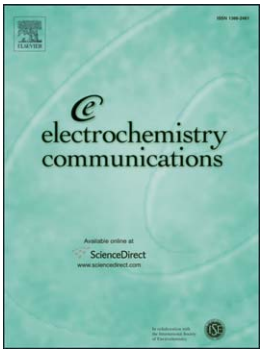

The effect of dielectric permittivity on the capacitance of nanoporous electrodes

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PII: S1388-2481(13)00266-X
DOI: doi: 10.1016/j.elecom.2013.07.009
Reference: ELECOM 4867

To appear in: *Electrochemistry Communications*

Received date: 12 June 2013
Revised date: 29 June 2013
Accepted date: 4 July 2013

Please cite this article as: S. Kondrat, A. Kornyshev, F. Stoeckli, T.A. Centeno, The effect of dielectric permittivity on the capacitance of nanoporous electrodes, *Electrochemistry Communications* (2013), doi: 10.1016/j.elecom.2013.07.009

The effect of dielectric permittivity on the capacitance of nanoporous electrodes

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By means of Monte Carlo simulations we show that a pore-width dependent dielectric permittivity, $\varepsilon_p(L)$, may diminish the pore-size dependence of the surface-specific capacitance. This is different from the case of a fixed dielectric permittivity, $\varepsilon_p = \text{const}$, which leads to an increase of capacitance when the pore width becomes comparable to the ions size.

Keywords: supercapacitors; nanoporous electrodes; anomalous capacitance

Electrochemical capacitors store energy in the electric double layers formed by an electrolyte in porous electrodes. The capacitance of such electrodes scales with the accessible surface area, which can be made very high by using porous carbons [1, 2]. The fundamental characteristic is therefore the capacitance per electrode's surface area, C_S. Two patterns have been reported regarding its pore-size dependence. In the case of $\text{TEA}^+\text{BF}_4^-$/AN an 'anomalous' increase in C_S with decreasing the pore width below 1 nm was reported [3, 4], while other measurements [5–7] suggested a constance capacitance in a range of pore sizes. Pore size distribution can weaken the possible anomalous increase of capacitance [8–11], but cannot eradicate it [12].

Recent Jiang et al. [8, 13] provided interesting clues regarding the role of a solvent in electrolyte solutions. They considered a density functional theory (DFT) for an electrolyte in metallic slit nanopores, and examine [8] the case of the solvent-free ionic liquid, where it is found a damped oscillatory behaviour of C_S and the 'anomalous' increase of C_S for the average pore width decreasing from 0.9 to 0.5 nm. In a subsequent paper [13], the same DFT approach was used for an ionic liquid dissolved in a polar fluid, with the polar molecules modeled as charged dumbbells. Here, the capacitance is nearly constant between 3 and 0.8 nm, increasing sharply only at 0.5 nm. This behaviour seems to resolve largely