

ION CONCENTRATION POLARISATION FOR PARTICLE MESOPOROSITY DIFFERENTIATION

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ABSTRACT

Microparticle porosity is an essential property e.g. determining particle catalytic properties. It is normally determined in bulk providing a porosity ensemble average that hinders establishing the individual role of each microparticle. On the other hand, single particle characterization needs expensive technology. We propose to use ion concentration polarization (ICP) as an inexpensive technology to differentiate mesoporosity at single particle level.

KEYWORDS: Ion Concentration Polarization, mesoporous particle differentiation

Polystyrene microparticles of different mesoporosities (3nm and 13nm average mesopore diameters) were immobilized via O₂ plasma treatment inside a straight PDMS microchannel filled with varying electrolyte concentrations and spiked with a fluorescent marker (Bodipy-BDP). AC potential pulses were applied and the extent of ICP (figure 1) as a function of the electrolyte concentration established by the BDP fluorescence amplitude (Figure 2).

To interpret the results, an approximative 1D theory describing ICP at single particle level was formulated. ICP occurs when a difference exists in the fraction of the current that is carried by the ionic species in particle and bulk solution, and involves gradients in the migration and diffusion fluxes (Fig 3b). The ion perm-selectivity of the particles is caused by the electrical double layer in the mesopores. Ignoring the convective flux contribution, we can write the flux J_e of BDP in the electrolyte as composed of a migration and a diffusion term,

$$J_{BDP}^e(x, t) = -\frac{\tau_{BDP}^e j}{F} - \hat{e}_x D \frac{\partial C_{BDP}^e(x, t)}{\partial x} \quad (1),$$

where τ_{BDP}^e is the dimensionless transport number of BDP in the electrolyte, F the faraday constant, j the current density, D the diffusion coefficient of BDP and $C_{BDP}^e(x, t)$ its concentration profile as a function of time and distance from the particle surface. The transport number is defined as the fraction of the total current carried by the species considered. For both the current density (conductivity) and the transport number, the concentration of each species is needed in the bulk and in the particle. Using the continuity equation and $C_{BDP}^e(\infty, t) = C_{BDP}^B$, $C_{BDP}^e(x, 0) = C_{BDP}^B$ and $\frac{\partial C_{BDP}^e(0, t)}{\partial x} = -\frac{j(\tau_{BDP}^P - \tau_{BDP}^e)}{FD}$ as boundary conditions, where C_{BDP}^B is the bulk concentration of BDP, we can solve equation 1 for $C_{BDP}^e(x, t)$ similar to Bergveld et al[1],

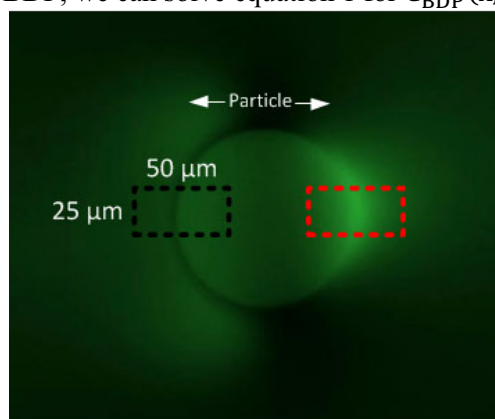


Figure 1- Fluorescent microscopy image of a typical measurement showing an accumulation zone on the right and the areas that were measured and averaged over a pulse duration of 4 seconds.

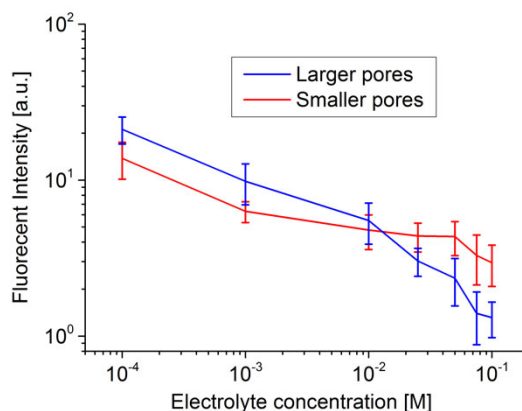


Figure 2 - Experimental results of ion concentration polarization vs electrolyte concentration as measured by the fluorescence intensity of BDP. The points on y-axis were found by subtracting the lower fluorescent intensity value (in the depletion zone) from the high intensity value (in the enrichment zone). The error bars correspond to 95% confidence intervals.

