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Electrochemical double-layer charging of ultramicroporous synthetic carbons in aqueous electrolytes

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ABSTRACT

We prepared synthetic porous carbons with a three-dimensional interconnected network of ultramicroporous particles; by adjusting the synthesis parameters the size of these particles was systematically varied from 13 nm to 1.4 μm. Cyclic voltammetry measurements using a cavity microelectrode (CME) were performed in different chloric aqueous electrolyte solutions. The CME allows for very fast measurements (up to 10 V/s) of carbon powders without the need of a binder or conductivity additive. Therewith we were able to investigate the accessibility of the ultramicropores and kinetics of the electrochemical double-layer (EDL) charging as a function of particle, inter-particular pore, effective ion and micropore size. We found, that the alkaline cations K^+, Na^+, Li^+ and the anion Cl^- can enter micropores down to a size of 0.4 nm at slow charging rates independent of the particle size. However, the accessibility is decreased due to kinetic limitations for the cations Na^+ and Li^+ at higher scan rates, which was not observed for the smaller K^+ ion. A simple model is presented, which explains the influence of the particle, inter-particular pore and micropore size on the kinetics of double-layer charging. This model suggests that first of all the carbon particle size is not a limiting factor for fast EDL charging as long as its size is smaller than a few hundred nanometers and secondly inter-particular pores with a size in the range of the particle size or larger are crucial for high-rate applications.

1. Introduction

In electrochemical double-layer capacitors (EDLCs), also called supercapacitors, energy is stored in the electrochemical double-layer (EDL) at the interface between the electrode surface and the electrolyte solution. Because of the pure electrostatic ion adsorption without charge transfer across the interface, supercapacitors achieve very long cycle lifetime ($\sim 10^6$) and high specific power density. Therefore supercapacitors can replace batteries as energy storage devices in low energy applications or boost the power capability of batteries when used as a complementary component [1,2]. Highly porous carbons are used as electrode material in EDLCs and its electrochemical characteristics such as the kinetics of EDL charging and specific capacitance show a complex dependence on various parameters, such as the (micro)pore size distribution, specific surface area, particle and inter-particular pore size [3–6] and also the nature of the electrolyte, viz. the ion size, solvent used and maximum voltage window [7–10].

Several authors suggested the use of neutral aqueous electrolytes in EDLCs due to their low cost, easy handling, safety and high intrinsic conductivity [11,12]. Earlier mentioned drawbacks due to the low decomposition voltage of water (1.2 V) are no longer valid, as a voltage window for Na_2SO_4 of up to 1.6 V was reported [13,14]. This enables a significant increase in energy density. Recent advances in understanding the charging mechanisms in subnanometer pores allow for high energy applications [15], which require the design of new carbon materials possessing a large amount of micropores smaller than 1 nm. The use of aqueous electrolytes in combination with ultramicroporous carbons may further increase the specific capacitance due to their small effective ion sizes [16]. However, the transport in such small micropores is very slow [17,18], which requires short transport paths for the ions to the storage sites in the micropores. Several publications deal with the role of mesopores as ion high-ways to the micropores or macropores as ion buffer reservoir, increasing the charging rate [4,19–21,6,3,22]. Portet et al. [23] investigated the effect of the particle size on the electrochemical performance of an EDLC and showed that smaller particles enhance the rate performance. However, the samples investigated with 20 nm and 600 nm particles performed nearly identical, which is not straightforward and was not explained in detail. Even more, Zeller et al. [24] found an improved charging rate for particles with a size of 75 nm compared to 10 nm or 20 nm particles.

Hierarchically structured carbons are interesting candidates for EDLCs, as they exhibit all types of pores; macropores as ion buffer reservoir, mesopores as ion channels and micropores

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accounting for high capacitances [25–27]. Synthetically derived carbon xerogels provide such a hierarchical structure consisting of a three-dimensional network of ultramicroporous particles [28,29]; in particular these materials allow for adjusting the structural characteristics over a wide range by controlling the synthesis parameters. This is also the reason why carbon xerogels are used as a model system within this study. We systematically varied the size of the microporous carbon particles, the inter-particular macro-/mesopores in between and further used chemical activation to modify the size and distribution of the micropores. The impact of these structural changes on the kinetics of EDL charging in aqueous electrolytes was investigated to provide a base for systematic optimization of future electrode materials. Additionally we used various alkaline and alkaline earth chloric electrolytes to establish a relation between the accessibility of the ultramicropores inside the particles and the ion size.

2. Experimental

2.1. Synthesis of model carbons

Carbon xerogels were prepared via a sol-gel process as described elsewhere [30,31]. Briefly, resorcinol (R) is dissolved in deionized water using a magnetic stirrer. After complete dissolution formaldehyde (F) is added in a molar ratio R:F = 1:2 and 0.1 N Na_2CO_3 is added to the yellow solution as a base catalyst (C). The prepared sol is sealed into a glass vial and cured for 24 h at 50 °C followed by 24 h at 85 °C. The aged monolithic organic RF gels are dried at ambient pressure and room temperature after a solvent exchange of the pore liquid (mainly water) by acetone. The final carbon xerogel is derived by pyrolysis of the RF xerogel at 850 °C in Ar atmosphere.

For this study we prepared eight carbon xerogels with different particle sizes and inter-particular pore sizes by varying the molar catalyst concentration in the range R/C = 500–8000. The reactant mass concentration ($M = (m_R + m_F + m_C)/m_{total}$) was M = 30–45. The micropore size and distribution of two samples having medium and large particles, respectively, were modified by chemical activation with potassium hydroxide as activation agent. The mass ratio of carbon to potassium hydroxide was set to C:KOH = 1. The activation was performed at a temperature of T = 850 °C for 1 h.

