinds of particles, using the average mesopore size determined by BET measurements (Table 1). As expected, the smaller mesopore shows a higher conductivity.

We calculate the total conductance of a particle ($G_p$) from the total number of mesopores ($N$) per particle, treating them as parallel conductors

$$G_p = NG_c \hspace{1cm} (23)$$

For the calculation of $N$ we use the specific pore volume ($V_s$ [m$^3$/g]) or specific pore surface area ($A_s$ [m$^2$/g]) and the density ($\rho$ [g/m$^3$]) values found via BET and pycnometer methods, as will be explained in the Experimental Section,

$$N = \frac{\rho V_{\text{particle}} V_s}{V_{\text{pore}}} \hspace{1cm} (24)$$

or

$$N = \frac{\rho V_{\text{particle}} A_s}{A_{\text{pore}}} \hspace{1cm} (25)$$

where $V_{\text{particle}}$ (m$^3$) is the volume of the particle and $V_{\text{pore}}$ (m$^3$) and $A_{\text{pore}}$ (m$^2$) are the volume and surface area of a single mesopore.
Figure 4b shows that the E-field remains relatively constant when the particle/pore conductivity is equal to the bulk conductivity. Once the bulk electrolyte concentration drops and the surface conductivity becomes the dominant conductivity contribution in the mesopore, the particle resistance increases slower than the resistance of the surrounding electrolyte resulting in a lower voltage drop and E-field across it. Now knowing the conductivity and the E-field as a function of bulk concentration and mesopore size, we can calculate the current density via eq 21.

Once the current density and transport numbers ($\tau_{\text{BDP}}^p - \tau_{\text{BDP}}^e$) are determined, eq 9 can be used to describe the temporal concentration profile of the fluorescent reporter, BDP$^{2-}$, as a function of distance from the surface of the particle ($C_{\text{BDP}}(x,t)$) in the enrichment zone. Figure 5a shows the calculated average BDP$^{2-}$ concentration of both particles over a distance of 25 $\mu$m in the bulk electrolyte over 4 s and at the edge of the particle (see Figure 5b). The shape of the graph is dominated by the value of the product $j/(\tau_{\text{BDP}}^p - \tau_{\text{BDP}}^e)$ in eq 9, representing the particle ion-permselectivity. At low concentrations, the cation-permselectivity is maximal; hence, the accumulation is governed by the conductance of the mesopores, with the larger pores being more conductive because of the larger pore volume. However, these pores lose their selectivity faster compared to the smaller pores as the bulk salt concentration increases. The two lines therefore cross, in the model at a bulk electrolyte concentration of 14 mM. In addition, at low concentrations the resistance of the particle is approximately 2 orders of magnitude lower than the resistance of the channel. Hence the resistance of the microchannel (Figure 4a) regulates the current through the system and particle resulting in the flattening of the BDP concentration at low concentration in Figure 5a.

**EXPERIMENTAL SECTION**

A PDMS microfluidic chip was fabricated by standard photolithographic techniques. First, a 200 $\mu$m SU8 layer was spun and baked on a 4 in. silicon wafer. Next, the photoresist was exposed for 50 s to UV light and developed. The chip design consisted of a straight channel of 200 $\mu$m height, 1 mm width, and 2 cm length, connecting two reservoirs. Polystyrene particles 50 $\mu$m in diameter with two mesopore sizes (10 and 50 nm) were purchased at https://www.chromspheres.com. Particles were submerged in ethanol, and with a pipet, they were deposited one by one on the PDMS channel. Thereafter, the PDMS with the particles was plasma treated for 40 s and bonded to a glass slide. The polystyrene particles were therefore stuck to the PDMS and sufficiently spaced between them in order to avoid interaction of the fluorescent reporter. A microscope Olympus IX51 and camera Grasshopper 3 were used with a Hg lamp for the fluorescent microscopy. Two platinum wires were used to connect the power supply (Keithley 2410) to the electrolyte solution at the reservoirs. BODIPY 492/515 disulfonate (BDP$^{2-}$; ThermoFisher) and phosphate buffered saline solution (PBS; Sigma-Aldrich) were used as a fluorescent molecule and background electrolyte, respectively. The PBS concentrations used were $10^{-4}, 10^{-3}, 10^{-2}, 2.5 \times 10^{-2}, 5.0 \times 10^{-2}, 7.5 \times 10^{-2},$ and $10^{-1}$ M, while the concentration of BDP$^{2-}$ was 750 nM in all experiments. Matlab and ImageJ were used to analyze the experimental data. Matlab was used to simulate the model. The power supply was operated via LabView software. BET and density measurements were performed in a Gemini.
VII from Micromeritics and AccuPyc II 1340 Micromeritics pycnometer, respectively. The ICP was measured by applying a step function of ±100 V across the channel and performing four cycles of 4 s each. During the experimental data analysis, a linear drop of fluorescence intensity in the bulk, which we assumed to be caused by the marker photobleaching, was observed and compensated for.

■ RESULTS AND DISCUSSION

Figure 6 shows SEM images of both types of polystyrene particles showing a clear difference in pore size distribution. To measure the average pore size as well as the pore volume, surface area, and density, BET and pycnometer measurements were performed, with the results being summarized in Table 1. A clear difference between both types of particles can be observed, with both having pores in the mesoporosity size range. Also, the similar pore volume indicates that the particles with smaller pores have more pores per unit volume.