$$C_{BDP}^e(x, t) = C_{BDP}^B - \frac{j(\tau_{BDP}^p - \tau_{BDP}^e)}{FD} \left\{ 2 \left(\frac{Dt}{\pi} \right)^{\frac{1}{2}} \exp\left(-\frac{x^2}{4Dt}\right) - x \operatorname{erfc}\left(\frac{x}{2(Dt)^{\frac{1}{2}}}\right) \right\} \quad (2)$$

In equation 2, only the current density (j) and the transport numbers ($\tau_{BDP}^e, \tau_{BDP}^p$ in the electrolyte and particle respectively) are unknown and depend on the electrolyte bulk salt concentration and the particle pore size and wall charge density. Assuming the particle as an array of parallel round nanochannels and following the approach of Rice and Whitehead[2], and Taghipoor et al.[3] we calculated concentration profiles of each species in the mesopores and hence their particle transport number. The predicted enrichment of BDP due to ICP as a function of the electrolyte concentration is shown on figure 4.

As can be seen from both figures 2 and 4, at low electrolyte salt concentration where both small and large pores are strongly permselective due to overlapping electric double layers, the more conductive larger pores result in a stronger ICP than the smaller pores. As the electrolyte concentration increases the large pores lose their selectivity earlier resulting in a drop in ICP compared to the smaller pores.

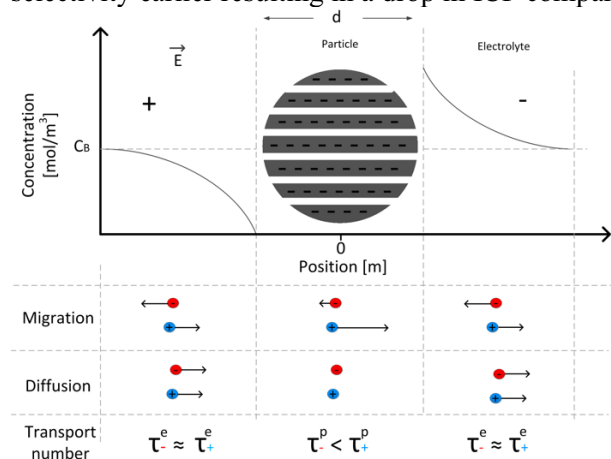


Figure 3 - Schematic of the porous particle under an electric field. ICP occurs as a result of the ion flux imbalance at the particle /solution interfaces as shown by the flux vectors and the electrical transport numbers τ in the particle and solution. At the anodic side, a depletion zone is formed close 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

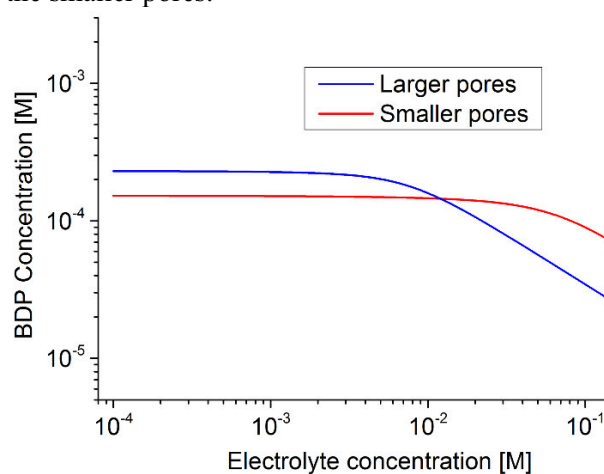


Figure 4- Averaged BDP concentration at different electrolyte concentrations on the enrichment side of the particle over 4 sec over 25 μ m from the particle/electrolyte interface. Similar to the theoretical graph, the ICP at low electrolyte concentration is larger for the large pore diameter particles, 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.

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