2.2. Structural characterization

The structural properties of carbon xerogels were characterized by means of scanning electron microscopy (SEM, Zeiss Ultra Plus), CO_2 and N_2 sorption measurements and small-angle X-ray scattering (SAXS).

SAXS measurements were used to determine mean values for the particle and inter-particular pore size (macro- and mesopores). The measurements on the carbon xerogel powders were performed at the German synchrotron radiation laboratory in Hamburg (HASYLAB) at the SAXS-beamline B1 (JUSIFA) [32]. Two detector/sample distances were applied (935 mm and 3635 mm) to cover a q-range between $6 \times 10^{-2}\,nm^{-1}$ and $8.6\,nm^{-1}$ and the energy of the incident X-rays was 12.6 keV. The obtained volume specific differential scattering intensity was normalized to the density ρ of the samples to provide mass specific values.

Using the two-phase media (TPM) model, various structural properties can be evaluated [33,34]. For $q < 1\,nm^{-1}$ the scattering intensity decreases with the power of 4 (Porod's law [35]) indicating a smooth particle surface. The Porod constant K is proportional to the specific external surface area S_{ext} of the carbon xerogels [29]:

$$S_{ext} = \frac{K}{2\pi\,\rho_{part}^2\,C^2}, \tag{1}$$

with the density of the microporous particles ρ_{part} = 1.4 g/cm^3 [36] and $C = 8.504 \times 10^{11}$ m/kg, the conversion factor between electron and mass density. Furthermore, the chord lengths l_{part} and l_{pore} corresponding to the mean particle and inter-particular pore size, respectively, were calculated:

$$l_{part} = \frac{4\,\Phi_{part}}{\rho\,S_{ext}}, \quad l_{pore} = \frac{4\,\Phi_{pore}}{\rho\,S_{ext}}, \tag{2}$$

with $\Phi_{part} = \rho/\rho_{part}$ and $\Phi_{pore} = 1 - \Phi_{part}$ being the volume fraction of the particles and the inter-particular pores in the system, respectively. The sample density ρ was calculated from the transmission T of the X-ray radiation as:

$$\rho = \frac{-In(T)}{\alpha d}. \tag{3}$$

Here d is the sample thickness and α the total attenuation coefficient for carbon, which is a function of energy of the incident X-rays (α = 1.252 cm^2/g for 12.6 keV).

N_2 sorption at 77 K and CO_2 sorption at 273.15 K were measured with a volumetric sorption instrument (Micromeritics, ASAP 2020). Prior to the measurements the crushed carbon xerogel powder was degassed at 300 °C for at least 24 h. Using both, N_2 and CO_2 as adsorptives allows for a detailed characterization of the micropores, because N_2 adsorption in pores $\leq$0.7 nm is very slow due to the low N_2 diffusion coefficient at 77 K. CO_2 isotherms are therefore complementary to N_2 measurements since pores smaller than 0.7 nm can be detected [37]. From the N_2 isotherm the specific surface area S_{BET} was calculated using the BET model [38] in the relative pressure range p/p_0 = 0–0.15. The external surface areas S_{ext} were obtained from the linear range of the t-plot [39]. Using the equation of Dubinin–Astakhov (DA) [40] the specific micropore volume V_{mic} and equivalent surface area S_{mic} were calculated from adsorption isotherms of both adsorptives. The mean micropore diameter d_{mic} can be calculated by means of the characteristic energy of adsorption E_{char} derived from the DA theory. For this purpose, different equations can be used [41–45]. Usually the one by Stoeckli et al. [44] is applied. However, the Stoeckli equation might lead to erroneous results, if applied to carbons having a notable external surface area S_{ext}. In this case, a linear relationship between S_{ext} and d_{mic} is observed, as demonstrated by Zeller et al. [24]. For that reason we employed an equation suggested by Terzyk and Gauden [42] providing a more suitable approach for the calculation of d_{mic}:

$$d_{mic} = \left(\frac{a_1}{1 + b_1 \exp(-c_1 n)} + \frac{a_2 + b_2 n + c_2 n^2}{E_{char}} \right) d_{N_2} \tag{4}$$

with $a_1 = 0.7775$, $b_1 = -9.5761$, $c_1 = 2.1227$, $a_2 = 53.7290$ kJ/mol, $b_2 = -13.8278$ kJ/mol, $c_2 = 1.7692$ kJ/mol, n being the exponent of the Dubinin–Astakhov adsorption isotherm equation [40] and $d_{N_2} = 0.3$ nm being the diameter of the N_2 molecule. In addition, the micropore size distribution was calculated with the non-local density functional theory (NLDFT) [46,47]. The ultramicropore size distribution (UPSD) determined by CO_2 adsorption was combined with the one for supermicropores larger than 1.0 nm (SPSD) as derived from N_2 adsorption [37,48,49]. In addition, the mean micropore diameter was calculated from the micropore size distribution.

2.3. Electrochemical characterization

The electrochemical measurements were carried out on an IVIUM NStat potentiostat. The measurements were performed in a three-electrode configuration with a graphite counter electrode and an Ag/AgCl reference electrode (3 M NaCl, 0.209 V vs. NHE). A cavity microelectrode (CME) was applied as working electrode [50,23]. This electrode was chosen, since it allows very fast measurements due to the small amount of material in the electrode cavity. Furthermore, the intrinsic electrochemical characteristics