Figure 7a shows an image of a typical concentration polarization measurement of a particle with an accumulation zone on the cathodic side and a depletion zone on the anodic side. The area- and time-averaged fluorescence intensities at both sides of a particle were measured as illustrated in Figure 7a. Equation 9 describes the spatiotemporal concentration profile of Bodipy, assuming a one-dimensional system. At any moment in time the magnitude of the concentration depletion and accumulation of Bodipy depends on the difference in Bodipy flux in the particle and in the solution, and hence on the particle properties that determine the Bodipy transport numbers in both. Since this is true for all times and all locations adjacent to the particle, averaging the concentration difference over time and space keeps the essence of this information intact. The data thus validate the model in a qualitative manner. In future a 3D simulation model could be constructed that is expected to provide more quantitative information. Figure 7b shows a typical experimental fluorescent intensity obtained in one positive and negative pulse.

The experimentally determined difference in fluorescence intensity between depletion and enrichment zones is plotted against the electrolyte concentration in Figure 8. It was found...
that the particles with larger pores have a higher fluorescence intensity at low salt concentrations. This was indeed predicted by our model, where it results from the larger pore volume. The fluorescence intensity values of both particles cross at a higher salt concentration, which was also predicted in the model, where it follows from the earlier drop in the ion-perselectivity of the particles with larger pores. This confirms that ICP can be used to differentiate between particles with different mesoporosity. The error bars in Figure 8 correspond to 95% confidence intervals.

Because some experimental verification of the model is now obtained, we will investigate its feasibility for future applications by modeling the effects of the following properties on the ICP: pore diameter, surface charge density, and total particle surface area. Figure 9a shows that an increase in pore size causes a faster decrease in fluorescent intensity with increasing electrolyte concentration which can be explained by the fact that smaller pores will be more permselective than larger pores at higher electrolyte concentrations, causing a higher transport number difference with the bulk electrolyte. It is worth noting that the total particle cross-sectional area was kept constant; hence, a constant current density is assumed on Figure 9a. In the case of varying surface charge, see Figure 9b, at low electrolyte concentration no difference is observed, that is caused by the limitation of the current due to high resistance of the bulk compared to the particle as commented on earlier. In contrast a difference is seen when the electrolyte concentration increases: the pores with high surface charge lose their permselectivity at higher electrolyte concentrations due to higher concentration in the double layer. Figure 9c shows the effect of total particle surface area on the reporter

**Figure 8.** Experimental results of ion concentration polarization vs electrolyte concentration. The points on the y-axis were found by subtracting the lower fluorescent intensity value (in the depletion zone) from the high intensity value (in the enrichment zone). Similar to the theoretical graph, the ICP at low electrolyte concentration is larger for the large pore diameter particles, while the ICP at high salt concentration is larger for the small pore diameter particles. The lines cross in both the model and the experiments at a concentration where the selectivity is lost for the larger pores. The error bars correspond to 95% confidence intervals.

**Figure 9.** Simulations of the model when changing (a) the mesopore size, (b) surface charge density, and (c) specific surface area. In each simulation, all of the other parameters not simulated are taken from the smaller pores’ particles. In panel a, the total cross-sectional area (no. of pores × pore size) is kept constant. σ corresponds to the surface charge density calculated for silicon dioxide as described previously.
concentration. As can be seen, a lower surface area causes an increase in fluorescent intensity. The total surface area is linearly (for a constant pore size) related to the number of pores. Since the total current through the particle is regulated by bulk resistance (microchannel), it is almost constant between particles. A decrease in the surface area translates in a lower number of pores which results in a higher current density through the particle. The conclusion is that differences in pore size and pore charge density lead to different concentration polarization behavior. In addition to a qualitative description of our system, also more specific information can be extracted from our model. As can be seen in Figure 9a, the cutoff point in the electrolyte concentration (intercept of red lines) where the concentration polarization effect starts to drop when increasing the electrolyte concentration is strongly correlated to the pore size as well as the surface area, with the effect of pore size being larger. On the other hand, the concentration polarization at very low electrolyte concentrations is dominated just by the specific surface area of the particle (Figure 9c); hence, by measuring the ICP at low electrolyte concentrations (10^{-4} M), the particles can be differentiated based on their specific surface area. As can be seen in the experimental data of Figure 8, the fluorescent intensity at low concentrations is slightly lower for the particle with smaller pores, indicating that their specific surface area is slightly larger. However, when evaluating the concentration at which the fluorescent intensity drops, a parameter that is largely dependent on the pore size, the ICP of the particles with larger pores drops at lower concentrations as predicted by our model.

**CONCLUSIONS AND OUTLOOK**

In conclusion, we demonstrated that ICP can be used to differentiate between particles with different mesopore dimensions. A model was developed demonstrating that both pore density and ion-permselectivity play a role in the magnitude of ICP. Subsequently, the ICPs of two types of particles with experimentally determined porosity and pore density were measured at different bulk electrolyte concentrations. Experimental and simulated results show similar trends. We conclude that the ICP method can be used to track differences in pore size between mesoporous particles such as catalysts or catalysts’ supports. Our model is currently a 1D model that provides qualitative results and allows understanding of the main factors affecting ICP. In the future it can be used as a foundation for numerical simulations in order to create a 3D (semi)quantitative model. Such a numerical approach can also include phenomena that are currently neglected in our analytical model such as the electro-osmotic flow.

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**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

We thank M. H. G. Eidhof and M. Derks for their contributions. This work was supported by The Netherlands Centre for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture and Science of the government of The Netherlands and by Horizon 2020 Framework Programme of the European Union under the project H2020-PHC-634013 (PHOCNOSIS).

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